



THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS

7-10 September, 1987

Sevilla, Spain

Organized by: Sociedad Española de Arcillas



BOOK OF SUMMARIES - PROCEEDINGS

SPONSORS

(As of July 31, 1987)

INSTITUTIONS

MINISTERIO DE EDUCACION Y CIENCIA

AYUNTAMIENTO DE SEVILLA

CONSEJERIA DE EDUCACION Y CIENCIA DE LA JUNTA DE ANDALUCIA

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS

DIPUTACION PROVINCIAL DE CADIZ

UNIVERSIDAD DE SEVILLA

UNIVERSIDAD DE GRANADA

INSTITUTO PARA LA CONSERVACION DE LA NATURALEZA (ICONA)

AGENCIA DE MEDIO AMBIENTE

DIRECCION GENERAL DE TURISMO DE LA JUNTA DE ANDALUCIA

FACULTAD DE QUIMICA DE SEVILLA

SOCIEDAD ESPAÑOLA DE ARCILLAS

SOCIEDAD ESPAÑOLA DE CERAMICA Y VIDRIO

ASOCIACION NACIONAL DE QUIMICOS

COLEGIO OFICIAL DE GEOLOGOS

BUSINESSES AND INDUSTRIES

BANCO DE SANTANDER

BENESA

CAOBAR, S. A.

CERAMICA DE SARGADELOS

ENRESA

INGEMISA

LA CRUZ DEL CAMPO, S. A.

MINAS DE GADOR, S. A. - GRUPO LAPORTE

PHILIPS IBERICA, S.A.E.

SIEMENS

TOLSA, S. A.



SUMMARIES - PROCEEDINGS

THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS

EUROCLAY'87

7-10 September 1987
Seville, Spain

Editors: E. Galán
J. L. Pérez-Rodríguez
J. Cornejo

SOCIEDAD ESPAÑOLA DE ARCILLAS

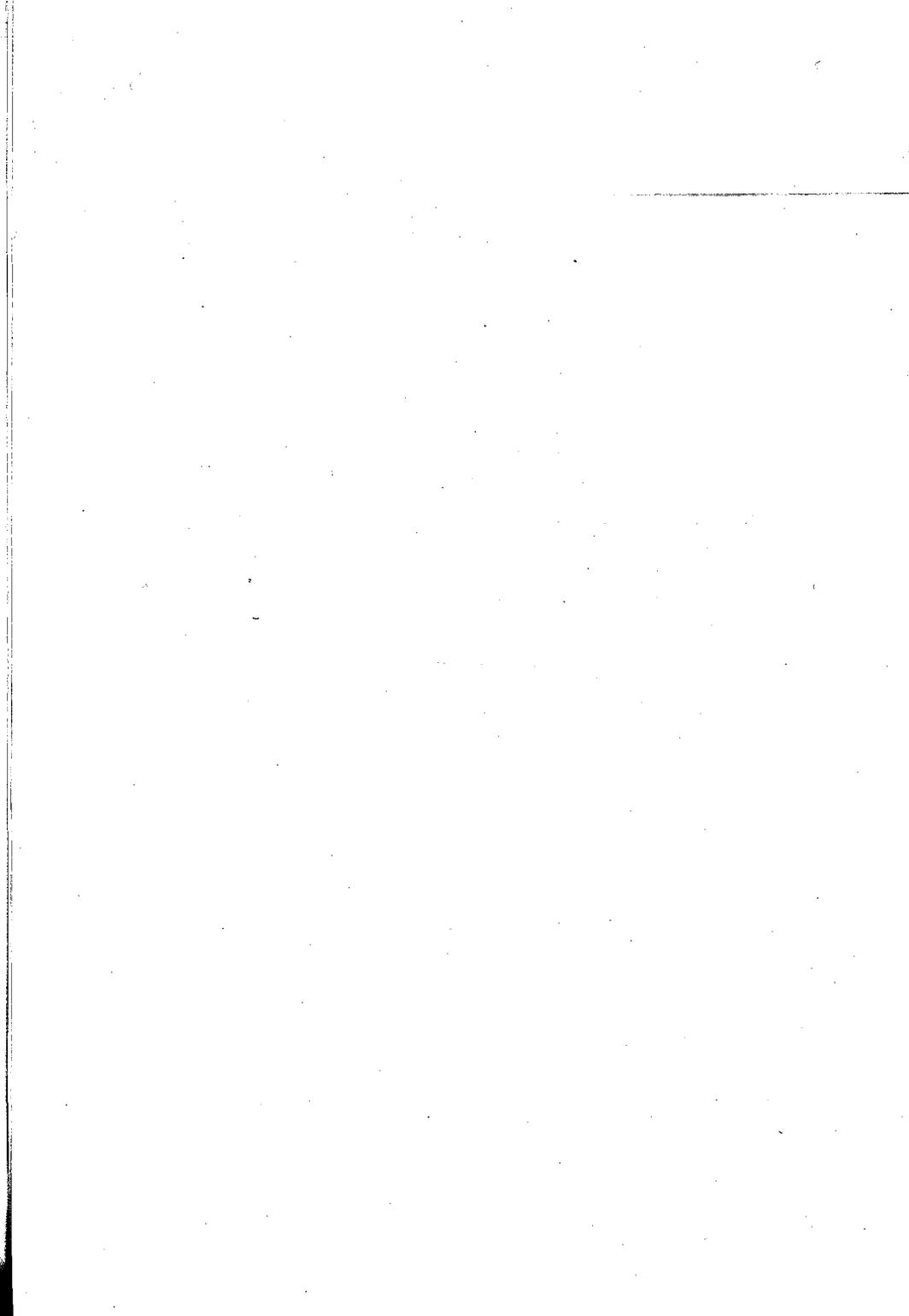
SUMMARIES ARRANGED ALPHABETICALLY
BY FIRST AUTHOR

Names of speakers or presenters
of poster are underlined

Sociedad Española de Arcillas
Facultad de Química
Apartado 553
SEVILLA

C O N T E N T S

PRESENTATION	5
PLENARY LECTURES	7
INTRODUCTORY LECTURES	19
SUMMARIES	57
OTHER ANNOUNCED PAPERS	615
AUTHORS INDEX	625



PRESENTATION

This Volume of Summaries - Proceedings of the Sixth European Clay Meeting, EUROCLAY'87, contains more than 200 extended abstracts of papers to be presented at the Conference, summaries of 14 Introductory Lectures, and 4 Plenary Lectures. It also includes a list of titles of other announced papers, whose authors have not confirmed their attendance at the Meeting at the edition closing date (1st of August).

Abstracts received for the Meeting were studied by the Scientific Committee, and about 50 % were sent back to the authors in order to improve the standard (information, extension, language, etc.). Around 10 % were also rejected. We think most of these extended abstracts published in this volume may be considered notes or short papers. This was our intention when we asked the authors for "very informative abstracts".

The edition of the present volume has been carefully prepared. Many originals were rewritten because they were not appropriate for reproduction. Others were corrected, or rearranged to homogenize standards.

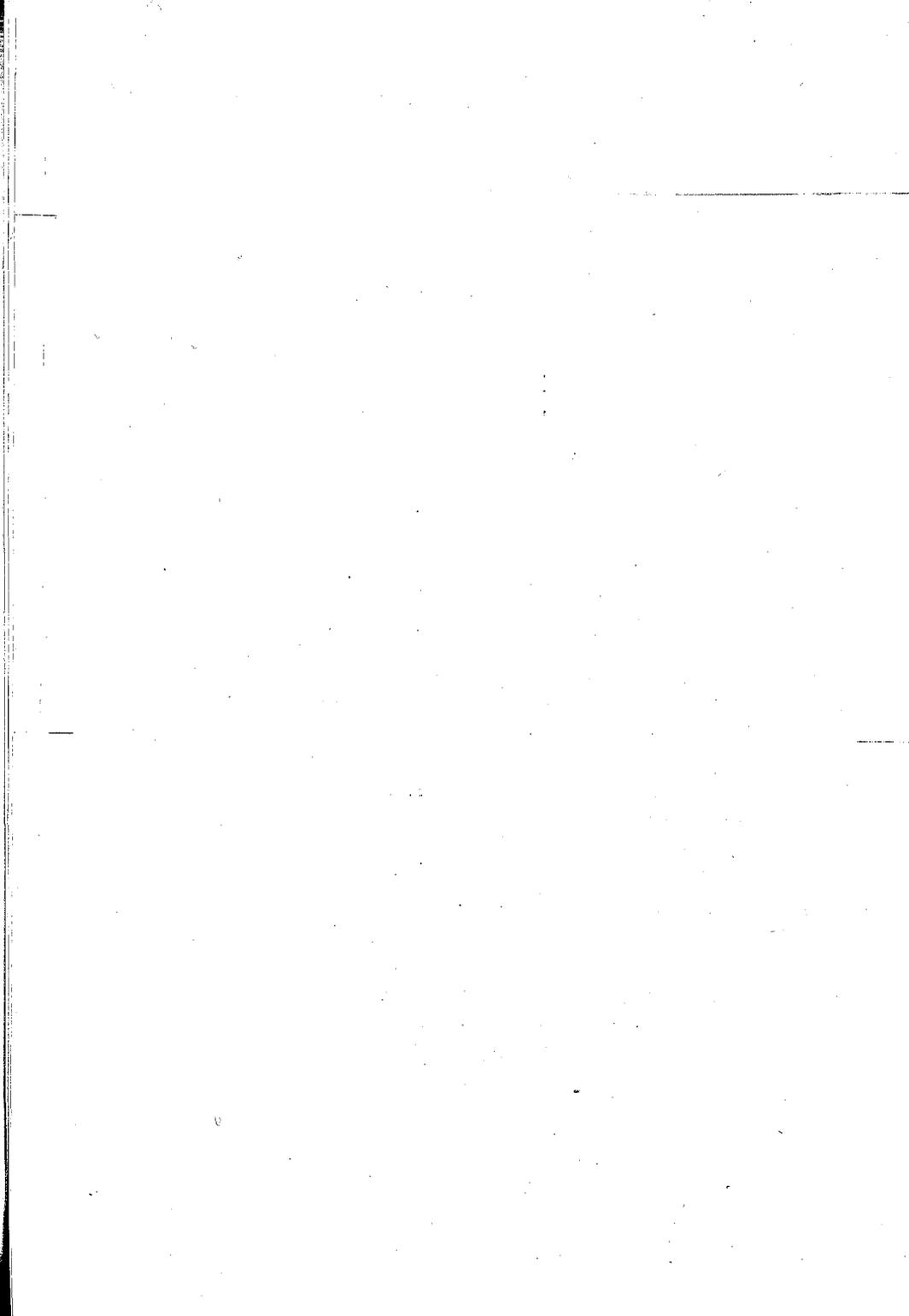
The cover reproduces the poster which was specially designed for this Meeting by Nicolás Forteza, a painter from Palma de Mallorca of international prestige.

Papers have been arranged by first author's name and all authors have been listed on the index.

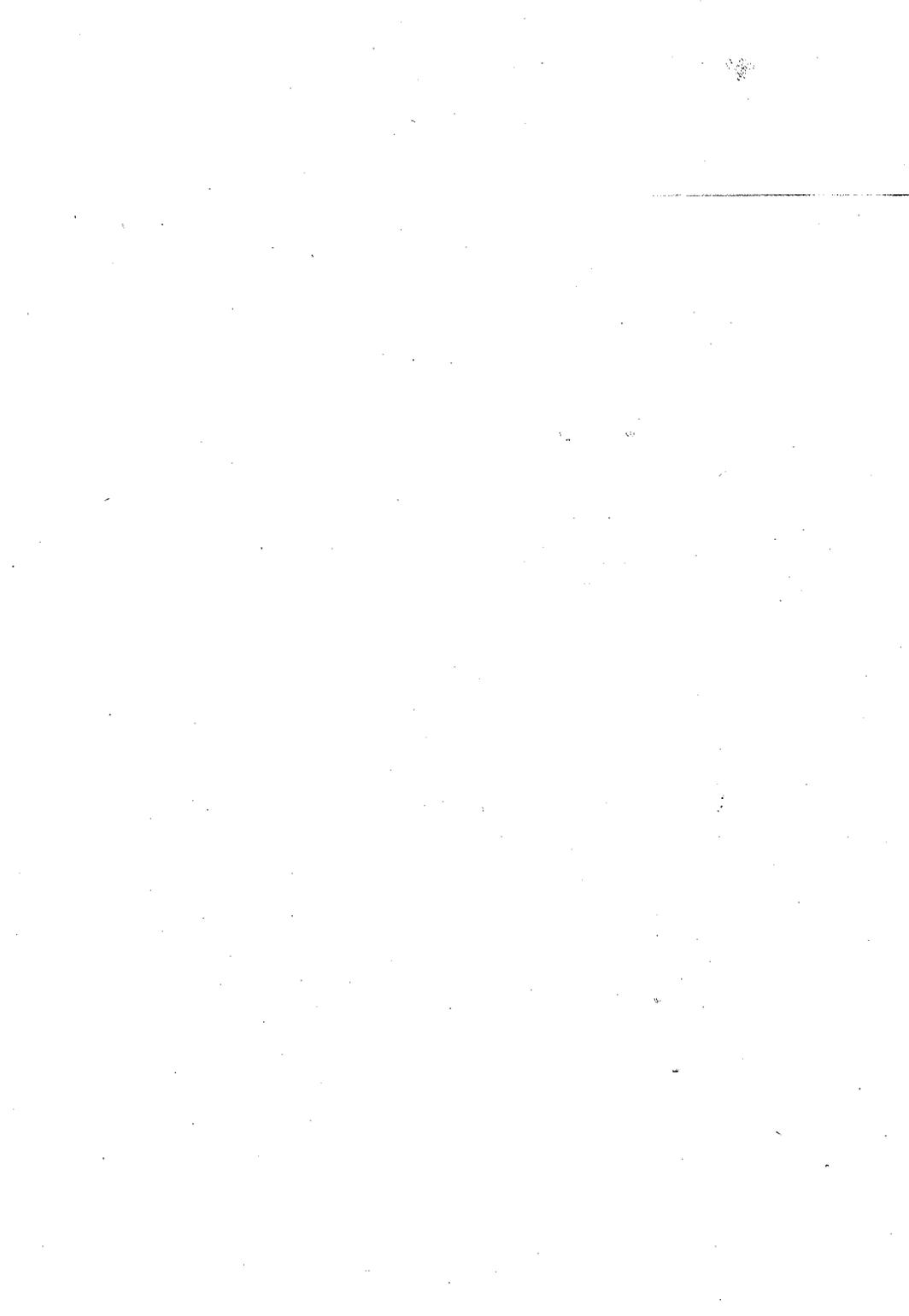
The Editors of this volume acknowledge the collaboration of authors, the assistance of Mr. Francisco Gayurt and the interest of the Publisher, Imprenta Raimundo, in improving the quality of the Edition.

EMILIO GALAN

Chairman



PLENARY LECTURES





Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ENVIRONMENTAL AND DIAGENETIC EXPRESSION OF CLAY SUCCESSIONS IN THE PAST
SEDIMENTARY RECORD

Hervé CHAMLEY

Dynamique sédimentaire et structurale, UA 719 CNRS, Université de
Lille I, 59655 Villeneuve d'Ascq (France).

INTRODUCTION

Multi-scale studies carried out on Meso-Cenozoic sedimentary successions of various boreholes and exposed sections allow to identify the respective influence of detrital input, of depositional factors and of diagenetic modifications on the clay record. The combination of basic sedimentological analyses with various mineralogical, micromorphological, geochemical and microgeochemical investigations, leads to delineate the sedimentary basins and geological periods marked by either major paleoenvironmental signature or dominant diagenetic imprint, or by the transition between both of them. Various examples are presented, largely based on data issued from sedimentary materials of the Deep Sea Drilling Project.

PALEOENVIRONMENT

Many series drilled in the oceans show only few diagenetic changes in the clay record since the late Jurassic. This is especially the case in the major areas of the Atlantic Ocean and of the Western Pacific, marked by strong terrigenous input or fairly rapid sedimentation rates. One of the rare significant in situ changes identified consists in the early diagenetic growth of lathed smectites at the periphery of detrital minerals (mainly smectites), without noteworthy quantitative modifications of the clay mineralogy and geochemistry.

Shatsky Rise, North-Western Pacific. The deep-sea red clays deposited since the uppermost Cretaceous on each side of the Shatsky Rise contain a large variety of clay minerals, which indicate the importance of eolian supply from Eastern Asia, and allow indirect stratigraphic correlations in the subzoic Cenozoic series.

New Zealand Basins. The Neogene sediments of the Lord Howe Rise area express the dependence existing between the climatic evolution of the Antarctic ice sheet, the aridification stages in Eastern Australia, and the atmospheric and oceanic circulation changes since 14 my. The post-Eocene clay successions around New Zealand reflect an alternation of tectonic events and relaxation stages, associated with modifications in the circulation regime.

Japan Trench Inner Wall. The clay mineral successions document the existence of a north/eastern landmass until the late Oligocene, its collapse and associated volcanism close the the early Miocene, and an increased detrital influence from Japanese islands during the late Cenozoic.

North Atlantic, late Jurassic to Quaternary. Since the Oxfordian, the clay stratigraphy of Hatteras and Cape Verde basins records only few volcanogenic signals. Many similarities exist in both basins from climatic, tectonic, pedogenical and morphological points of view, and the history of the adjacent continents can be usefully documented. The main differences between both domains result from the migration of plates in different climatic zones along the time, and from the timing of the Atlantic enlargement in the North and in the South. The Albian period shows a clear opposition between both western and eastern basins, which is interpreted mainly as the result of distinct tectonic and morphological situations on the landmasses..

DIAGENESIS

Noticeable diagenetic changes in the large-scale clay sedimentary record characterizes some areas or periods marked by active fluid migration processes, by volcanic and hydrothermal activity, or by thermodynamical constraints.

Nankai and Kuril Trenches, North-Western Pacific. The frequent volcanic activity and sediment permeability determine locally, in spite of the generally strong detrital input, the rapid halmyrolysis of glass and ashes, and the formation of Al- to Mg-Fe-rich smectites characterized by various shapes and chemical compositions.

Mariana Basin, Central Western Pacific. The volcanoclastic and pelagic sediments deposited from Aptian to Maastrichtian reveal a complex sequence of geochemical and geodynamical events : proximal volcanism and local supply from exposed archipelagoes, early marine diagenesis during lithospheric subsidence and plate migration, increase of terrigenous supply from distant asian sources.

Senegal and North-Eastern Atlantic Basins. The transition from terrigenous to diagenetic influences with the depth of burial, identified in the thick series deposited during the Cretaceous and the Paleogene in the Senegal Basin, is complicated by the tectonic instability of the African margin, which gives way to similar clay assemblages (illite and chlorite groups). As the deep-sea sediments of Cape Verde Basin are only slightly affected by diagenetic changes, the comparison between both series allows to distinguish the respective effects, depths and ages of the changes due to lithostatic pressure, tectonics and paleoenvironment.

Tyrrhenian Sea, Western Mediterranean. The Central Tyrrhenian Basin, which opened during the late Miocene in a global compressive context, experienced a strong geothermal gradient, responsible for an acceleration of clay diagenetic changes related to the depth of burial. Similar thermodynamical modifications occurred neither on the eastern Sardinia margin whose clay record expresses at the same period the local tectonic instability, nor in South Sicily marked by climatic peculiarities related to the Messinian salinity crisis.

MAIN REFERENCES

- H. Chamley, Geologische Rundschau, 1986, 75 : 271-285.
- H. Chamley, P. Debrabant, Sedimentary Geology, 1984, 40 : 151-167.
- H. Chamley, P. Debrabant, Tectonophysics, 1987 (in press).
- H. Chamley, P. Debrabant, R. Flicoteaux, Sedimentol., 1987 (in press).
- H. Chamley, J.-F. Deconinck, C.R.Ac. Sci., 1985, 300 : 1007-1012.
- H. Chamley, J.E. Meulenkamp, W.J. Zachariasse, G.J. Van der Zwaan, Oceanologica Acta, 1986, 9 : 227-238.
- H. Chamley et al., Init. Repts DSDP, 1987, 107 (in press).
- T. Holtzapffel, H. Chamley, Clay Minerals, 1986, 21 : 133-148.
- C. Robert, H. Chamley, Palaeo-geogr., -clim., -eol., 1987 (in press).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ROLE OF THE CLAY IN THE PETROLEUM GENERATION AND EXPLORATION

E. ROALDSET

University of Oslo, Box 1047, Blindern, 0316 Oslo 3 (Norway)

Clay minerals and clay sediments play an important role in the petroleum industry, in particular in exploration, drilling, and reservoir engineering. The state of the art, aims, and expectations from research and development, now in progress, will be reviewed.

An improved understanding of the distribution and properties of clays and clay minerals is of importance in the following fields: basin evaluation, reservoir quality and yield predictions, drilling technology, well-logging, and log interpretation.

Literature on the different aspects of clay sediments and clay minerals in petroleum technology is published in a variety of scientific journals, symposia proceedings, patent documents, and in company reports often of limited distribution. The special clay journals frequently report research results applicable for the petroleum industry. The journal of the European Clay Groups, *Clay Minerals*, in 1982, 1984, and 1986, published special issues on clays, and clay mineral diagenesis, in the discovery and recovery of petroleum.

Database search on topics within the clay sciences of relevance for petroleum generation, exploration, and production, gave for the period 1978-1986 approximately 20.000 references including publications, reports, and abstracts.

EXPLORATION - BASIN EVALUATION

The distribution of clays and shales in sedimentary basins is influenced by tectonic conditions, subsidence,

and depositional rates. The clay mineralogy reflects paleoclimate, provenance, and depositional environment, and appears useful for stratigraphic correlation.

In a sedimentary basin implications for hydrocarbon exploration are the existence of

- reservoirs (sand, sandstones, carbonates)
- source rocks (claystones and shales with high organic matter content)
- traps (structural and/or stratigraphic)
- sealing cap rocks (claystones, shales)

The subsidence versus geological time, geothermal gradients and heat flow, are key figures in modelling the thermal history and diagenetic processes of buried sediments, and thus for predicting the maturity of hydrocarbon source rocks, and the quality of reservoir rocks.

The role of clay and clay-organic matter interactions in the generation of hydrocarbons is considered extremely important. The clay minerals, their colloidal and surface chemical properties, may catalyze the thermal degradation of the organic matter.

Sealing layers in sedimentary sequences control the accumulation of hydrocarbons in reservoir structures. The hydrocarbon seals are characterized by having high contents of smectite and smectite/illite with particle sizes less than 1 μm , average porediameters of 0.1-1 μm , low diffusion rates, and high capillary pressures.

RESERVOIR TECHNOLOGY

Aspects of clay sedimentology and mineralogy of major importance for reservoir evaluation and hydrocarbon production are

- the distribution of clay- and siltstone barriers within the reservoir
- the amount and composition of primary and diagenetic clay minerals in the pores of reservoir rocks

The geometry of clay- and siltstone beds within a reservoir strongly affect the drainage pattern during

production. Shale management, i.e. modelling of the effects of low- and impermeable layers on reservoir performance, has become increasingly important in reservoir simulation.

Clay minerals in sandstone pores can generate severe production problems by swelling, migration, and clogging of pore throats, thereby reduce the permeability. Theoretically calculated stability diagrams for the most important clay minerals combined with field observations and core data, represents a valuable tool for prediction of reservoir quality, and for pre-assessing possible gains by improved oil techniques (incl. enhanced oil recovery).

DRILLING

Drilling through active, smectitic claystones is frequently followed by formation problems. The clays may swell in contact with the drilling fluid, and cause well-bore damage. Furthermore, clay, preferably bentonite, is a major constituent of drilling fluid.

WELL LOGGING

Facies interpretations from gamma-log analysis can be misleading when non-radioactive clay minerals, or K-feldspar, occur. The conductivity of clay sediments may change as the clay minerals swell, and this influences the resistivity log.

ADVANCING RESEARCH

Although clay and shales make up at least 75 % of most sedimentary basins, they still are considered to be the least understood rock type in terms of physical properties that affect seismic and well-log responses (Oil & Gas Journal, Nov. 3, 1986).

The ongoing research related to clays in the petroleum industry emphasize on: mathematical modelling of clay/hale distributions, experimental studies on the physical and chemical properties (i.e. surface phenomene, catalytic effects), clay-organic matter reactions, and maturation.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

METHODOLOGY AND ANALYTIC TECHNIQUES OF CLAY MINERAL
RESEARCH

M. STÖRR

Department of Geological Sciences, Ernst-Moritz-Arndt-
University Greifswald (G.D.R.), F.-L.-Jahnstr. 17 a,
Greifswald, 2200, G.D.R.

Like in every experimental science also in clay science advances are largely dependent upon the development of analytic techniques. The wide-spread occurrence of clays and clay minerals in nature, their varied applications in industry, their specific structures and the corresponding physical, chemical and technological properties etc. require the use of nearly all examination techniques available. Under this aspect the study of the relationships between knowledge, methods, objects, theories and ideas on the methodology of clay science, i. e. the analyses of its methods and rules is gaining particular interest.

Of the tree entities



each one can be the driving force in the development of science. Of special importance for the interactions between these three entities as well as for achieving relevant advances in science are new ideas on theory and methods and new aspects arising from objects. Improved accessibility to such new objects as clay samples from deep drillings has led to new theories on the diagenesis

of clays (cf. Clay Minerals, vol. 21, No. 4, Oct. '86), though predominantly only conventional analytic techniques were used. At present most new objects are investigated by means of conventional techniques, as KONTA emphasized at the VIIIth ICC in Bologna.

New theories, such as plate tectonics have initiated the renewed discussion of the genesis of bauxite (BARDOSSY) and kaolin (STÖRR), which has meanwhile led to essential new findings. New methods and their close relationship to analytic techniques have produced the largest gain in knowledge (cf. FRIPIAT, Advanced Techniques for Clay Mineral Analysis, Elsevier 1981), therefore they will be discussed in greater detail.

In clay research the most important method is the experiment whether in the laboratory, in industry or in the field. The character of such experiments may be:

- analytical (to determine the state of the object)
- synthetic (to utilize or change the state).

Accordingly, the analytic techniques as such are primarily aimed at determining the state. These techniques are usually divided into:

- the laboratory analytic techniques and
- the field analytic techniques.

The latter have gained increasing significance in the past few years. Recent advances in analytic techniques are mainly based on

- improved devices
- computer aided analytic control and data interpretation.

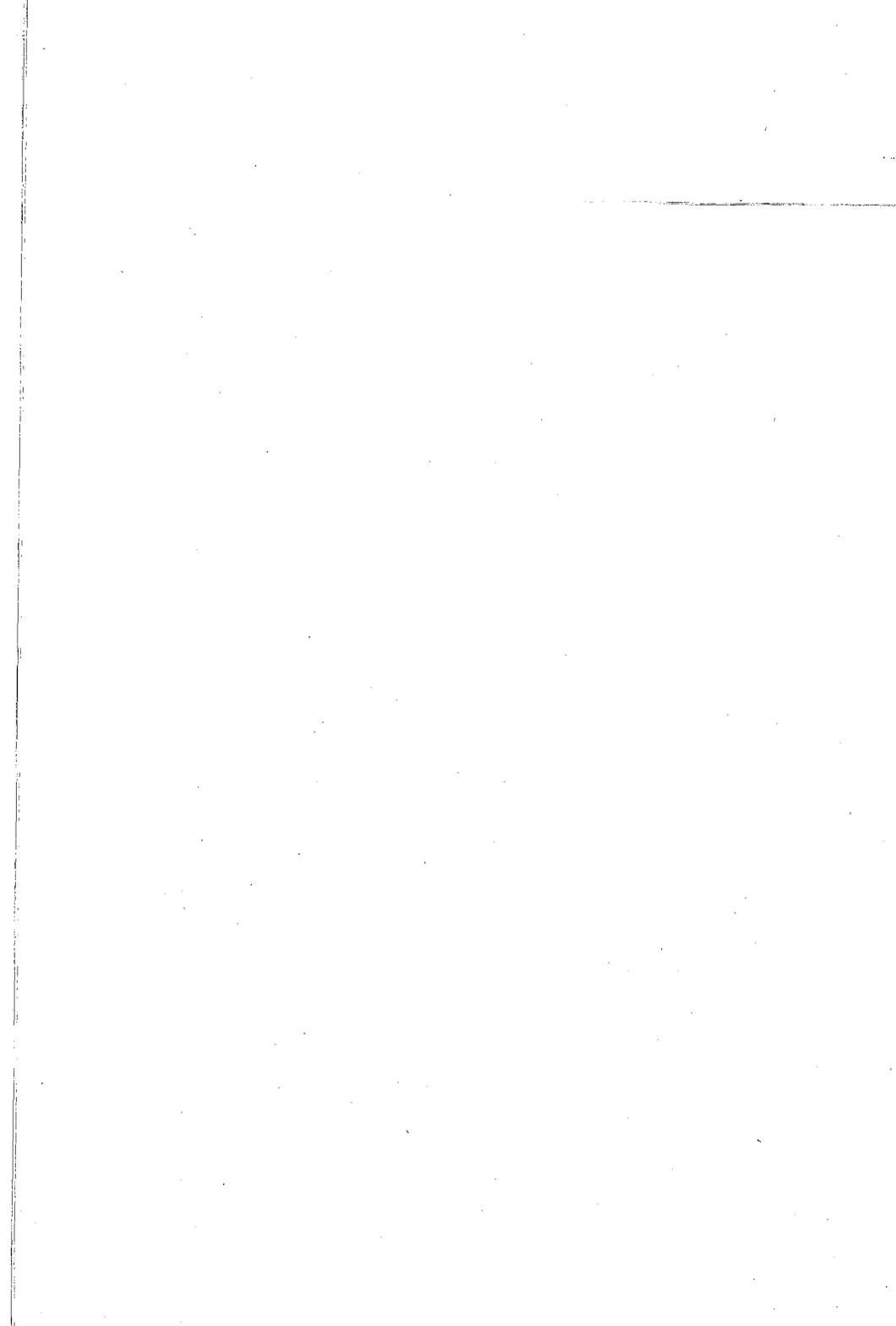
The impact of new laboratory techniques on the development of knowledge is illustrated using several examples taken from the literature and own investigations, such as HRTEM, high-temperature dilatometry, IR-FTS-ellipsometry, measurement of magnetic susceptibility, EPR, SEM, micro-

probe analysis and STEM.

The main concern of the field analytic techniques is to measure in situ, and these techniques are closely related to the ever increasing in situ treatment of minerals, rocks and deposits as well as to the large-scale utilization of nature (waste disposal, water filtration, soil consolidation etc.).

The following examples of modern field analytic techniques are discussed:

- chemical analysis by means of well logging
- substantial interpretation of geophysical data
- in situ measurements of physical and chemical parameters related to the alterations of bentonite properties within the framework of the Stripa Project, Sweden.



INTRODUCTORY LECTURES





Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

X-RAY IDENTIFICATION OF THE POLYTYPES OF 1:1 LAYER SILICATES

S. W. BAILEY

Department of Geology and Geophysics, University of Wisconsin, Madison,
WI 53706, USA

Twelve standard polytypes can be derived for trioctahedral 1:1 layer silicates on the basis of (1) distribution of octahedral cations either in the same set of positions in every layer or (2) regular alternation between the I and II sets in successive layers and by formation of interlayer hydrogen bonds by (3) shifts of adjacent layers by $\pm a/3$ along X_1 , X_2 , or X_3 or by (4) shifts of zero or $\pm b/3$ along Y_1 , (assuming regular stacking and no intermixing of types of layer shift). These four variables subdivide 1:1 layer silicate structures into four groups A-D. In groups A and B the layer shifts are $\pm a/3$, and in groups C and D the shifts are zero or $\pm b/3$. In groups A and C the octahedral cations are in the same set of positions in every layer, and in groups B and D the cations alternate regularly between the I and II sets of positions.

All of the octahedral cations and anions repeat at intervals of $b/3$ and thus contribute strongly to x-ray reflections of index $k = 3n$ (assuming indexing on orthohexagonal axes). For these strong reflections the periodicity along Z will either be 7 Å or 14 Å, corresponding to variables (1) or (2) above. The intensities of these $k = 3n$ reflections are different for groups A-D and assure easy identification of the four groups. The intensities are the same for the three polytypes within each group, however, and their identification requires study of weaker reflections of index $k \neq 3n$. The basal oxygen atoms do not repeat at intervals of $b/3$ and thus contribute primarily to $k \neq 3n$ reflections. The periodicity within these reflections will be $n \times 7$ Å, where n indicates the number of layers before a repeat of identical basal oxygen planes is met along Z,

and this periodicity plus the symmetry identifies the individual trioctahedral polytypes. If the stacking of layers is random, the $k \neq 3n$ reflections will be streaked along Z^* , and only the groups A-D can be identified from the remaining discrete reflections.

For 1:1 layer silicates the stacking of layers is often random. Even in cases of regular stacking the $k \neq 3n$ reflections for trioctahedral species may be too weak to observe on x-ray powder patterns. Those for dioctahedral species are normally visible, but ordering of the octahedral vacancy in adjacent layers may change the layer periodicity and symmetry relative to that of the equivalent trioctahedral species. Illustrations will be presented of the periodicities and relative intensities needed to identify the 12 standard polytypes by use either of single crystal or powder x-ray patterns.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**NATURE OF DEFECTS AND STRUCTURAL PECULIARITIES OF LAYER
SILICATES**

V.A. DRITS

Geological Institute of the USSR Academy of Sciences,
Moscow, USSR

Theory of polytypism plays an important role in structural studies of layer silicates. It helps to predict all possible for this family polytypes and calculate their diffraction characteristics which are to be compared with experimental ones. This approach provides idealized structures and finds successful practical applications. However, polytypism theory is as a rule unable to assess the relative stability of the polytypes outlined. Refined crystal structures of specific layer silicates suggest their fine structural peculiarities whose analysis helps to define the factors controlling variable distribution of various polytypes in different geological environments. The same approach is feasible in defining the nature of various defects in real structures of layer silicates. Peculiarities of crystal structures taken into account considerably limit the set of possible stacking defects. Application of profile analysis based on the comparison of experimental diffraction patterns with simulated ones for the models with variable stacking defects, is an effective means to confirm the inferred nature of defects in the structure of mineral under study.

Stability of one-layer chlorites has been evaluated qualitatively by Bailey in terms of changing cation-cation repulsion and cation-anion attraction resulting from differing 2:1 and brucite-like layers superpositions. Calculations of electrostatic energy for the point charges model show that 12 one-layer polytypes can be subdivided in-

to three groups, different only in the mode the brucite-like layers cations are imposed on the adjacent tetrahedral cations of 2:1 layers. Real distortions of tetrahedral sheets show that reduction of hydrogen bond lengths is the second major factor that controls natural occurrences of chlorites. Widely spread semi-ordered structures, e.g., due to the presence in crystal of fragments of 11b-2 and 11b-4 and 11b-6 polytypes, may be accounted for by the fact that their inter-growth does not affect hydrogen bonds and positions of the closest cations of neighbouring layers.

Analysis of structural peculiarities of kaoline minerals (kaolinite, dickite, nacrite) has led to the revision of existing notions of the nature of stacking faults in kaolinite structure. Defects produced by equally probable shift of 1:1 layers to $\pm b/3$ are not equivalent from the energetic point of view, i.e., they lead to differing imposition of the nearest octahedral and tetrahedral cations of neighbouring layers. Growth defects due to $\pm 120^\circ$ rotation of layers must lead to commensurability in ab plane of adjacent layers. A vacancies displacement model with equally probable occurrence of layers A, B and C in the extreme case makes kaolinites with different unit cell parameters possible. In addition, kaolinites composed of A layers are characterized by unfavourable imposition of Si and Al cations of neighbouring layers. Stacking faults models are discussed that do not contradict the existing chemical notion of kaoline minerals.

Stacking defects in dioctahedral one-layers micaceous minerals depend on the specific structure of 2:1 layers, particularly on the mode of distribution of isomorphous cations, on the structural mechanism of their formations and other factors. If for individual 2:1 layers $b = a\sqrt{3}$, stacking defects may be due to neighbouring layers rotations. Rotations to $n120^\circ$ do not change the coordination of K cations whereas rotations to $n60^\circ$ lead to different anion surroundings of K in interlayers. If $b \neq a\sqrt{3}$, each pair of adjacent layers that form a stacking defect is

connected with each other either by a slide plane or by a 180° rotation relative normal to (001).

The calculations of X-ray powder patterns for various defect models suggested diffractive criteria which determine the nature of stacking defects in 1M dioctahedral K-micas, at least on the qualitative level. Analysis of diffraction patterns of natural micaceous minerals is discussed.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CHANGES IN SPECIFIC CATALYTIC ACTIVITY DURING ILLITIZATION
AND BURIAL DIAGENESIS. THE CASE OF THE VIENNA BASIN

W. D. JOHNS

Department of Geology, University of Missouri, (U.S.A.)

Specific catalytic activities were measured on Tertiary shales and extracted illite-smectite clay fractions from the Vienna Basin of Austria. Sca measurements were made also on homoionic K-, Na-, Ca-, and Mg-smectites and illites.

The source of catalytic activity was determined to be due to the dissociation of water molecules bonded to exchangeable cations in the interlayers of smectite and external basal surfaces of primary illite particles. In both smectite and illite sca increased with polarizing power of the exchangeable cation in the order $K^+ < Na^+ < Ca^{+2} < Mg^{+2}$. In the mixed-layer phases increased sca is associated with and accompanies the increase in interlayer and tetrahedral charge associated with illitization during diagenesis.

External basal surfaces of illite are associated with especially high sca as a result of high charge density and cation population and tetrahedral source of charge. A cation site associated with tetrahedral substitution has an activity about 40 times one of octahedral origin.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAYS IN THE 21st CENTURY

M. KUŽVART

Department of Mineral Deposits, Charles University,
128 43 Praha (Czechoslovakia).

Few countries have all kinds of clays on their respective territories. To these belong the U.S.A., the Soviet Union, Spain, U.K., and several other countries. These countries will also produce greater part of the 750 mil.tons of all types of clays in the year 2000, compared with 500 mil.tons in 1983. The first figure and all considerations on future technological improvements in following text are results of projection of contemporary trends to the future. It is not a prophecy which should materialize to the last iota. Remember the prices of oil and predictions of oil deposits depletion ten years ago, and compare with present situation !

The structural clay products will be used in broader scale provided that the present efforts for promoting the loadbearing potential for brick construction and the use of factory-built panels will continue. On the other hand, we must take into consideration the competition of alternative construction materials, such as wood, glass, aluminium, plastics, and sand-lime brick made from fly ash.

The production of clays and shales of low quality used as corrective agent in making cement clinker will not rise very rapidly, as in most countries pozzolanic material, fly ash, blast-furnace slag, aluminum drosses and pyritic cinders will be used. Reinforced concrete will partially give way to structural steel with lightweight panel fillings. Asphalt pavement will compete with concrete. Expanded clay and shale in the form of lightweight aggregate will be used in concrete in bridge

decks, high rise buildings and unsupported roof spans. New end use of expanded aggregates is in top course of asphalt roads, and in landscaping and horticulture.

Refractories will have to cope with higher operating temperatures demanded by technological advances in metallurgical processes. For this purpose high alumina kaolins and highest quality fire clays will be used. The shift to the base oxygen process in steelmaking requires basic (magnesite-chrom) rather than alumina-type firebricks. The electric-arc-furnace steel-making process requires high-alumina or mullite-type refractory roofs.

Paper production will grow, and with it the consumption of washed kaolin, which makes 30 % in high-quality paper. Unfortunately, there is a great danger from the side of calcium carbonate fillers and extenders which are cheaper, and brighter, thereby requiring less loading for comparable opacity. Growing use of calcined kaoline in paper products might help to cope with this trend. The drive to produce very lightweight coated paper has led to the development of plastic pigments which are uniform in size, lightweight and are spherical. These pigments give superior gloss, opacity and improved printability to coated paper but are much more expensive than kaolin, at least for the time being.

Bentonite used in pelletizing taconite iron ore might be partially replaced by organic and lime materials, which do not contaminate the batch; organics even add heat in the process. In the drilling mud bentonite is indispensable, but there is a gloomy future for exploration for oil and ores because their prices are low. Oil prices might continue to decline as a result of conservation efforts, construction of more fuel efficient automobiles, and building smaller and better insulated houses. Synthetic mica-montmorillonite or randomly interstratified alumina montmorillonoid, used presently in catalytic cracking, hydrogenation (dehydrogenation), and double-bond isomerization, will find new applications, and new competing materials as well. Organic-clad hydrophobic bentonites (with alkyl amine) are used in making paint, to gel organic liquids, to produce

greases having superior adherence to metal, ability to repel water and to resist to high temperatures. Their application will grow.

Halloysite will be used in petroleum catalysts as long as high-quality deposits can be mined at a reasonable cost. The competition of materials manufactured from kaolin and synthetic materials containing alumina and silica will grow.

Ceramics and glass utilization grows and will continue to grow with new construction. Sanitary ware, ceramic tile, pottery dinnerware and electrical porcelain are indispensable for civilized habitation. Contemporary trend in residential construction with more elaborate appointments such as tiled kitchens and baths will add to consumption of ceramic clays. Increased use of glass containers instead of plastic ones for the softdrinks and beer could have positive effect on long-range glass demand.

Absorbent clays will be used as toxic and low-level nuclear waste absorbents in buried disposal sites, and, of course, also as pet waste absorbents.

The competition of clay fillers for rubber with other cheaper materials might be very hard, because precipitated silica gives better reinforcement to rubber, produces higher tensile strenght, modulus of elasticity and resistance to abrasion. Their cost is twice of washed kaolin.

The demand for bentonite as a sand binder in foundries will continue to grow with the growth of production of automobiles, trucks, trains and heavy equipment for construction and farming.

The use of high-alumina clays and washed kaolin for production of alumina or aluminum is technically feasible but in comparison with bauxite as raw material still too expensive.

Future production of synthetic zeolites for petroleum refining, gas pollutant absorbing and substituting of phosphates in detergents will be based on kaolin, fuller's earth and bentonite more than today.

Improved processing technology will allow the utilization of lower quality clays as paper coater, paint filler, rubber filler, and high-quality ceramic raw materials.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SURFACE CHEMISTRY AND CATALYSIS

G. LAGALY

Institut für anorganische Chemie, Universität Kiel,
Olshäusenstraße 40, D-2300 Kiel, FRG

Recent studies on clay minerals as catalysts refer to the minerals in their pristine form (with or without exchanging interlayer cations) or in chemically modified form, in particular as pillared clays. Much effort has been made to prepare pillared clays and to find out their catalytic activities (Ballantine, 1986; Barrer, 1986; Pinnavaia et al., 1984, 1986; Poncelet and Schutz, 1986).

Clay minerals containing (OH) groups are not very stable thermally which is a serious disadvantage for practical applications. Synthetic fluor micas with high cation exchange capacity exhibit high temperature stability and may be used instead of clay minerals containing (OH) groups (Barrer, 1986).

Clay minerals without chemical alterations (excepting cation exchange reactions) catalyse a large variety of reactions (Adams et al., 1983; Adams et al. 1986; Ballantine, 1983, 1986). Many reactions are catalysed by the increased Brönsted acidity in the interlayer space due to an enhanced degree of dissociation of water around interlayer cations (cf. Fripiat, 1986). An other type of sites with increased acidity is produced by Al-O-Si linkages when a clay with tetrahedral substitution (beidellite) is heated (Schutz et al., 1986). The list of reactions which are catalysed by acidic centers, is impressive. I only mention the transformation of limonene into p-menthene and p-cymene

(Frenkel and Heller-Kallai, 1983) and the hydration of ethylene (Atkins et al., 1983) or production of ethyl acetate from ethylene and acetic acid (Gregory et al., 1983).

The presence of distinct amounts of water is often imperative for increased activity (Adams et al., 1979; Almon and Johns, 1976; El-Amamy, 1984). An interesting observation was made by Perez-Rodriguez et al. (1985) during studies of the interaction of the pesticide chlordimeform with decylammonium vermiculite in aqueous and butanol solution. Type and distribution of products in closed systems can be notably different from those in open or semi-closed systems (Galwey, 1970; Heller-Kallai, 1985).

The central topic to be discussed refers to the influence of geometrical conditions. Despite of the swelling properties of smectites, there is only limited space available for the reacting molecules, and the reactants can be held under geometrical constraints. A strong relation should exist between possible orientations of the reacting molecules in the interlayer space and the type of products. However, there are only very few examples illustrating such effects (Brunner, 1979; Abdo et al., 1981; Adams et al., 1981; Cruz et al., 1982; Pinnavaia, 1983). An interesting alternative is the reaction in wedge-shaped pores of layered materials, for instance of crystalline silicic acids (Lagaly et al., 1986). In contrast to flat surfaces where the distance between reacting sites is invariable, the wedge-shaped opening of the pores provides sites in different distances. For instance, any molecule that needs two centres of reactions will find two reacting sites at the required distances.

Another important influence is the texture of the system, that is, the way in which the particles are aggregated and, in case of smectites, the degree of delamination. The method used to dry flocculated clay dispersions can be

far more important than the choice of the chemical pathways in modifying the clay minerals (Pinnavaia et al., 1984). The importance of the system architecture for light-induced electron transfer and catalytic reactions in a complex colloidal medium has been established by Nijs et al. (1983). The possibility that delaminated sodium smectite particles can be re-aggregated in different ways (Frey and Lagaly, 1979) allows an optimization of the particle structure. This "clay particle engineering" (Nadeau, 1987) may find diverse applications and may also provide a pathway to increase selectivity and activity of clay catalysts. (Nadeau, 1987).

References

- ABDO, S., CANESSON, P., van DAMME, H., CRUZ, M.I., and FRIPIAT, J.J. (1981) Photochemical and photocatalytic properties of adsorbed organometallic compounds. II. *J. Phys. Chem.* 85, 797-809.
- ADAMS, J.M. et al (1979) Selective chemical conversions using sheet silicate intercalates: low temperature addition of water to 1-alkenes. *J. Catalysis* 58, 238-252.
- ADAMS, J.M., BYLINA, A., and GRAHAM, S.H. (1981) Shape selectivity in low-temperature reactions of C₆-alkenes catalysed by a Cu²⁺-exchanged montmorillonite. *Clay Min.* 16, 325-332.
- ADAMS, J.M., CLAPP, T.V., and CLEMENT, D.E. (1983) Catalysis by montmorillonites. *Clay Min.* 18, 411-421.
- ADAMS, J.M., MARTIN, K., McCABE, R.W., and MURRAY, S. (1986) Methyl t-butyl ether production: a comparison of montmorillonite-derived catalysis with an ion-exchange resin, *Clays Clay Min.* 34, 597-603.
- ALMON, W.R. and JOHNS, W.D. (1976) Petroleum forming reactions: clay catalyzed fatty acid decarboxylation. *Prov. Internat. Clay Conf. Mexico, 1975*, Appl. Publ. Ltd. Wilmette, 399-409.
- ATKINS, M.P., SMITH, D.J.H., and WESTLAKE, D.J. (1983). Montmorillonite catalysts for ethylene hydration. *Clay Min.* 18, 423-429.

- BALLANTINE, J.A. (1986) The reactions in clays and pillared clays. In: Setton, R. (ed.) Chemical reactions in organic and inorganic constrained systems. D. Reidel Pub. Comp. Dordrecht, 151-164.
- BALLANTINE, J.A. (1983) Organic reactions in a clay micro-environment. Clay Min. 18, 347-356.
- BARRER; R.M. (1986). Expanded clay minerals: a major class of molecular sieves. I. Inclusion Phenomena 4, 109-119.
- BRUNNER, P. (1979), Thesis University Munich (A. Weiss)
- CRUZ, M.I., NIJS, H., FRIPIAT, J.J., and van DAMME, H. (1982) Photochemical and photocatalytic properties of adsorbed coordination compounds. III. J. Chim. Phys. (Paris) 79, 753-757.
- EL-AMAMY, M.M. and MILL, T. (1984) Hydrolysis kinetics of organic chemicals on montmorillonite and kaolinite surfaces as related to moisture content. Clays Clay Min. 32, 67-73.
- FREY, E. and LAGALY, G. (1979) Selective coagulation in mixed colloidal suspensions. J. Colloid Interf. Sci. 70, 46-55.
- FRENKEL, M. and HELLER-KALLAI, L. (1983) Interlayer cations as reaction directors in the transformation of limonene on montmorillonite. Clays Clay Min. 31, 92-96.
- FRIPIAT, J.J. (1986) Internal surface of clays and constrained chemical reactions. Clays Clay Min. 34, 501-506.
- GALWEY, A.K. (1970) Reactions of alcohols and of hydrocarbons on montmorillonite surfaces. J. Catalysis, 19, 330-342.
- GREGORY, R., SMITH, D.J.H., and WESTLAKE, D.J. (1983) The production of ethyl acetate from ethylene and acetic acid using clay catalysts. Clay Min. 18, 431-435.
- HELLER-KALLAI, L. (1985) Do clay minerals act as catalysts in the thermal alteration of organic matter in nature? Problems of simulation experiments. Miner. Petrogr. Acta 29A, 3-16.
- LAGALY, G., RIEKERT, H.-M., and KRUSE, H.-H. (1986) Crystal-line silicic acids, in: Setton, R. (ed.) Chemical reactions in organic and inorganic constrained systems. D. Reidel Pub. Comp. Dordrecht, 361-379.
- NADEAU, P.H. (1987) Clay particle engineering: a potential new technology with diverse applications. Clay Min. 2, 83-93.

- NIJS, H., van DAMME, H., BERGAYA, F., HABTI, A., and FRIPIAT, J.J. (1983). Structural aspects in the photooxidation and photoreduction of water in clay mineral suspensions. *J. Mol. Catalysis* 21, 223-232.
- PEREZ-RODRIGUEZ, J.L., MORILLO, E., and HERMOSIN, M.C. (1985) Interactions of chlordimeform with a vermiculite-decylammonium complex in aqueous and butanol solution. *Miner. Petrogr. Acta* 29A, 155-162.
- PINNAVAIA, T.J. (1983) Intercalated clay catalysts. *Science*, 220, 365-371.
- PINNAVAIA, T.J., TZOU, M.-Sh., LANDAU, S.D., and RAYTHATHA, R.H. (1984) On the pillaring and delamination of smectite clay catalysts by polyoxo cations of aluminium. *J. Mol. Cat.* 27, 195-212.
- PINNAVAIA, T.J. (1986) Pillared clays: synthesis and structural features in: Setton, R. (ed.) *Chemical reactions in organic and inorganic constrained systems*. D. Reidel Pub. Comp. Dordrecht, 151-164.
- PONCELET, G. and SCHUTZ, A. (1986) Pillared montmorillonite and beidellite. Acidity and catalytic properties. In: Setton, R. (ed.) *Chemical reactions in organic and inorganic constrained systems*. D. Reidel Publ Comp. Dordrecht, 165-178.
- SCHUTZ, A., PLEE, D., BORG, F., JACOBS, P. PONCELOT, G., and FRIPIAT, J.J. (1986) Acidity and catalytic properties of pillared montmorillonite and beidellite. *Proc. Intern. Clay Conf. Denver, 1985*, in press.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

NEW APPLICATIONS OF KAOLINS AND FUTURE TRENDS

HAYDN H. MURRAY

Department of Geology, Indiana University
Bloomington, Indiana 47405

The major industrial applications of kaolins continue to be as coaters and fillers for paper, as an essential component in ceramic whitewares, insulators, high alumina refractories, and sanitaryware, as an extender in paint, and as a functional filler in rubber and plastics. New or improved products for each of these applications continue to be developed largely as a result of the development of new and/or improved beneficiation processes. For example new flotation techniques, improved selective flocculation processes, and the development of a super conducting high intensity magnetic separator with a range of 2 to 5 tesla have made it possible for kaolin processors to make high brightness and low iron and titanium content kaolins. These products are used to make high quality coated paper, as feed to make high brightness calcined kaolin extenders for TiO_2 , and for high whiteness, translucent whiteware products.

High brightness, fine particle size calcined kaolins are used as extenders for both anatase and rutile grades of TiO_2 . The price of TiO_2 is approximately 80 cents per pound and the price of the high brightness calcined kaolin is in the range of 15 to 20 cents per pound. Replacement of up to 50% of the TiO_2 is possible in paper and paint systems without a significant decrease in the opacity and at a significant cost savings.

Special kaolins with high green, dry, and fired strengths are used in the body of the ceramic support for the automobile catalytic converters. A predetermined mixture of talc, alumina, silica, and high strength kaolin will, when fired, form cordierite which has an exceptionally low thermal expansion which is a necessary requisite in order that the ceramic support last for at least five years.

Another rapidly expanding market for kaolin is in petroleum refining where the kaolin is used as a catalyst support or as the raw material to make special types of molecular sieves. Another special use for calcined kaolin is to make granular products that are used in special foundry applications to replace silica, olivine, or chrome sands.

With the ever increasing postal rates all over the world the paper industry is moving to lighter weight coated paper. The most effective kaolin product that can produce a lightweight coated paper that will print well is

a delaminated kaolin. This product is produced by separating large stacks or books of kaolin into large diameter thin plates by shearing action. These large diameter, thin plates are also effective in paint and as a filler for special rubber compounds.

Kaolin clays are used in many other applications including the pharmaceutical and drug industry, the pencil industry, as a filler in inks, crayons, mastics, detergents, and many other special uses. The surface chemistry of kaolins which are naturally hydrophyllic can be altered by special treatments to make the surfaces organophyllic or hydrophobic. These specially modified kaolins are used in many applications where better dispersion and higher volume loadings are required.

Kaolin is a versatile and useful industrial mineral. Each year new and modified uses are discovered and the growth of the kaolin industry worldwide will continue in the foreseeable future. Improved beneficiation techniques, modified chemical treatments, locating additional good quality kaolin deposits, and continued industrial growth and development will continue to increase the utilization of this versatile industrial mineral - kaolin.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAY MINERALS AND THE EVOLUTION OF THE SUBBETIC ZONE (BETIC CORDILLERA, SE SPAIN): JURASSIC PELAGIC SEDIMENTATION AND CRETACEOUS SEDIMENTS DEPOSITED IN AN EXTENSIVE PALEOMARGIN ENVIRONMENT.

M. ORTEGA HUERTAS

Dpt. Mineralogy and Petrology. University of Granada (Spain).

INTRODUCTION AND GENERAL GEOLOGICAL CONTEXT

The Betic Cordillera is the westernmost chain of the Mediterranean Alpine Cordilleras. Two well-defined geological complexes have been recognised within the chain, the External Zones and the Internal Zones. The External Zones, made up of Mesozoic and Cenozoic materials deposited upon the continental crust, form part of the southern margin of the Iberian Plate, the geodynamic evolution of which has been interpreted in several different ways (Bourgeois, 1980; Vera, 1981; Malod, 1982, etc.). The External Zones have been subdivided into two palaeogeographic realms, the northern Prebetic Zone and the southern Subbetic Zone and within this latter Zone three separate Jurassic domains are recognised: the External Subbetic, the Middle Subbetic and the Internal Subbetic.

Since 1980 a team of geologists from the University of Granada has been studying the mineralogy and geochemistry of the clay minerals belonging to the lithofacies in the Subbetic Zone. Our general aims have been to understand the palaeogeographic conditions that controlled the sedimentation and determined its spatial and temporal evolution and also to discover the possible source-areas of the sediments.

Two different examples have been chosen as an illustration in point: Lower-Jurassic marls and marly limestone lithofacies deposited in a pelagic marine environment and black-shale deposited in an anaerobic, deep-marine environment during the Middle-Cretaceous.

THE MINERALOGY, SEDIMENTARY ENVIRONMENT AND SOURCE-AREAS OF THE LOWER JURASSIC SEDIMENTS.

The mineralogy of the bulk samples consists of varying quantities (%) of calcite+(dolomite)=50-52, quartz+K-feldspar=12-9 and clay minerals=38-39. The calcite, which is an essential constituent of the carbonate phase, has an average content of 1.80% moles of $MgCO_3$ and corresponds

to a non-magnesian calcite, typical of a pelagic marine environment, in which the carbonate contribution came essentially from foraminifera and coccolithaceae. The temporal and spatial evolution of the bulk mineralogy indicates that the Lower-Toarcian is the most heterogeneous age in the Subbetic Zone (Ortega et al.,1985; Palomo,1987).

The following clay minerals associations have been established (Palomo et al.,1985; Ortega et al.,1985; Palomo,1987):

Association A: illite, chlorite, kaolinite; Association B: illite, chlorite;
Association C: illite, chlorite, (smectite); Association D: illite, chlorite, smectite; Association E: illite, chlorite, mixed-layers I-Sm;
Association F: illite, smectite; Association G: illite, kaolinite, smectite.

The spatial and temporal distribution of the clay minerals suggests that the sedimentation in the easternmost extreme of the Subbetic Zone was initially influenced by emerged areas, while later the sequences become more pelagic. In general, the environment was one of a pelagic marine trough with several swells at different ages and in different parts of basin (Palomo,1987). An analysis of the clay minerals has also shown that any of the lithofacies, whether they be marls and marly limestones or the Ammonítico Rosso, were deposited in various different palaeogeographical conditions with little or no relationship between the lithology and the mineralogy.

When determining the source-areas of the Jurassic sediments it is important to bear in mind not only the distribution of the clay mineral associations but also some crystallochemical parameters such as, the b_0 and the basal spacing of the phengites and the iron content and the basal spacing of the chlorites. This latter parameter is of special interest as it is affected neither by erosion nor weathering and its variations depend directly upon the lithology of the source-area (Liebling and Scherp,1976,1980; Nieto García, 1983). It would appear that the Jurassic sediments in the Subbetic Zone derived from several different source-areas (Palomo,1987). The most general source-rocks were very-low to low grade metamorphic Precambrian, graywacke schists from the Central Iberian Zone of the Meseta (Palomo, op.cit.; López Munguira and Sebastián Pardo,1987). Locally, in the easternmost sector of the Subbetic Zone, there is some influence from the Prebetic Triassic Keuper, which, according to some authors (García Hernández et al.,1980) was

emerged during the Mesozoic. In the same way some Ammonítico Rosso and marls and marly limestone deposits could well have been influenced by emerged areas, possibly the so-called "Dorsal Medio Subbética" (Busnardo, 1979). In other areas the high iron content in the chlorites and their basal spacing (14,16 Å) in a turbiditic sequence suggest that they derived from the Lower-Liassic carbonate platform and, in fact, similar values have been described by Whittle (1986) for sedimentary chlorites.

THE MINERALOGY AND SEDIMENTATION OF THE DARK-MUDSTONE FACIES

The geodynamic conditions and the sedimentary contribution during the Cretaceous in the Betic Cordillera are clearly different from those of the Lower-Jurassic. The relationship between the African and European plates was transtensive and there was also an open communication between the Atlantic and the Tethys. For this reason it is not possible to refer to the geological subdomains that existed during the Jurassic.

In this context the anaerobic black-shale type facies which were deposited during the Aptian-Coniacian both on the continental margins and in the oceans troughs are of great palaeogeographical significance. This type of facies, containing hemipelagites and turbidites with bentonitic clay as their principal component, is well represented in the Subbetic Zone and has similar characteristics to those of other Tethyan margins.

The sedimentology of these facies has been studied by Comas (1979), the mineralogy of "Fardes Formation" by Sebastián Pardo et al. (1984) and López Aguayo et al. (1985) and the mineralogy and sedimentology by López Galindo et al. (1985) and López Galindo (1986a). This author (op. cit.) distinguishes four mineral associations characteristic of different palaeogeographic subdomains:

Association I, to be found in the northern sequences, is made up of "clay minerals (illite, kaolinite, chlorite, smectites and mixed-layers)-calcite-quartz-feldspars". Illite is the dominant clay mineral in proportions of up to 90%. Smectites and mixed-layers are present in minor quantities.

Association II, to be found in the central sequences, corresponds to "clay minerals (smectite, illite, palygorskite, kaolinite)-quartz-calcite-

-feldspars". Smectite is the dominant mineral in proportions of more than 50%. In the hemipelagic samples phyllosilicates are more abundant, while in the turbiditic pelites calcite is.

Associations III and IV are to be found in the southern Subbetic sequences. The former contains "clay minerals (smectite, illite, kaolinite, palygorskite)-quartz-opal CT-calcite-clinoptilolite-feldspars" and the latter "calcite-clay minerals (smectite, illite, palygorskite, kaolinite, mixed-layers)-quartz".

López Galindo (1986a) suggests that, bearing in mind this disposition of this various sequences on the Southern Iberian paleomargin, the distribution of the gravitational sediments and the characteristics of the mineral associations it is possible to distinguish between two main trough environments during the physiographical evolution of this margin in the Middle-Cretaceous.

The hemipelagic and turbiditic materials which were deposited in the northern trough and which have been defined as Association I came essentially from paleocontinent. The southern trough, on the other hand, is where the mineral Associations II, III and IV appear. Here the frequent absent of calcite in the hemipelagic levels indicates deeper deposit, probably below the CCD. In this palaeogeographical environment the distribution of the clay minerals was influenced by bottom and/or contour currents, as witnessed by the compositional uniformity of the Subbetic samples and their analogy with coetaneous Atlantic facies (cf. Brosse, 1982; Debrabant et al., 1985). The chemical composition and crystallinity of the smectites and the association with clinoptilolite and palygorskite suggest that these components come mainly from the submarine alteration of basic volcanic rocks (López Galindo, 1986a, b).

REFERENCES

- Bourgeois, J. (1980). Pre-triassic fit and alpine tectonics of continental blocks in the western Mediterranean: discussion. Geol. Soc. Amer. Bull. 99, 332-334.
- Brosse, E. (1982). Contribution à la minéralogie et à la géochimie des sédiments pélagiques profonds. Comparaison des "black-shales" du Crétacé dans l'Atlantique central nord et des dépôts du Malm et du Crétacé en Briançonnais. Thesis Ecole Nat. Sup. Mines de Paris. 474 p.

- Busnardo, R. (1979). Prebétique et Subbétique de Jaén à Lucena (Andalousie). Lias.Doc.Lab.Géol.Fac.Sc.Lyon, 74, 140 p.
- Comas, M.C. (1979). Sobre la geología de los Montes Orientales: sedimentología y evolución paleogeográfica desde el Jurásico al Mioceno inferior (Zona Subbética-Andalucía). Tesis Doctoral. Universidad de Bilbao, 323 p.
- Debrabant, P.; Delbart, S. et Lemagner, D. (1985). Microanalyses geochimiques des minéraux argileux de sédiments prélevés et Atlantique Nord (Forages du DSDP). Clay Minerals, 20, 125-145.
- García Hernández, M.; López Garrido, A.C.; Rivas, P.; Sanz de Galdeano, C. and Vera, J.A. (1980). Mesozoic palaeogeographic evolution of the External Zones of the Betic Cordillera. Geol.Mijnb. 59, 155-168.
- Liebling, R.S. and Scherp, H.S. (1976). Chlorite and mica as indicators of depositional environment and provenance. Bull.Geol.Soc.Am., 87, 513-514.
- Liebling, R.S. and Scherp, H.S. (1980). Chlorite and mica as indicators of provenance. Clays and Clay Minerals, 28, 230-232.
- López Aguayo, F.; Sebastián, E.; Huertas, F. and Linares, J. (1985). Mineralogy and genesis of the bentonites of the "Fardes Formation" Middle Subbetic, province of Granada, Spain. Miner.Petr.Acta, 29-A, 303-311.
- López Galindo, A. (1986a). Las facies oscuras del Cretácico Medio en la Zona Subbética. Mineralogía y sedimentación. Tesis Doctoral. Universidad de Granada, 267 p.
- López Galindo, A. (1986b). Mineralogía de series cretácicas de la Zona Subbética. Algunas consideraciones paleogeográficas derivadas de la composición química de las esmectitas. Estudios Geológicos, 42, 231-238.
- López Galindo, A.; Comas, M.C.; Fenoll Hach-Alf, P. and Ortega Huertas, M. (1985). Pelagic Cretaceous black-greenish mudstones in the Southern Iberian paleomargin, Subbetic Zone, Betic Cordillera. Miner.Petr. Acta, 29-A, 245-257.
- López Munguira, A. and Sebastián Pardo, E. (1987). Characterization of the phyllosilicates in metamorphic rocks of the SE Hesperian Massif (Ossa Morena and Central-Iberian Zones). (In this book).
- Malod, J.A. (1982). Comparaison de l'évolution des marges continentales au nord et au sud de la Péninsule Ibérique. Thèse d'état Mém. Sci.Terre, Univ. Curie, Paris.
- Nieto García, F. (1983). Las cloritas de las Cordilleras Béticas. Tesis Doctoral. Universidad de Granada, 249 p.
- Ortega Huertas, M.; Palomo, I. and Fenoll Hach-Alf, P. (1985). Mineral composition of the Jurassic sediments in the Subbetic Zone, Betic Cordillera, SE Spain. Miner.Petr.Acta, 29-A, 23-243.
- Palomo, I. (1987). Mineralogía y geoquímica de sedimentos pelágicos del Jurásico Inferior de las Cordilleras Béticas (SE de España). Tesis Doctoral. Universidad de Granada, 344 p.

- Palomo, I.; Ortega Huertas, M. and Fenoll Hach-Alí, P. (1985). The significance of clay minerals in studies of the evolution of the Jurassic deposits of the Betic Cordillera, SE Spain. Clay Minerals, 20, 39-52.
- Sebastián Pardo, E.; López Aguayo, F.; Huerts, F. y Linares, J. (1984). Las bentonitas sedimentarias de la Formación Fardes, Granada, España. Clay Minerals, 19, 645-652.
- Vera, J.A. (1981). Correlación entre las Cordilleras Béticas y otras Cordilleras Alpinas durante el Mesozóico. En: Programa Internacional de Correlación Geológica, PIGC. Real Acad.Ciencias Exactas Fís.Nat. Madrid, 2, 125-160.
- Whittle, C.K. (1986). Comparison of sedimentary chlorite compositions by X-ray diffraction and analytical TEM. Clay Minerals, 21, 937-947.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ORGANISATION, MOBILITY AND REACTIONS OF ORGANIC MOLECULES ON CLAY SURFACES.

R. A. SCHOONHEYDT

Senior Research Associate of the National Fund of Scientific Research (Belgium); Laboratorium voor Oppervlaktechemie, K.U. Leuven, K. Mercierlaan, 92, B-3030 Leuven (Heverlee), Belgium.

In the area of surface chemistry and catalysis of clays 2 main topics have emerged from the literature in recent years. They are : (1) the use of fluorescent probes to study static and dynamic aspects of the adsorption process; (2) the preparation and characterisation of pillared clays.

Our research group is actively involved in the first subject. Up to now the organisation of molecules on the clay surface was studied by static spectroscopic means and by X-ray diffraction. It was impossible to obtain on the dynamics of the adsorption process; organisation of molecules on the surface at very small loadings and the organisation of the clay platelets in colloidal suspension.

To tackle these problems we and other research groups have applied static and dynamic fluorescence spectroscopies of adsorbed probe molecules. The advantages of these techniques are their extreme sensitivity so that very small loadings can be investigated and their time resolution allowing the study of fast physical and chemical processes. The disadvantage is that only luminescent molecules can be studied and this is only a small fraction of the molecules we want to study in the adsorbed state. There are 2 ways to circumvent this problem : fluorescent molecules can be used as probes for the environment in which they are embedded. They give therefore indirectly information about the state of the coadsorbed, non-luminescent molecules; fluorescent chromophores can be built in molecules one wants to investigate in the adsorbed state. This is especially suitable for adsorption of polymers and biological

molecules. Another limitation to the use of these luminescence techniques is that the clays must be practically free of iron.

Three molecules will be discussed in this review : Ru(bipy)₃²⁺, (RuBP), proflavine and 3-(1-pyrenyl)-propyltrimethylammonium(PN). The luminescence of RuBP is quenched by structural Fe³⁺, co-adsorbed Cu²⁺ and Fe(CN)₆³⁻ in solution. In the first case a Perrin mechanism is followed, indicative of the immobility of probe and quencher on the time scale of the excited state lifetime (600 ns). The quenching by Fe(CN)₆³⁻ follows essentially Stern- Volmer behavior. The quenching by Cu²⁺ is peculiar. It must be assumed that part of the Cu ions are preferentially located in the neighborhood of RuBP on the surface.

Proflavine is a cationic dye. Its interest lies in its possibility to protonate and to dimerize. Thus, acid sites and distribution of the molecules at very small loadings can be studied. Absorption spectra as well as luminescence spectra indicate that the synthetic mica-type montmorillonite Barasym is an acid clay : 1 to 2 moles/g sites are present with a pKa of .5. However similar acidity is also observed for Hectorite, exchanged with NH₄⁺, Cs⁺ and K⁺, although the number of sites is less. On the other hand dimerisation occurs on all clays even at extremely small loadings of <0.2 % of the CEC. As the dimer is not emitting, the quenching of the monomer emission by dimerisation can be quantitatively followed. When the logarithm of the monomer quantum yield is plotted against dimer concentration (Perrin mechanism of quenching), straight lines are obtained, the slope of which is a measure of the available surface area in aqueous suspension. We can distinguish between external and total surface areas and obtain ideas about the aggregation of the clay platelets in aqueous suspension. For instance, the total available surface area of K-Hectorite is 470 m²/g and for Na-Hectorite 750 m²/g. Their external surface areas are 120 m²/g.

The dimerisation or non-random distribution of aromatic molecules on the clay surfaces in aqueous suspension is confirmed by the fluorescence spectra of PN. Indeed excimer-like fluorescence is detected, indicative of ground- state complexes. However, detergent molecules like CTAC form micellar-like aggregates on the surface, which solubilize PN preferentially and suppress the excimer formation. The number of excimers on the surface initially increases

and then decreases over a time scale of a few thousands of seconds. This decrease is characteristic of the type of clay and the type of exchangeable cation. It indicates that initially adsorption occurs preferentially on the external surface and that a reorganisation occurs over the total surface area with a decrease in excimer formation. The same redistribution of PN molecules occurs between PN-loaded and unloaded clay particles, when the latter are added to the former in aqueous suspension. The time scale is now several hundreds of seconds

We may conclude that the application of luminescence techniques, both static and time-resolved, allow to obtain detailed information on the adsorption processes on clay surfaces. Up to now the picture is largely qualitative but, as more data are being gathered, a quantitative picture will emerge. At that time models of surface organisation and clay platelets organisation can be developed and quantitatively tested.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**NEW ASPECTS OF IRON OXIDE PROPERTIES AND THE FORMATION OF
IRON OXIDES IN VARIOUS ENVIRONMENTS**

U. SCHWERTMANN, E. MURAD AND L. CARLSON*)

Lehrstuhl für Bodenkunde, Technische Universität München,
8050 Freising-Weihenstephan, F.R.G.

The formation of iron oxide associations in nature is only in part governed by thermodynamic stability relations; very often kinetic favours or hindrances play a more important role. The result is the formation of metastable or instable phases. The formation of such phases must therefore be explained through elucidation of the formation mechanisms.

Examples for transitional phases are presented. The transition between organically bound iron and ferrihydrite in a creek transecting a bog will be described. In another example, the presence of silicon inhibited the formation of crystalline iron oxides during the weathering of a volcanic glass. In deep-sea nodules from the Pacific Ocean, an intimate association of iron and manganese seems to affect iron oxide formation. In all cases, Mössbauer spectroscopy proved to be a valuable tool for phase identification, since the iron concentrations are often so low that the phases in question do not show up in X-ray diffraction, and concentration procedures such as peroxidation to remove

* Geology Department, University of Helsinki, SF-00171
Helsinki, Finland

organic carbon or hydroxylamine extraction to remove manganese may produce artefacts.

In the past, the concept of hematite formation has been based on the presence of ferrihydrite as a necessary precursor, although the close association of both minerals has so far not been observed in natural systems. During the investigation of environments of active iron oxide formation, such as young volcanic ash soils in Hawaii and young ferriferrous sediments from the Atlantis Deep in the Red Sea, the coexistence of ferrihydrite and hematite has been indicated. In the special environment of active iron oxide formation from acid mine waters (pyrite oxidation), in addition to goethite an iron oxide was observed which, according to XRD and Mössbauer spectroscopy, had some but not all characteristics of ferrihydrite.

Finally, experiments conducted to explain the factors which favour goethite or lepidocrocite formation in the same environment showed that the nature of the anions in the solution containing Fe^{2+} may play a decisive role. These anions possibly influence the type of linkage between double bands of $\text{Fe}(\text{OH})_2\text{O}_2$ octahedra which make up the structures of both these FeOOH forms (see separate contribution).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ILLITE/SMECTITE IN THE ROCK CYCLE

J. ŚRODON

Institute of Geological Sciences, Polish Academy of Sciences
Senacka 3, 31-002 Kraków, /Poland/.

According to geochemical calculations, the clay minerals of smectite-illite group account for 30% of the total mass of sedimentary rocks. More recent, precise measurements indicate that the end-member smectite and illite minerals are relatively less abundant: the bulk of this mass consists of mixed-layer illite/smectite.

Pure smectite crystallizes in surface and near-surface environments, both subaerial and submarine. The biggest concentrations of this mineral form in the weathering zone on volcanic rocks, both basic and acidic, but it is well documented that feldspars of plutonic rocks may also weather into smectite. The weathering of sheet silicates /degradation/ may also produce smectite, but more often the process does not go to completion and a mixed-layer clay is formed.

Neoformed smectite is eroded and transported to sedimentary basins, but - for some reasons - even the youngest sediments do not contain smectite but highly expandable illite /smectite. This is, for example, the case of all Tertiary basins of Poland. In sedimentary basins, pure smectite is present only in bentonites. K/Ar dating shows that this phenomenon cannot be explained in some instances by mixing of smectite with illite/smectite - either recycled or formed during weathering of sheet silicates. To explain the data, a mechanism of low-temperature, pre-burial illitization of smectite has to be postulated. Laboratory experiments indicate that illitization takes place in surface temperatures

during alternate wetting and drying of smectites in the presence of potassium-bearing minerals, such as feldspars or micas. Field data are needed to verify this hypothesis. Illitization on the contact with seawater is not supported by laboratory data.

Illitization of smectite is the dominant inorganic diagenetic reaction in most sedimentary basins. The process is well documented in terms of the succession patterns of illite and smectite layers /mixed-layering/, but the evolution of tridimensional organization /polytypes/ has not been studied thoroughly so far. The use of the illitization curve for paleogeothermometry must be very cautious, because of the evident kinetic control of this reaction in the geological time scale.

Several studies have been devoted to tracing the chemical evolution of the expandable clay undergoing illitization. All the papers report the increase of tetrahedral Al and some report also the octahedral Al increasing.

The fixed cations content of the illite layer is still disputable. The value of $0.75/K+Na//O_{10}/OH/2$ obtained by Hower and Mowatt by extrapolation of their fixed cations vs expandability plot has been widely accepted. In a recent study, we argued that this relationship is not linear, and two different illite layers must be present: 0.55 layers, forming at the random stage of illitization, and 1.0 layers, forming at the ordered stage of illitization. This result is reliable, as long as the expandabilities measured by XRD method are correct. TEM measurements of expandability, following the interparticle diffraction concept, are questioning the XRD data. Restricted number of measurements available so far indicates that the fixed cations vs expandability plot becomes a straight line if TEM expandabilities are used. This line means a stable fixed cations content of about $0.9/O_{10}/OH/2$. More measurements are required to verify this result and make it more accurate. NH_4^+ measurements have to be included, because there is growing evidence that it is a common minor member of the fixed

cations population.

A tentative explanation is offered for this systematic discrepancy between TEM and XRD measurements of expandability /overestimation of illite by XRD/. Our present model of mixed-layer diffraction may be inaccurate. Some illite crystallites may not articulate with other illite crystallites and they would diffract as discrete illite, and not as a mixed-layer illite/smectite. TEM measurement cannot see that, but XRD measurement will give overestimated illite content.

Interparticle diffraction concept puts the problem of defining illite into new perspective. Ordered illite/smectites differ from the end-member illite only by the size of crystallites. When the size is big enough, the interparticle diffraction effect /mixed-layering/ becomes negligible. According to our observations of hydrothermal sericites, it happens at temperatures higher than 300°C, when the individual illite crystallites become significantly more than 50 layers thick.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

RHEOLOGY OF ALUMINUM HYDROXIDE GELS

JOE L. WHITE and STANLEY L. HEM

Department of Agronomy and Department of Industrial and Physical Pharmacy, Purdue University, West Lafayette, Indiana 47907 U.S.A.

Recent developments in the understanding of the nature and properties of aluminum hydroxide and aluminum hydroxycarbonate gels have provided a reasonable basis for explaining and predicting the rheological behavior of aluminum hydroxide gels. The contributions provided by the following developments will be described and illustrated: (1) recognition of carbonate as an integral component of the structure of carbonate-containing aluminum hydroxide, (2) establishment of the role of carbonate in influencing the point of zero charge (PZC) of aluminum hydroxide gels, (3) the application of fiber optic Doppler anemometry (FODA) for measuring particle interactions and for quantifying the relationship between the surface potential and the rheological behavior of aluminum hydroxide gels, (4) the use of transmission electron microscopy, together with rates of reaction of aluminum hydroxide with protons and phosphate ions to provide information on the morphology and organization of primary particles into secondary particles and aggregates, and (5) application of scanning electron microscopy with cold-stage and cryostat facilities for freeze/fracture-freeze/thaw studies to establish the three-dimensional arrangement of particles of aluminum hydroxycarbonate in liquid gels when $PZC = pH$ and when $PZC \neq pH$. Some implications and practical applications of these concepts will be given.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

POLYTYPES OF PHYLLOSILICATES: TYPOMORPHIC IMPORTANCE, CRYSTAL CHEMISTRY AND X-RAY IDENTIFICATION

A. WIEWIÓRA

Institute of Geological Sciences, Polish Academy of Sciences, Al. Żwirki i Wigury 93, 02-089 Warszawa, Poland

Several layer silicates have their synthetic monographs in which crystal chemistry and polytypism were taken into account. It is not intended to discuss these data. The goal of the present paper is to draw the attention to some novelties in the crystal chemistry of polytypes of the layer silicates, in the methods of their identification and to remark on the possible implications for the genetic mineralogy.

An important task of the genetic mineralogy is to discover the truly indicative structural features and to use them to define the relationships between the structure and the conditions of crystallization of minerals. Such a "structural typomorphism" (Frank-Kamenetzky, 1968) is developing relatively slowly because the precise data on structure deformations in a function of the crystallization conditions are scarce and because, generally, the polytypism of the layer silicates was underestimated. Usually, the geologists studying the petrogenesis have the valuable informations on a chemistry of the environment and p-T conditions but they are short of informations on the structure. And vice-versa the crystallographers do not have enough field observations to indicate which structural features are typomorphic and how they may be used by the mineralogists.

Until a purposely directed co-operation of the petrologists and crystallographers is established on a larger scale it is timely to perform the systematic analyses of the available structural data in order to select the most pros-

pective typomorphic features. Such a job was partially done by several scientists. But the growing number of the structure refinements and the rapid development of the computer techniques create still better possibilities for preparing synthesis from the structure refinement data. For example, Weiss et al. (1985) analysed 66 refined crystal structures of micas in order to characterise the geometry of the octahedral layer. This may be fully characterised by metal - anion bond length, two ratios of anion - anion octahedral edges, mean fictive ionic radii (MEFIR), octahedral flattening angle and counter rotation of top and bottom anion triads. Amongst the features characterising the geometry and distortions of the octahedral, tetrahedral layers and the interlayer are some which are straight-forward related to the chemical composition and may be predicted from chemical composition. It is not clear which features are controlled by physical parameters.

Recently appeared several publications inspired by the so called "order-disorder" theory which were very helpful in making the real order in our understanding of the crystallochemical foundations of the phyllosilicates structures, classification and identification of their polytypes. First of all should be mentioned papers of dr Ďurovič and his co-authors, Dornberger-Schiff, Mikloš, Backhaus, Weiss, in which they promoted the new look into the octahedral layer from the point of view of the equivalence-nonequivalence of M(1), M(2), M(3) occupations. We should accept their division: homo-, meso-, heterooctahedral structures (see e.g. Ďurovič et al., 1984) as this concept is in the background of the classification of polytypes of all groups of phyllosilicates and of X-ray methods of their identification. Accordingly, the principles of X-ray identification of polytypic structures may be summarised as follow.

Unambiguous identification of any polytype including heterooctahedral polytypes may be done via structure refinement. Meso- and homooctahedral polytypes may be identified by the visual comparison of the calculated and experimental F_{201}^2 together with F_{021}^2 values from single-crystal

experiments. Application of the powder methods is strongly limited due to great similarities, not to say identity of the diffraction patterns of some polytypes, as it was shown for micas by Weiss and Wiewióra (1986). Nevertheless, some layer silicates are available only in powders. Therefore, the great interest is in some advanced techniques, namely, the oblique texture diffractometry with $\theta, 2\theta$ non-coupling (Plancon et al., 1982), with $\theta, 2\theta$ coupling aided by the computer simulated patterns (Wiewióra and Weiss, 1985) and in the oblique texture photography (Rieder, 1986). It should be mentioned that all these methods, including the single-crystal ones, are burdened by the statistical effect the greater the bigger is the irradiated volume during experiment. The only technique which is free of this effect and may be used to identify the polytypic structures is HRTEM.

REFERENCES

- Durovič S., Weiss Z., Backhaus K.O., 1984, *Clays and Clay Minerals*, 464-474.
- Frank-Kamenetzky V.A., 1968, *B.D.G. geol. Wiss.*, Berlin, Bd. 13, 3.
- Plancon A., Rousseaux F., Tchoubar D., Tchoubar C., Kri-nari G. and Drits V.A., 1982, *J. Appl. Cryst.* 15, 509-512.
- Rieder M., 1986, *Abstracts IMA*, Stanford.
- Weiss Z., Rieder M., Chmielova M., Krajiček J., 1985, *Am. Mineral.*, 747-757.
- Weiss Z. and Wiewióra A., 1986, *Clays and Clay Minerals*, 53-68.
- Wiewióra A. and Weiss Z., 1985, *Clay Minerals*, 231-248.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERAL WEATHERING IN COOL TEMPERATE CLIMATES AND ITS IMPLICATIONS FOR
"ACID RAIN" AND CATCHMENT STUDIES

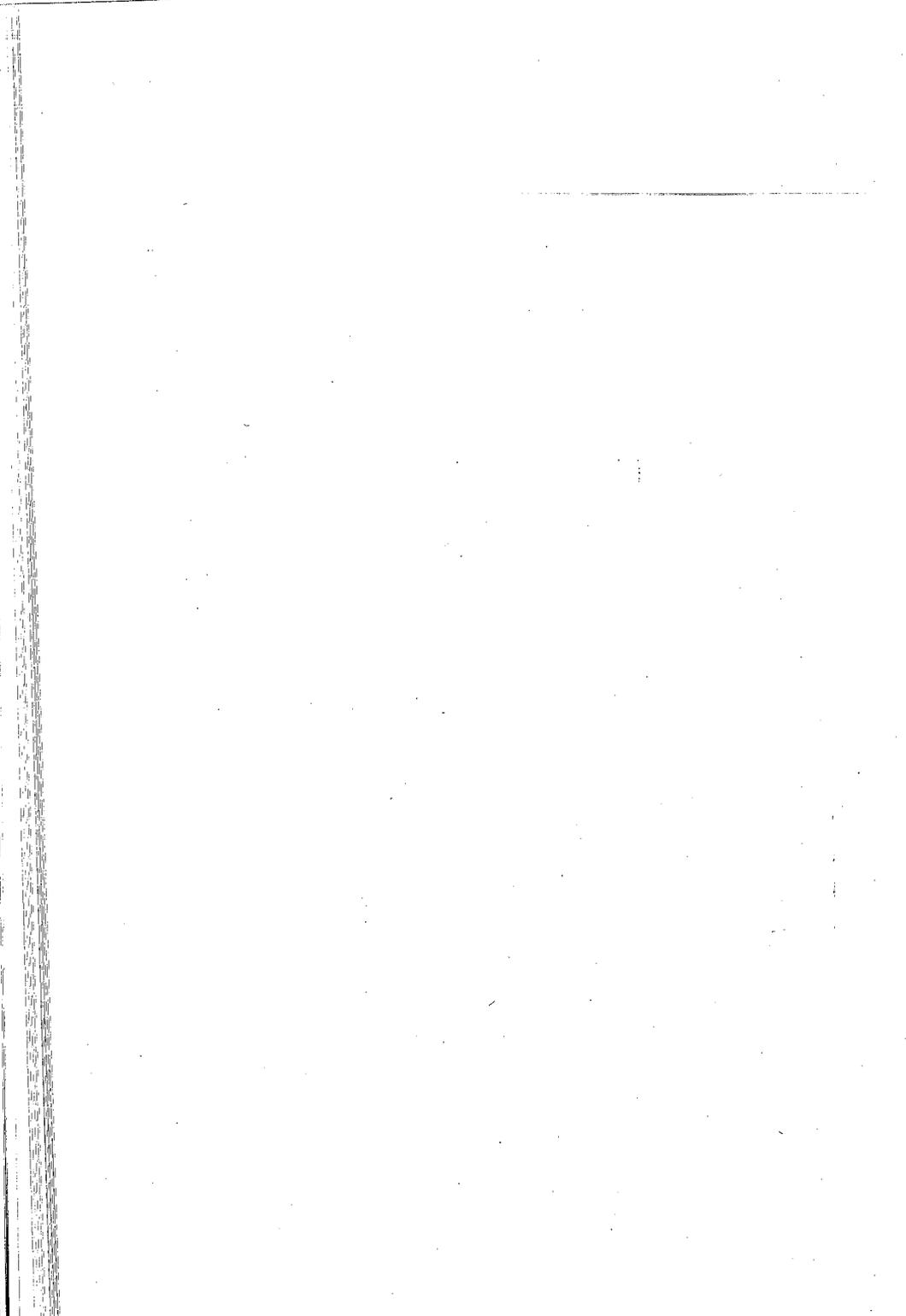
M.J. WILSON AND A. MELLOR

The Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen,
AB9 2QJ, Scotland, U.K.

The deleterious effects of acid precipitation on the environment have been widely recognized, research and documented, particularly by Scandinavian scientists, since the early 1970s. Evidence has accumulated to show that there is a connection between acid precipitation and the acidification of soils, surface waters and groundwaters, with consequent impacts on forests, aquatic life and groundwater quality respectively. Mineral weathering is an important factor to be taken into account when considering the susceptibility of catchment areas to the effects of acid precipitation, because it is the principal means of replenishing exchangeable bases in the soil and also results in the formation of fine-grained clays which dominate exchange and adsorption in mineral soils. Under the auspices of SWAP (Surface Water Acidification Programme) weathering and mineralogical studies have been made of the soils in three upland catchments in Scotland and Norway which are representative of heavily acidified, moderately acidified and pristine sites and are developed on parent material derived from schists, granite and granitic gneiss respectively. In the prevailing cool, temperate climate, podzols and podzolic soils, with well-developed A, B and C horizons, are dominant. Major mineral weathering processes in each of the three catchments tend to be similar and involve (a) total decomposition of chlorite, particularly in A horizons, (b) vermiculitization of dioctahedral mica, sometimes via a regularly interstratified mica-vermiculite (c) hydroxy aluminium interlayering of vermiculitic minerals, particularly in B horizons (d) precipitation of poorly ordered imogolitic/allophanic material in B horizons and (e)

intense corrosion of plagioclase feldspar and decomposition of biotite in A horizons. In some soils, gibbsite and kaolinite also occur but these minerals are interpreted as relicts of a previous weathering cycle. Mechanisms of weathering as well as long- and short-term mineral weathering rates in the catchments will be discussed and their significance with regard to future acidification trends assessed.

SUMMARIES





Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

EPITAXIAL GROWTH OF ACICULAR MAGHEMITE CRYSTALS ON QUARTZ

MARIA M. ABREU, M.O. FIGUEIREDO, J.C. WAERENBORGH & J.M.P. CABRAL

Inst. Sup. Agronomia, Tapada Ajuda, 1399 Lisboa (Portugal)
Centro Crist. Miner., IICT, 1000 Lisboa (Portugal)
Dept. Quím., ICEN-LNETI, 2685 Sacavém (Portugal)

In previous works /1,2/ maghemite with a particular needle-like morphology and arranged in a star-like pattern was identified, associated with hematite and quartz in the sandy fraction of B horizons of Alfisols and one Ultisol from Alentejo (Southern Portugal). Crystals with this same morphology were obtained when the synthesis was carried out on a solution of ferrous and ferric chlorides and catalysed by fresh quartz surfaces. By contrast, on the absence of quartz, maghemite crystals formed in solution were sub-rounded, with dimensions forty times smaller than the acicular ones.

The formation of needle-like maghemite occurs only at reactive, fresh-surface, sites of quartz by a surface complex formation, through ligand exchange with iron compounds (probably green-rust). Maghemite without a particular morphology was observed (SEM) at the non-active quartz surfaces and in this case represents only a deposition.

The relative orientation of the individual maghemite needles could not be ascertained but it is clearly seen from ultrathin sections in TEM to be close to 60° /1,2/. Considering the structural arrangements in both quartz and maghemite, and the existence of donor oxygens at quartz surfaces, a possible mechanism is advanced to explain the oriented crystallization of maghemite with unusual acicular morphology and hexagonal star-like pattern. α -Quartz has a trigonal crystal structure that can be described in terms of a lacunar packing of oxygen atoms with a three-stored layer sequence /3/

deserving close similarities to the cubic close-packing of oxygen atoms in the keno-spinel arrangement of δ -Fe₂O₃. However, such structural control at active surfaces could not yet be proven. In fact, electron microdiffraction patterns of acicular maghemite from soil samples showed to be polycrystalline /1/, and, up to now, single crystal X-ray work on quartz grains retaining maghemite was not conclusive in what concerns the existence of a particular texture.

⁵⁷Fe Mössbauer spectra of soil samples, taken at room temperature show two unresolved hyperfine split patterns that can be fitted with two magnetic splittings, one characteristic of α -Fe₂O₃ /4/ and the other of γ -Fe₂O₃ /5/. On the other hand, the very low absorption at velocities corresponding to the two low velocity peaks due to octahedral iron in stoichiometric Fe₃O₄ /4/ seems to confirm both chemical analysis and X-ray diffraction data pointing to the presence of a highly oxidized member of the series Fe₃O₄ - γ -Fe₂O₃. Room temperature spectra of synthetic samples were very poorly defined due to their low degree of crystallinity; low temperature measurements are now in progress.

- /1/ ABREU, Maria M. & ROBERT, M. (1985). Geoderma, 36, 97-108.
- /2/ ABREU, Maria M. & ROBERT, M. (1985). Congr s Internat. Micromorphologie des Sols, Paris (in press).
- /3/ FIGUEIREDO, M.O. (1977). Com. Ser. Geol. Port., LXII, 19-34.
- /4/ GREENWOOD, N.N. & GIBB, T.C. (1971). "M ssbauer Spectroscopy". Chapman and Hall, Ltd. London, pp. 239-254.
- /5/ TOPSOE, H., DUMESIC, J.A. & BOUDART, M. (1974). Journ. Physique C, 35, C6:411-413.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FLUORINE IN CLAY MINERALS AND ITS BEHAVIOR DURING FIRING

H. ACKERMANN, H. KROMER

Staatl. Forschungsinstitut für Angewandte Mineralogie bei der TU-München,
D-8400 Regensburg, West-Germany

Problems of pollution by toxic trace elements have become more and more important. The investigations concern the fluorine contents of various clays of different geological formations from the Triassic to Diluvium Age which are used in the ceramic industries. Moreover the loss of fluorine of the fired samples was studied. The investigated materials concern kaolins, clays for the production of technical porcelains, white wares and stone wares, refractory clays, clays and loams for the production of bricks and roof-tiles.

The fluorine was determined by melting the materials with five to ten times the quantity of potassium-sodium-carbonate, dissolution of the cooled melt in sulfuric acid and distillation in superheated water steam. The fluorine in the distillate was determined by a fluorine sensitive electrode.

Kaolins show fluorine contents from 100 to 3000 ppm. The amounts seem to be related to the genesis and to the original rocks. For example the kaolins of Hirschau-Schnaittenbach generated from sediments by weathering and circulating groundwaters have low fluorine contents (200 ppm). Kaolins formed from in situ disintegrated granitic rocks commonly have higher fluorine contents and can show values up to several thousands ppm F, as can be demonstrated by kaolins of Cornwall.

The fluorine of ceramic clays of various geological formations ranges from 300 to 1500 ppm. Also a correlation between geological formation, age, and mineralogical composition is observed. Tertiary kaolinitic clays show an average of F-values of 500 ppm but the contents can vary with contents of quartz and also with the local deposit. Illite and montmorillonite-bearing diluvial loams vary from 600 to 800 ppm fluorine. Keuper-clays high in illite and mixed-layer minerals show 800 to 1000 ppm F and smectite-rich clays vary between 1000 and 1400 ppm F depending on the mineral composition.

Talcs and steatites range from about 100 ppm to more than 2 % fluorine. The amounts in materials formed by metasomatic processes are fairly high, compared with talcs generated from ultrabasic rocks.

Feldspars and feldsparsands show fluorine amounts between 80 to 200 ppm whereas in feldsparporphyric rocks 250 to 325 ppm fluorine are found.

The emission of fluorine from clayey materials during firing was investigated by analyzing samples heated in air to temperatures from 1000 to 1300 °C. The release of fluorine is related to the mineralogical composition and the particle size distribution of the starting material. This in turn controls the formation of a molten phase which keeps the fluorine in the body. Therefore the emission of fluorine reaches its maximum at about 1000 °C whereas remaining fluorine is fixed in the vitrified body. Calcia supports the fixation of fluorine but this needs the presence of calcia in an extremely fine grain size.

INTERACTION OF PHOTOCHROMIC MATERIALS WITH SMECTITES

J.M. ADAMS** AND A.J. GABBUTT*

Edward Davies Chemical Laboratories, University College of Wales,
 Aberystwyth, Dyfed (United Kingdom).

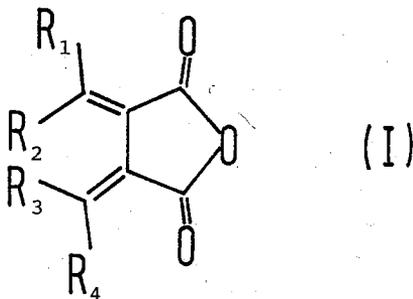
Present addresses:

**Central Research Laboratories, ECC International Ltd., St. Austell,
 Cornwall (England).

*Laporte Inorganics, Moorfield Road, Widnes, Cheshire (England).

INTRODUCTION

Reversible light-induced colour changes have been observed in a wide variety of organic and inorganic systems: The phenomenon is termed photochromism. Molecules having the generalised structure (I) are termed fulgides.

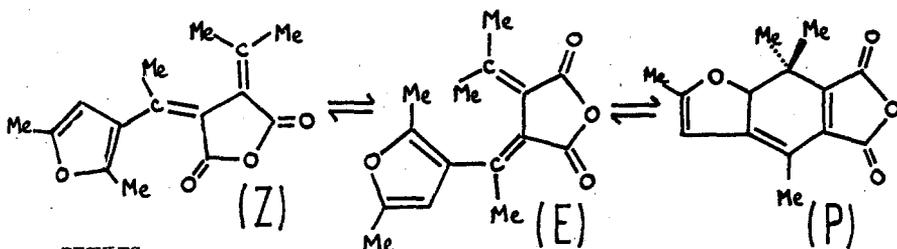


When at least one of the substitutes $R_1 - R_4$ is an aryl group, the materials are photochromic, exhibiting colour changes dependent upon the particular substituents.

There are numerous potential applications of these organic photochromic materials, ranging from data storage to packing labelling. The properties of interest include the particular colours involved and the degree of fatigue-resistance, i.e. the number of reversible colour changes possible with little degradation.

In 1981 Trundle showed that when certain fulgides were absorbed on smectite clays, they showed significant shifts in the wavelength of visible absorption spectra, e.g. fulgides which produced a photochrome which was normally red in organic solution, gave a photochrome which was blue when supported on a clay. This effect can be of significance in many applications.

In the present work we have studied the interaction between the fulgide α -2,5-dimethyl-3-furyl ethylidene (isopropylidene) succinic anhydride and a variety of smectite clays. In solution, the following forms of this organic species can exist



RESULTS

Preliminary studies were carried out by heating the fulgide and clay in toluene reflux; these experiments showed that the various clays examined could be divided roughly into two groups in regard to their interaction with the fulgide. For some clays the fulgide was able to penetrate the interlayer region, while for the remainder the organic molecules were confined to the surface of the clay. Complexes formed with this latter group were found to be highly sensitive towards moisture. The former group were less sensitive to moisture levels and stabilized the photochrome towards the light induced reverse reaction. Typically, and significantly, the absorption maximum of the fulgide and photochrome were shifted by 20 and 80 nm respectively, relative to values in organic solution.

More detailed studies demonstrated that the clays were catalyzing several reactions on very different time scales:

- (i) Z-E isomerization of the fulgide. This process was found to be an acid-catalyzed interlayer reaction, strongly sensitive to the presence of polar molecules, even at very low concentrations. The most effective catalysts were clays exchanged with trivalent interlayer cations, equilibrated at

low relative humidity before use. In toluene reflux reactions were complete in ~ 1 hour.

- (ii) The ring closure reaction to give the photochrome (i.e. $E \rightarrow P$) was found to be a surface catalyzed, thermal reaction. These reactions were much slower than the $Z - E$ isomerizations, taking of the order of a day in toluene reflux. The reaction rate did not depend to any great extent upon the type of spectite used, or, within reasons, any pre-treatment of the clay.
- (iii) The decomposition of both forms of the fulgide and also of the photochrome. These reactions were found to be acid-catalyzed and gave at least four different products. The reactions occurred in the interlayer region of the clay, but were much slower than the previous reactions, taking days or months to reach levels at which the product could be detected.

DISCUSSION

The $Z - E$ isomerization reaction is of practical importance, being complete on a much shorter timescale, and with less complexity than the solution process, which is multi-stage and takes ~ 5 days. Alternative procedures attempted using a variety of acids in place of the clay catalyst failed, as the acid not only protonated the carboxyl oxygen (a pre-condition for the isomerization to occur), but also cleaved the furan ring.

The ring-closure, which led to formation and stabilization of the photochrome has also been shown to occur over carbon. The molecule itself is planar and appears to be stabilized when sorbed on surfaces. This interpretation is consistent with the lack of variation shown with modified and natural smectites.

While the decomposition products were not identified with complete certainty, they most likely result from acid catalyzed attack on the anhydride ring of the fulgide.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**LATE QUATERNARY DEPOSITIONAL PATTERNS OF CLAY MINERAL IN THE EBRO
MARGIN (WESTERN MEDITERRANEAN): PALEOCLIMATIC INTERPRETATION**

Belen ALONSO

Departamento de Geología Dinámica, Geofísica y Paleontología.
Universidad de Barcelona. Gran Via, 585. 08007 Barcelona.

INTRODUCTION

During the last twenty years numerous studies have been performed on the nature, occurrence and meaning of Mediterranean clay minerals (1,2). The purpose of this paper is to show that temporal variations in clay composition can be used to reconstruct climatic changes that have existed since the Late Quaternary. These changes are noted at depth between 1100 and 1800 meters in cores of the Ebro distal margin. Distribution of clay mineralogy has been compared with various parameters such as texture, carbonate influence and microfauna in order to determine its geological significance (3).

CLAY MINERALOGY AND SEDIMENT CHANGES WITH TIME

Vertical distribution

The changes observed in clay mineralogy of 55 cores are associated to many parameters. The illite crystallinity index above 2 (poorly-crystallized) is found in surficial layers (< 50 cm) of cores formed by brown and yellow hemipelagic muds. These layers are usually at the top of most western Mediterranean cores and are characterized by low chlorite/kaolinite and illite/kaolinite ratios and high calcite/quartz ratio. A reverse pattern occurs when illite is well crystallized (index < 2) in underlying layers of gray hemipelagic mud and gray turbiditic mud. These deposits contain high chlorite/kaolinite and illite/kaolinite ratios and low calcite/quartz ratio (Fig. 1). These differences suggest a decrease in detrital content (mica, quartz, illite) and an increase in illite crystallinity index in the less than 2 μm fraction toward the top of sedimentary sequences. This also indicates that the depositional

evolution of sediments reflects an increase in biogenic components of the $> 63 \mu\text{m}$ fraction.

Paleoclimatic significance

Changes in the composition of clay mineral associations of marine sediments and corresponding environmental changes on adjacent landmasses are mostly climate-controlled (4). This study shows that during the Late Quaternary there has been a temporal variability of clay mineralogy related to changes between glacial and interglacial periods. Cores in the Ebro distal margin penetrating only the Late Pleistocene (< 17000 years) allow reconstruction of climatic conditions. In the paleoclimatic curve as determined from mineralogical data, two different climatic periods are evident: 1) a cold-dry period and 2) a warm-humid period (Fig. 1). During the cold-dry climate the particles transported to the sea had a well crystallized illite and thus an increase of chlorite/kaolinite, illite/kaolinite ratios and decrease in calcite/quartz ratio. The most recent period is represented by warm-humid climate, with poorly formed crystallized illite and sediment of low chlorite/kaolinite, illite/kaolinite ratios and high calcite/quartz ratio. The uppermost layers (< 50 cm) of the cores are attributed to the Holocene period and show clay mineralogy and sediment composition different from that of underlying layers of the Late Pleistocene/Early Holocene.

In addition, yellow and brown hemipelagic muds with poorly crystallized illite of Post-glacial sediment are attributed to climatic fluctuations during the Atlantique Phase. The grey hemipelagic and grey turbiditic deposits with well-crystallized illite are related to Late Pleistocene/Early Holocene deposition (Fig. 1).

- (1) Monaco, A. Thèse Sci.Nat.Montpellier, 2 vol. 1971.
- (2) Blac-Vernet et al., *Palaeogeogr.Palaeoclimat.Palaeoecol.* 6:215-235. 1969.
- (3) Alonso, B. Tesis Doctoral. Univ, Barcelona: 384. 1986.
- (4) Chamley, H. *Utrecht Micropal. Bull.*, 30:71-91. 1983.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF THE UNDERCLAYS OF THE
"PAQUETE MARIA LUISA" (CENTRAL COAL BASIN, ASTURIAS, SPAIN)

O. E. ALONSO AND C. BRIME

Departamento de Geología, Universidad de Oviedo, Spain.

The mineralogy and geochemistry of the underclays between the coal beds of the "Paquete Maria Luisa" have been investigated in order to determine if they could help to establish a discrimination between the underclays that allow their use as correlation markers in the basin. Samples were obtained from underclays corresponding to nine different coal beds of the "Paquete Maria Luisa" in the Aller valley (Asturias, Spain). The underclays were sampled at two, three or more positions to determine if vertical changes were present. Each sample was analyzed for 24 elements by either X-ray fluorescence spectrometry and atomic absorption. The clay mineralogy is described based on powder and oriented aggregates of the whole rock samples and clay sized fractions subjected to standard treatments.

The mineralogy of the underclays is mainly illitic, more than 55 % of the sample, with smaller amounts of chlorite, kaolinite (chlorite always more abundant than kaolinite) paragonite, pyrophyllite and mixed-layers illite/smectite and muscovite/paragonite. This mineralogical association is clearly anchizonal (FREY 1970) and similar to that described by ALLER and BRIME (1985) in pelitic samples from the southern part of the Central Coal Basin. The measurement of the illite crystallinity index of the clay fraction yielded also anchizonal values. The scarcity of kaolinite could be due to the transformations undergone by the rocks under anchemetamorphic conditions. There is no consistent variation with increasing depth below the coal

The data, 38 mineralogical and geochemical variables, were treated by stepwise discriminant analysis (BMDP 7M, JENRICH and SAMPSON 1983).

The variables that serve as the best discriminators between underclays are: illite and mixed-layer I/S content on both whole rock and clay fraction, illite crystallinity of the clay fraction, pH of the samples, and the elements (in order of atomic number) Na, Al, K, Ti, V, Co, Sr, Zr, Nb, Ba. These are the variables that have different values from underclay to underclay, but relatively small ranges of concentrations within underclays.

REFERENCES

- ALLER, J. & BRIME, C. 1985. Deformación y metamorfismo en la parte sur de la Cuenca Carbonífera Central (NO de España). Compte Rendu Dixieme Congres International de Stratigraphie et de Géologie du Carbonifere, Madrid 1983, vol. 3, 541-548.
- FREY, M. 1970. The step from diagenesis to metamorphism in pelitic rocks during alpine orogenesis. Sedimentology, vol. 15, 261-279.
- JENNRICH, R. & SAMPSON, P. 1983. Stepwise discriminant analysis. In DIXON W. J. et al. (Eds) BMDP Statistical software. University of California Press, Berkeley, 519-537.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**PREPARATION AND CHARACTERISATION OF IRON OXIDE PILLARED
MONTMORILLONITE**

J.E.M. ALLAN, J.M.D. COEY, D.H. DOFF*, AND N.H.J. GANGAS**

Department of Pure and Applied Physics, Trinity College, Dublin 2,
(Ireland)

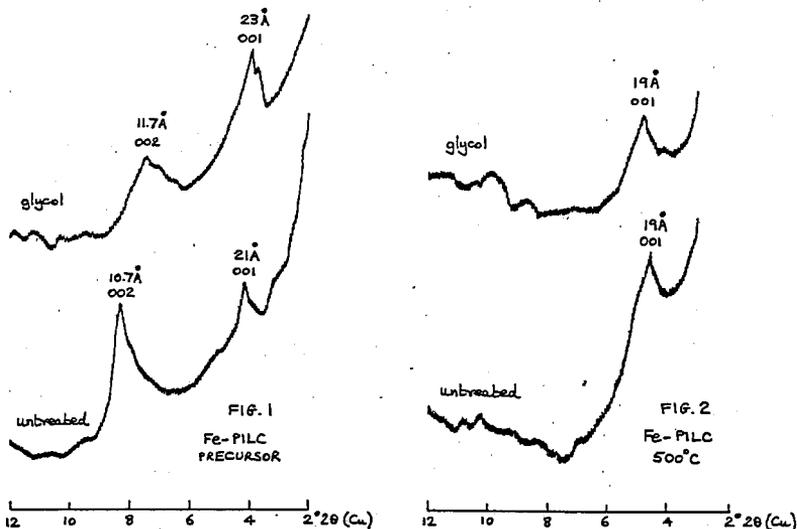
*Department of Geology, Trinity College, Dublin 2, (Ireland)

**Kifissias Avenue 108, GR-11526 Athens, (Greece).

Pillared or cross-linked smectites in which the interlayer is converted into a two dimensional zeolite-like structure have recently attracted much interest because of their catalytic and molecular sieving properties. The pillared clays (PILCs) which are best understood so far are those in which aluminium oxide pillars act as molecular-sized props permanently separating the silicate layers of the clay. If, however, the pillars are formed of iron oxide interesting and novel magnetic properties may also be expected (Gangas et al., 1985). Large iron cations and polycations which can occupy the exchange sites in smectite interlayers include hydroxy-Fe (III) and phenanthroline-Fe (II) complexes but in these cases calcination does not result in formation of a PILC. On the other hand, reaction of smectites with trinuclear Fe(III) carboxylate complexes forms an expanded precursor which does yield a PILC on firing.

In the present study an iron oxide pillared montmorillonite was prepared by a modification of the method of Yamanaka et al. (1984). $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] + \text{Cl}^-$, was prepared by crystallisation from mixed solutions of ferric chloride and sodium acetate. Texas bentonite (STx-1) was chosen as the starting clay material because of its low iron content. Three to five successive treatments (1meq Fe (III) complex per g Na⁺ clay) were carried out with washing in between

each step in order to ensure complete displacement of Na^+ ions. The product, or PILC precursor, was brown in colour and its x-ray diffraction pattern showed two orders of reflection ($I_{002} > I_{001}$) corresponding to a layer spacing of 21\AA . Treatment with glycol increased this spacing to 23\AA (Fig. 1). On firing at 500°C the clay does not collapse to the 9.6\AA spacing expected of a smectite but remains at 19\AA and this spacing is not affected by treatment with glycol (Fig. 2), confirming that cross-linking has occurred.



The magnetic susceptibility of the trinuclear ferric salt was $0.22 \text{ J/T}^2/\text{Kg}$ of sample and that of the exchanged montmorillonite was $0.19 \text{ J/T}^2/\text{Kg}$ of sample. After firing, however, the magnetisation curve showed a small ferromagnetic component of $0.4 \text{ J/T}^2/\text{Kg}$ of sample in addition to the paramagnetic component.

The Mossbauer spectrum at room temperature of both the trinuclear iron (III) chloride and the PILC precursor showed a quadrupole doublet with isomer shift $\delta = 0.39$ (3) mm/s and quadrupole splitting $\Delta = 0.64$ (5) mm/s consistent with the trinuclear species being preserved in the clay. After firing, however, the

room temperature spectrum was broad and asymmetric, showing signs of incipient magnetic relaxation.

REFERENCES

- Gangas, N.H.J., van Wonterghem, J., Morup, S., and Koch, C.J.W. 1985. *J. Phys, C: Solid State Phys.*, 18, L1011-L1015.
- Yamanaka, S., Doi, T., Sako, S., and Hattori, M. 1984. *Mat. Res. Bull.*, 19, 161-168.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CRYSTALLINITY OF LOWER CRETACEOUS KAOLINITES OF TERUEL,
SPAIN.

J.M. AMIGO, J. BASTIDA, M.J. GARCIA AGRAMUNT, A. SANZ & J.
GALVAN*.

U. Cristalografía y Mineralogía. Dep. Geología. Universidad de Valencia (España).

* Instituto de Edafología y Biología Vegetal. CSIC (Madrid España).

In the present work 30 kaolinite samples from kaolinitic clays of the Lower Cretaceous in the area of Teruel (Iberian Range, Spain) have been studied.

X-ray diffraction patterns with a fast goniometer speed ($1^\circ 2\theta/\text{mn}$) registering the 001 and 002 peaks and the 0211 bidimensional band have been performed, and the crystallinity has been obtained by comparing the fast patterns with classifications based on the appearance of diffraction patterns, which are given in the bibliography (THOREZ, 1976)

The 001 and 002 reflections have also been studied in X-ray diffraction patterns of oriented powder aggregates with a low goniometer speed ($1/10^\circ 2\theta/\text{mn}$), and the crystallite size in the $[001]$ direction has been calculated by the WILLIAMSON & HALL (1953) method and by the program SI ZE (SIEMENS DIFRAC 310), and the results of both methods have been compared.

The extent of the hidrazine intercalation has been tested by the TCHOUBAR et al. (1982) index, and the particle size has been observed by T.E.M.

The crystallinity criteria proposed to date, are difficult to apply to polimineralic samples like those studied in this work.

A good relationship between the progressive lack of resolution of the (hkl) peaks forming the 0211 bidimensional band and the line broadening of the 001 and 002 reflections has been observed. Because of that relationship we propose the half-maximum line breadth ($B_{1/2}$) of the 001 and 002 reflections to be a good crystallinity index.

The WILLIAMSON & HALL (1953) method and the results obtained by the program SIZE show the non-existence of internal strain in the |001| direction in the reported kaolinites. So $B_{1/2}$ can be applied to calculate the crystallite size in that direction. This can be seen in the plot of crystallite size calculated by the WILLIAMSON & HALL method versus the results of the program SIZE, which gives a straight line with $\rho=0.97$.

The extent of the hydrazine intercalation reaction is closely connected with the crystallite size in the c^* direction but seems not to be related with the particle size observed by T.E.M. The plot of TCHOUBAR index (TCHOUBAR et al., 1982) versus crystallite size in the c^* direction gives a straight line with $\rho=0.94$.

BIBLIOGRAPHY:

- TCHOUBAR, C. et al. (1982). Bull. Minéral. 105, 477-491.
- THOREZ, J. (1976). "Practical Identification of Clay Minerals". Ed. G. LELOTTE. Belgique.
- WILLIAMSON, G.K. & HALL, W.H. (1953). Acta Metallurgica 1, 22-31.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**FIRST STEPS OF SMECTITE-ILLITE TRANSFORMATION WITH
HUMECTATION AND DESSICATION CYCLES.**

C.Y. ANDREOLI(1), M. ROBERT(1) and C.H. PONS(2)

(1) Station de Science du Sol, I.N.R.A., 78000 - Versailles (France), (2) Laboratoire de Cristallographie, Université d'Orléans, 45046 Orléans (France)

Potassium fixation by 2:1 phyllosilicates is an important phenomenon in term of its agronomic impact and its consequence in desimentology concerning transformation of smectite into illite.

This selectivity in K-fixation is related to the weak cation hydration energy and dehydration phenomena.

Recent studies (Gaultier and Mamy, 1975 ; Eberl, 1984) have shown that collapse of smectite layer to 10 Å, associated with the development of tridimensional ordering of the initially turbostratic smectite structure can be obtained by wetting and drying cycles.

The purpose of the present report is to better understand and determine these sequences by using High Resolution Transmission Electron Microscopy (HRTEM) and small-angle X-ray Scattering (SAXRS).

Low charge montmorillonite (Wyoming), 2:1 soil clays (interstratified illite-smectite, used as a reference), saturated with potassium, were investigated during wetting and drying cycles (dessication at 60°C).

The characteristics examined were related to external and internal surface area and to the clay organization.

Clay paste samples were prepared at given water suction pressure (pF 1.5) and studied using SAXRS and HRTEM.

Results obtained by transmission electron microscopy show that the first phase of smectite transformation is a "textural clay transformation" (Tessier and Pédro, 1987). We could observe a particle reorganization by regrouping and alignment of the elementary particles leading to the formation of thick pseudocrystals similar to those of mica particles (photos 1-5).

Small-angles XRS indicates at every step (before the

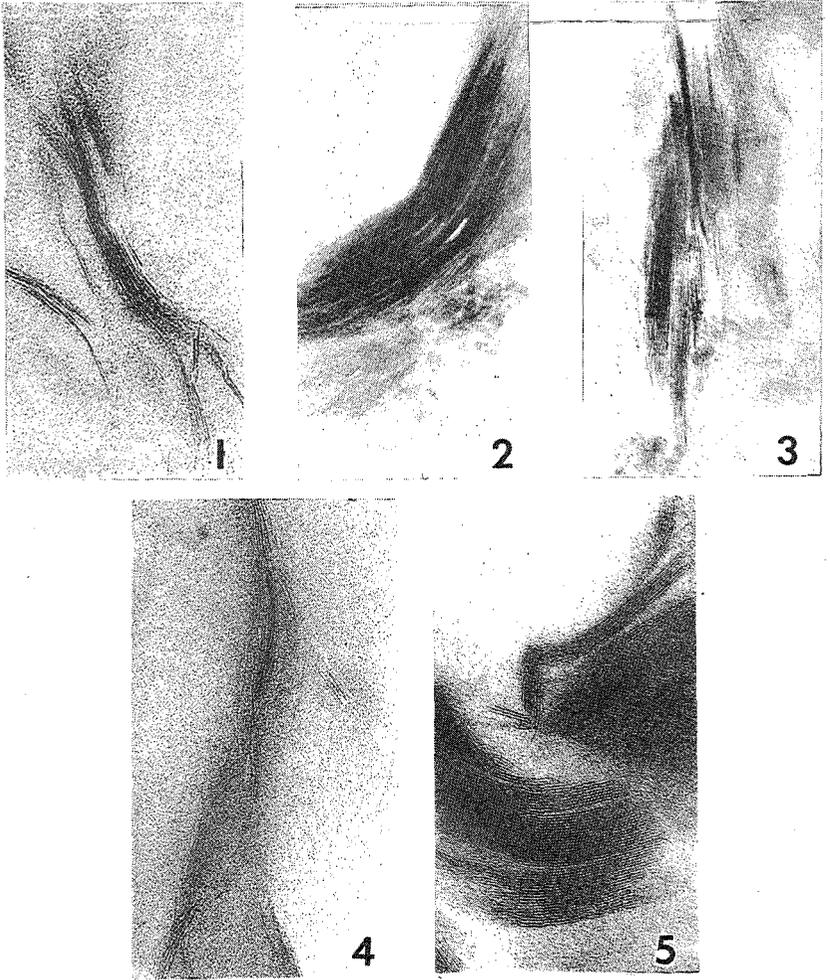
first dessication, 1st, 10th and 20th dessications) the number of particle layers and the proportion of layers of 10 or 14 A.

A correlation was found between textural rearrangement, layer collapse and the variations in external and internal area.

These results are complementary to those of Nadeau (1985, Nadeau et al., 1984a, 1984b) and Eberl (1980, 1984) concerning the interstratified minerals and allow the determination of the first steps of smectite to illite transformation.

REFERENCES

- EBERL D.D. (1980). Alkali cation selectivity and fixation by clay minerals. *Clays and Clay Minerals* (28), 161-172
- EBERL D.D. (1984). Clay mineral formation and transformation in rocks and soil. *Philos. Trans. Roy Soc. London A-311*, 241-157
- MAMY J. et GAULTIER J.P. (1976). Les phénomènes de diffraction des rayonnements X et électronique par le réseau atomique. Application à l'étude de l'ordre cristallin dans les minéraux argileux. II Evolution structurale de la montmorillonite associées au phénomène de fixation irréversible du potassium. *Ann. Agron.* (27) 1-16
- NADEAU P.H. (1985). The physical dimensions of fundamental clay particles. *Clays Minerals* (20) 499-514
- NADEAU P.H., WILSON M.J., Mc HARDY W.J. and TAIT J.M. (1984). Interparticle diffraction : a new concept for interstratified clays. *Clay Minerals* (19) 757-769
- NADEAU P.H., TAIT J.M., Mc HARDY W.J. and WILSON M.J. (1984). Interstratified XRD characteristics of physical mixtures of elementary clay particles. *Clay Mineral* (19) 67-76
- TESSIER D. et PEDRO G. (1987). Mineralogical characterization of 2:1 clays in soils : importance of the clay texture. In *Proc. Int. Clay Conf. Denver 1985* (in press)



24 nm

Photographs 1-5: Transmission electron microscope lattice fringe images showing the first phase of smectite transformation with the regrouping and alignment of elemental particles. 1) 2:1 soil clay-K <math>K < 0.2\mu</math>, pF 1.5, before the first desiccation; 2) after 1st desiccation, pF 2.5; 3) after 5th desiccation, pF 2.5; 4) Montmorillonite (Wyoming)-K <math>K < 2\mu</math>, before the first desiccation, pF 1.5 ; and 5) after 10th desiccation, pF 2.5.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FORMATION OF AMINO ACIDS FROM HYDROLYSIS OF KCN IN A WATER SUSPENSION OF KAOLINITE.

A. DE ANDRES GOMEZ DE BARREDA, P. MENENDEZ APARICIO and F. ARAGON DE LA CRUZ.

Instituto de Química Inorgánica "Elhuyar", C.S.I.C., Serrano 113.
28006 Madrid (Spain).

We are interested to study the role of clay minerals as catalysts in biological molecules synthesis. Formation of amino acids has been studied in the presence of different molecular sieves, like montmorillonite, graphite oxide (lamellar materials) and sepiolite or zeolite (1,2).

Now we have studied the formation of amino acids from a 2.2 M KCN aqueous solution maintained at 70 °C for 26 days with kaolinite (3).

In this work, the kinetics of the reaction has not been studied, emphasis has been placed on the nature of the reaction products.

The crystallinity of kaolinite was checked by X-ray diffraction.

Kaolinite was first treated for 4 days in a 10% H₂O₂ solution at 70 °C in order to remove most of the organic impurities contained in these materials (4). The layer and the solution were separated, after the reaction, by centrifugation. The solid was dried at 70 °C and we worked in the best way to elude their contamination.

Furthermore, we realized a control blank, without sieve, in order to observe if amino acids were detected, and the result was negative.

The solution was analyzed by thin-layer chromatography (5), using two mixtures: butanol-acetic acid-water (1:4:1) and propanol-NH₄OH (3:1); cellulose and silica gel aluminium sheets. But a very important problem is the salt excess; for this reason we wanted to use different ion exchange resins, and on the other hand we are realizing the reaction with a 1M KCN solution in the same described conditions.

Actually we have identified alanine and aspartic acid.

We will analyse the original products (KCN, kaolinite) and treated kaolinite by infrared spectroscopy, and then confirm the absence or presence of characteristic amino acid bands.

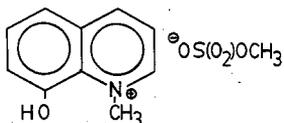
We will study the same samples by thermogravimetric analysis.

- (1) Aragón de la Cruz, F. and Vitón Barbolla, C. Formación de aminoácidos a partir de la hidrólisis de KCN en presencia de montmorillonita o de óxido grafitico. (1979). An. Quím., 81B, 22-25.
- (2) De Andrés Gómez de Barreda, A., Menéndez Aparicio, P. and Aragón de la Cruz, F. Formación de aminoácidos a partir de una solución acuosa de KCN, en presencia de sepiolita y zeolita. An. Quím. (in the press).
- (3) Oró, J. and Kamat, SS. Amino acid synthesis from hydrogen cyanide under Possible Primitive Earth Conditions. (1961). Nature, 190, 442-443.
- (4) Fripiat, J.J., Poncelet, G., van Assche, A.T. and Mayaudon, J. Zeolite as catalysts for the synthesis of amino acids and purines. (1972). Clay Minerals, 20, 331-339.
- (5) Stahl, E. Thin-Layer Chromatography. (1969). Springer-Verlag, N.Y.

A DIFFUSE REFLECTANCE STUDY OF THE ABSORBING POWER (NEAR-U.V. RANGE) OF THE SMECTITE/N-METHYL 8-HYDROXY QUINOLINE METHYL SULPHATE SYSTEM
 M. DEL ARCO**, M. HERNANDEZ-BLANCO#, C. MARTIN**, V. RIVES** AND M.A. VICENTE*

*Centro de Edafología y Biología Aplicada, CSIC, Apdo. 257, 37081-Salamanca; **Dpto. de Química Inorgánica, Facultad de Farmacia, Universidad de Salamanca; #Dpto. de Química Analítica, Universidad Autónoma, Cantoblanco, Madrid. SPAIN

The interaction between smectite and N-methyl 8-hydroxyquinoline methyl sulphate (hereafter MHQMS), as well as the stability of the adsorption complex thus formed, have been studied previously (Vicente et al., 1985). This drug is known to strongly absorb the erythematogenic near-u.v. radiations; in addition, it is not toxic, and then suitable to be used against sunburns and harmful radiations in soldering, u.v. lamps, etc., and it is indeed used in collyria and protective creams. On the other hand, smectite is widely used as a carrier in creams and pomades manufacturing. The aim of the present communication is to investigate the improved absorbing power (and thus, the shielding and protective properties) of the MHQMS/smectite system, well as an adsorption complex or a mechanical mixture. V.-u.v./diffuse reflectance is a very useful tool to study light-absorbing solid materials.



N-methyl 8-hydroxyquinoline methyl sulphate (MHQMS)

Fig. 1 displays the spectra of the pure drug (curve a), smectite (b) and a drug/smectite adsorption complex (c) containing 95 mEq/100 g (a saturated sample). Blank was MgO, and curve d corresponds to spectrum c recorded vs. unloaded smectite. The drug exhibits a

strong absorption between 470-250 nm, while smectite shows a weaker absorption between 300-200 nm. The complex, on the contrary, absorbs more strongly in a wider range (540-200 nm), despite the drug content

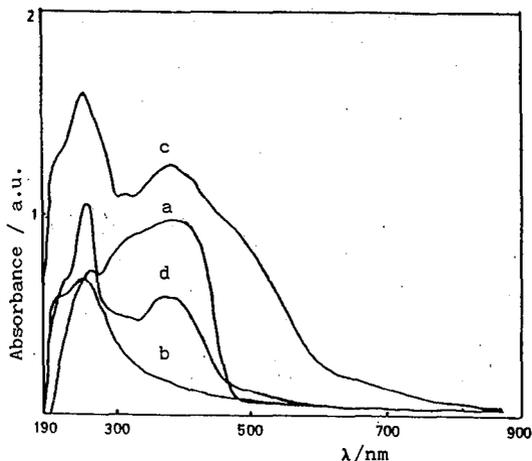


Fig.1.-V.-u.v. spectra (diffuse reflectance) of (a)MHQMS; (b) smectite; (c) MHQMS/smectite adsorption complex (95 mEq/100 g). Blank was MgO. Spectrum (d) corresponds to sample (c) recorded vs. smectite.

is obviously lower (ca. 26% w/w) than in the pure compound. When lower loadings of drug are adsorbed on smectite, the absorption power increases as the drug content does, reaching a maximum for 60 mEq/100 g; higher drug loadings do not significantly improve the absorption capacity of the complex.

When comparing drug/smectite mechanical mixtures and adsorption complexes (with the same drug/clay ratio), the former display lower capacities for absorbing the radiations in the near-u.v. range. While in the complex, the N-methyl 8-hydroxyquinoline cation is located in the interlayer space of the smectite, saturating the exchange sites, in the mixture the drug is not dissociated and the molecules are randomly located on the external surface of the clay. The different structure of the dissociated and the undissociated moieties, together with the restricted orientation of the cations in the interlayer space may be related to the improved absorption ability of the complex.

Finally, it should be mentioned that the high stability of the adsorption complex delays the extraction of the drug from the interlayer space, extending its protective properties; on the contrary, the

drug itself is very soluble in water, and is easily lost.

REFERENCE

M. A. VICENTE, M. S. CAMAZANO, M. J. SANCHEZ-MARTIN, J. VICENTE-HERNANDEZ; "Absorption of N-methyl 8-hydroxyquinoline methyl sulphate by montmorillonite"; International Clay Conference (1985), Abstract 249.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PARTICLES AGGREGATION AND IRON OXIDES RELATIONSHIP IN B HORIZONS OF SOME ITALIAN SOILS

E. ARDUINO, E. BARBERIS AND V. BOERO

Istituto di Chimica Agraria, Università di Torino, Via P. Giuria 15, 10126 Torino, (Italy).

The role of iron oxides in soil particles aggregation is still being discussed. Even though a positive correlation was shown by several Authors, Borggaard (1983) recently objected that iron oxides only play a secondary role.

In order to assess the relative importance of various forms of iron oxides in aggregates formation, the present work was performed by selectively removing iron oxides. The clay produced and the sand disaggregated by these treatments were evaluated.

Thirteen soil samples were selected from B horizons of Alfisols and Inceptisols in Northern Italy: Fe_0 ranged from 0.06 to 1.25%, Fe_d from 2.60 to 5.85% and the Hm/Hm+Ght ratio ranged from 0 to 0.84%. The colours of the soils were 10YR, 5YR, 2.5YR and 10R.

Three different procedures were carried out: (i) dispersion with Na-hexametaphosphate (ii) dissolution with NH_4 -oxalate (Schwertmann, 1964) followed by dispersion with Na-hexametaphosphate (iii) dissolution with DCB (Mehra and Jackson, 1960) and dispersion with Na-hexametaphosphate. After each treatment, particle size distribution was measured by pipette method.

For all the soils, both oxalate and DCB extractions resulted in an increase of clay and a decrease of coarse sand ($>200 \mu m$) contents, the DCB being more effective than the former.

The quantity of soil material which was disaggregated into clay-size particles ranged from 0 to 6.9 g/100g of soil by oxalate treatment and was as high as 21 g by the DCB treatment.

The correlation between total iron oxide, Fe_d , and the quantity of soil material which was disaggregated into clay-size was poor. A significant correlation was found between this quantity and Fe_d content of the fractions $> 2 \mu m$. For all the soils 1.0 g of Fe_d in the fractions $> 2 \mu m$ aggregates 7.0 g of clay material.

The quantity of coarse sand disaggregated by DCB was higher for soils with only goethite (7.7 g/100 g of soil) than for ones with goethite and hematite (2.2 g/100 g of soil); no differences resulted in the quantity of clay produced.

REFERENCES

- Borggaard O.K., 1983. Iron oxides in relation to aggregation of soil particles. *Acta Agric. Scand.*, 33: 257-260.
- Mehra O.P. and Jackson M.L., 1960. Iron oxide removal from soils and clay by a dithionite-citrate system buffered with bicarbonate. *Clays Clay Miner.*, 7: 317-327.
- Schwertmann U., 1964. The differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. *Z. Pflanzenernähr. Bodenkd.*, 105: 194-202.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE DIAGENESIS IN THE ANTICLINE OF BILBAO, BASCO-CANTABRIAN BASIN (SPAIN).

AROSTEGUI, J. (1); VELASCO, F. (1); NIETO, F. (2,3) & ORTEGA-HUERTAS, M. (2,3).

(1) Dpto. Mineralogía y Petrología. Universidad del País Vasco. Aptdo. 644. Bilbao.

(2) Dpto. Mineralogía y Petrología. Universidad de Granada (Spain).

(3) Instituto Andaluz de Geología Mediterránea. Universidad de Granada-C.S.I.C.

The Bilbao anticline is a NW-SE structure located within the Basco-Cantabrian basin. Three great groups of lower-Cretaceous materials are identifiable: a deltaic terrigenous Weald complex of black and grey coaly shales with intercalated sandstones, an Urgonian complex of marine carbonated and terrigenous shales and sandstones, and a supraurgonian complex made up mostly of coarse detrital materials (sandstones and conglomerates of deltaic and fluvi-deltaic environment).

Four traverse stratigraphic sequences, in the SW side of the anticline have been studied. Bulk rock and both 2-20 μm and $< 2 \mu\text{m}$ fractions mineralogy of 75 pelitic samples have been analysed by means of X-ray powder diffractometry.

The mineralogical bulk-rock compositions plotted in the $Q+FG/CO_3$ / clay minerals define two fields: Most of them with 30% $Q+FD$, 70% clay.min. average composition and the other ones with 40% CO_3 , 21% $Q+Fd$, 39% clay.min. average composition.

The mineralogical $< 2 \mu\text{m}$ composition is very similar in all the samples. Illite proved to be the dominant mineral with an average content of around 80%. Kaolinite and/or chlorite appear in minor quantities. The shift in the 10 \AA reflection with different chemical treatments revealed the presence of variable amounts of illite/smectite mixed-layers of ISII ordered structure with less of 15% swelling layers (Środoń, 1984). In the lateral parts of anticline, IS ordered (allevardite like) mixed layers, near 30% swelling layers, are present. The negative correlation of Kübler's index in the 10 \AA reflection (Kübler, 1968), known as "illite crystallinity (IC)" and BBI parameter (Środoń, 1984) with burial depth is interpreted as diminution of swelling layers with burial.

The various intensities of the reflections for mica (002), (004) and (0.0.10) fitted to the Rey and Kübler (1983) triangular diagram showed and illitic mica in all the samples analysed. However, after etilenglicol treatments all samples shift to phengite field. The spacings of reflections (060) and (0.0.10) are corresponding to phengite range.

2-20 μm fractions of various samples has been checked in Rey and Kübler diagram and its d_{060} and d_{0010} has been measured. The plot of intensities showed phengitic mica and the reflections spacings showed moscovitic mica. These differences may be interpreted as being due to the presence in 2-20 μm fraction of mixed layers illite/smectite in very small quantities, that enhanced specially the intensity of 10 \AA reflection moving the plot of moscovitic mica to phengitic field. The different proportions of mixed layers may explain the different plots of 2 μm and 2-20 μm in the diagram and the phengitic d_{060} and $d_{0.0.10}$ for $< 2 \mu\text{m}$ fraction, as average values between illitic and moscovitic ones.

The Kubler's index values for all samples in $<2 \mu\text{m}$ fraction vary from 0.40° to 1.20° 2θ values which correspond to late-middle diagenesis and late diagenesis, however in the Weald materials of the central sector there are some values of anchimetamorphism (after Kubler, 1968, the upper limit of anchimetamorphism correspond to $IC=0.42^\circ$ 2θ). The Kubler's index values, for all the samples in $2-20 \mu\text{m}$ fraction, correspond to the anchi-epizone range.

Therefore, bearing in mind the relation of intensities, d_{060} , d_{0010} and IC an herited character, for $2-20 \mu\text{m}$ fraction and neofomed, herited one for $<2 \mu\text{m}$ fraction are proposed.

According to Kübler index values for $<2 \mu\text{m}$ fraction the level of burial maturation is too weak in relation to the strong thickness of lower Cretaceous and upper materials, around 9.000 m. The explanation may be a lighth geothermal gradient which could correspond with strongly subsidence area. At the same time this could explain the great acumulation of materials in the stratigraphic register. Moreover, bearing in mind the above and the stratigraphic observations, less tickness in the lateral sections, may be interpreted as being due to basin being separated into different compartments, probably with diferences in subsidence levels, above all in the central sector.

REFERENCES

- Kübler, B. (1968). Evaluation quantitative du metamorphisme par le cristallinité del'illite: etat des progrès réalisés ces dernières années. Bull.Cent.Rech.Pan.-SNPA 2, 387-397.
- Rey, J.Ph. et Kübler, B. (1983). Identification des micas des séries sédimentaires par diffraction X à partir de série harmonique (0.0.1) des préparation orientées. Schweiz. Mineral. Petrogr. Mitt. 67, 13-36.
- Srodoń, J. (1974). X ray powder diffraction identification of illitic materials. Clays and Clay Minerals, vol. 32. No 5. 337-349.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PHENYL DERIVATIVES OF SEPIOLITE

A.J. AZNAR and E. RUIZ-HITZKY

Instituto de Ciencia de Materiales, C.S.I.C., c/ Serrano, 115 bis.
28006-MADRID (Spain).

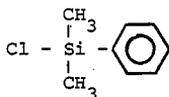
INTRODUCTION

Organosilicic materials obtained by grafting of organosilanes on silica and silicates have received a great attention specially due to their potential use in industrial applications (1-3). Alkyl and alkenyl derivatives of sepiolite have been synthesized by grafting reactions of organo-chloro or -alkoxy silanes following different experimental conditions (4).

The objective of this work consists in the synthesis, characterization and study of the reactivity of a new family of organosilyl derivatives of sepiolite obtained by grafting of $\text{>Si(CH}_2\text{)}_n\text{C}_6\text{H}_5$ ($n=0-2$) groups. The coverage of a silicic substrate by phenyl groups open ways to the preparation of a wide variety of new organic derivatives due to the latent reactivity of the phenyl grafted groups.

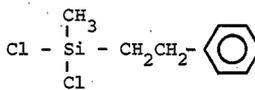
SYNTHESIS AND CHARACTERIZATION

Sepiolite (from Vallecas-Vicálvaro) has been cohydrolyzed in a mixture of isopropanol and hydrochloric acid together with the following reagents:



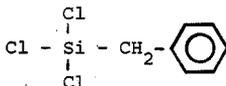
Phenyldimethyl-chlorosilane

(I)



2-Phenylethylmethyl-dichlorosilane

(II)



Benzyl-trichlorosilane

(III)

The reagents have been selected because: i) they are mono-, di- or tri- functionals and consequently they can produce derivatives with the organosilyl groups arranged in monolayers (I), chains (II) or as polymeric tridimensional species (III), and ii) the phenyl group is separated from the silicon atom by 0-2 methylene groups, which is an important factor affecting the latent reactivity of the aromatic ring.

Kinetics, carried out at 60°C, indicate that the grafting of the organosilyl groups and the extraction of Mg^{2+} ions of sepiolite are controlled diffusion mechanisms. The use of the monofunctional reagent (I) permits to reach rapidly a plateau corresponding to monolayer coverages of the silica produced by the hydrolysis of the silicate. In contrast, the trifunctional reagent (III) shows a continuous increase of the grafted species with the time of treatment, indicating the formation of polymeric organosiloxanes (Table 1). The extraction of Mg^{2+} ions is favoured in the sequence III<II<I in agreement with the more homogeneous protection of the substrate by the coverage of mono- or di- functional silanes.

Table I

Amounts of grafted species and Mg^{2+} extracted from sepiolite in the grafting reactions after 200 minutes of treatment at 60°C. Experiments carried out in the HCl/Pr¹OH system.

organosilane reagent	grafted groups (10^{-3} mole/g)	Mg^{2+} extracted %
I	80	50
II	82	75
III	126	100

Chemical analysis, X-ray diffraction, NMR-MAS ¹³C and IR spectroscopies and LAMMA technique have been used to characterize the organo-mineral compounds. In this way, information about the quantities and nature of the grafted species as well as the modifications of the starting sepiolite have been obtained.

PROPERTIES

The most salient feature of these new organo-mineral materials is their latent reactivity towards electrophilic reagents. Thus, typical reactions of the aromatic ring as the nitration and sulphonation are operative to transform the phenyl grafted groups in the corresponding nitro or sulphonic derivatives. Nitrocompounds are easily obtained in the conditions adopted usually in homogenous organic synthesis, whereas the extent of the sulphonation processes is strongly dependent on: i) the experimental conditions, and ii) the distance between the phenyl group and the silicon atom. The highest yield are obtained when the aromatic ring is uncoupled to the Si atoms.

REFERENCES

- (1) FRIPIAT, J.J., CHAUSSIDON, J., JELLI, A. "Chimie physique des phénomènes de surface, applications aux oxydes et aux silicates". Ed. Masson, Paris (1971)
- (2) UNGER, K.K. "Chemical modification of the silica surface" in Porous Silica, Elsevier, Amsterdam (1979)
- (3) Technical Information Bulletins from: Union Carbide Corporat. "Silane adhesion promoters in mineral-filled composites"; Dynamit Nobel Chem. "Bonding agents Dynasilan: organo-functional silanes".
- (4) RUIZ-HITZKY, E., FRIPIAT, J.J., Bull.Soc. Chim. 48 (1976); Clays Clay Min. 24, 25 (1976)



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

BEHAVIOUR AND MICROSTRUCTURE OF SMECTITES

ROLE OF SUCTION PRESSURE AND MECHANICAL STRESSES

M. Azzaoui*, C.H. Pons**, D. Tessier*

* Station de Science du Sol, INRA 78000-Versailles (France)

**Université d'Orléans, Laboratoire de Cristallographie
45067-Orléans (France)

In a previous work Ben Rhaïem et al. (1986) reported results on the behaviour and microstructure of the calcium montmorillonite. In this paper the influence of suction and unidimensional mechanical pressure on the behaviour and microstructure of the same montmorillonite is undertaken.

MATERIAL AND METHODS

Curves of first drying of Ca-Wyoming montmorillonite pastes were obtained by applying air pressure in a ultrafiltration cell described by Tessier et al. (1979), or using unidimensional mechanical pressure in a oedometric cell. Rehydration effects were studied by rewetting at decreasing air pressures. Transmission electron microscopy (MET) was carried out on ultra thin sections of about 500 Å in thickness. These sections were prepared by successive replacements of the liquid phase by methanol, propylene oxide and, finally an epoxy resin. Small angle X-ray scattering experiments were carried out with a Rigaku apparatus with a rotating anode. Using such an X-ray source, the experimental diagrams can be compared with theoretical curves. Computation models were used which assumed the particles to be stacks of M parallel silicate layers. The internal structure of such a particle is given by the degree of order in the succession of layers (Pons et al., 1981).

RESULTS

Dehydration-rehydration behaviour

At stress $\leq 3,2$ bar, the water content after unidimensional mechanical pressure is higher than the one obtained when a suction pressure is applied (Fig.1). At 10 bar however, the water content remained the same for the two types of stress. As shown in figure 2, the water content recovered at 0.032 bar after drying the sample at 10 bar is 115 % and 140 % for the mechanical and suction pressure respectively.

Changes in interlayer spacing and particle size distribution

SAXS data obtained show that interlayer spacing was not affected by suction or mechanical pressure at a stress < 10 bar. The inter-

layer distance with highest probability is 18.6 Å. Moreover, for suction pressures ≤ 1 bar, the number of layers (M) in each particle (55 layers) remained unchanged. Above 1 bar to 10 bar, the number of layers increased markedly and led to the formation of particles having 225 layers at 10 bar. On the contrary, with a mechanical pressure $M = 23$ layers from 0.032 up to 10 bar indicating that the number of layer per particle remained constant.

DISCUSSION

Sample deformation and hydration behaviour

During the first drying the two types of stress applied to the samples resulted into two main types of deformation. With a suction pressure, a substantial lateral shrinkage of the sample (mainly isotropic) is observed. On the contrary, with a unidimensional mechanical pressure, deformation of the sample is determined by the geometry of the oedometric cell and is therefore anisotropic. In the range of ≤ 3.2 bar, the water content is systematically lower with the suction pressure than with the mechanical pressure treatment. As a result, it is easier to deform the sample isotropically than anisotropically.

There was a considerable hysteresis during rewetting and it was after a unidimensional pressure that the water content recovered was lower. It seems therefore that, after a mechanical unidimensional stress at 10 bar, the material lost a greater part of its elasticity than after suction pressure at the same pressure value.

Microstructure changes

During the first drying it was observed that in the mechanical experiment, water which is withdrawn from the sample is at atmospheric pressure. It seems that the water activity remained constant in the range of stress under study and was roughly # 1 indicating that hydration forces could prevent the regrouping of the particles. With a suction pressure, the water activity is modified in the total range of stress under study. This leads to the regrouping of the particles which in turn provoke the existence of a higher elasticity in the system thus increasing the water content during the rewetting process.

CONCLUSION

This work showed that in studying the behaviour and microstructure of clays, it is very important to take into account the state of water in relation with the different types of stresses applied to the systems, especially mechanical stresses.

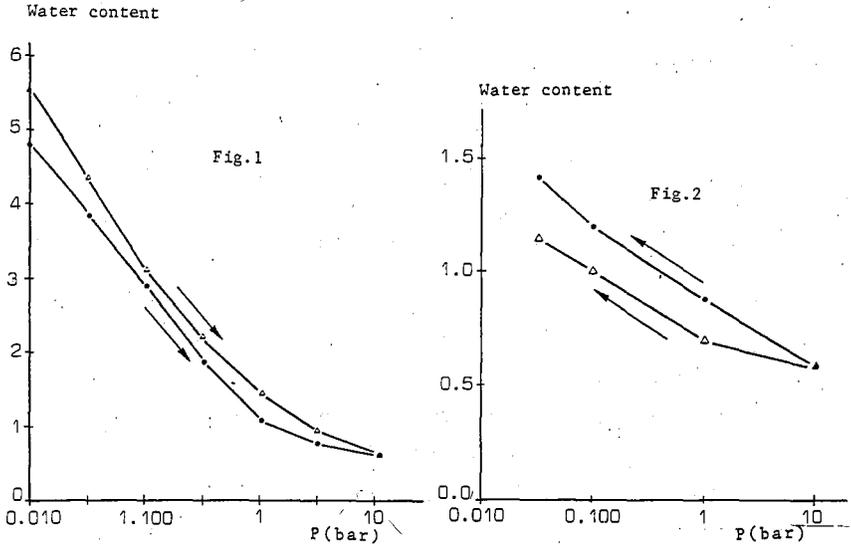


Fig. 1 - Water content changes for the Ca-Wyoming montmorillonite 10^{-3} M CaCl_2 , first drying ; (.) suction pressure (Δ) unidimensional mechanical pressure

Fig. 2 - Rewetting suction curves for the Ca-Wyoming montmorillonite 10^{-3} M CaCl_2 from 10 bar ; (.) initially dried under suction pressure (Δ) initially dried under mechanical pressure

REFERENCES

Ben Rhalem H., Tessier D. and Pons C.H. (1986) - Clay Minerals, 21, 9-19
 Pons C.H., Roussaux F. and Tchoubar D. (1981) - Clay Minerals, 16, 23-42
 Tessier D. and Berrier J. (1979) - Science du Sol, 1, 67-82



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGY AND ORIGIN OF THE GLAUCONITE IN THE MIOCENE CALCARENITE CALLED "PIETRA LECCESE" FROM LECCE PROVINCE, SOUTHERN ITALY.

F. BALEZANO, L. DELL'ANNA AND R. LAVIANO

Dipartimento Geomineralogico, University of Bari - (Italy)

In the "Pietra Leccese", a calcarenite of Miocene age which occurs only in the Lecce province (Puglia, Southern Italy), are found several grains of Glauconite with different colour, chemical composition and degree of crystallization.

The grains occur mainly as replacement of foraminifera and the white, yellowish green, pale green and green colours shown are related to the compositional and structural characteristics. From white to green grains it is noted that: a) SiO_2 decrease (81.7% to 53.3%) with increasing of $\text{Fe}_2\text{O}_3 + \text{FeO}$ (3.5% to 19.5%) and K_2O (1.4% to 6.8%); b) the refractive indices range from 1.54 to 1.62; c) the X-ray pattern shows more numerous and slightly sharper reflections; d) the thermal behaviour of the Glauconite is better outlined; e) the P_2O_5 of the associated phosphorite become more abundant.

The green grains are made up of microcrystalline aggregates of platlets, pale green in thin section, with α about 1.60 and $\beta = \gamma$ about 1.62; they have 1Md structure with some percentages of expandable layers.

On the basis of investigation a model for the origin of the Glauconite grains from "Pietra Leccese" is proposed. The white grain could be the starting material, the iron and potassium of which is supplied by a marine environment which has become a reducing environment inside foraminiferal tests.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**CRYSTALLOCHEMISTRY AND SURFACE PROPERTIES OF BRAZILIAN
OPALS**

F. BARTOLI⁽¹⁾, D. BITTENCOURT ROSA⁽²⁾, M. DOIRISSE⁽¹⁾,
R. MEYER⁽³⁾, R. PHILIPPY⁽¹⁾ and J.C. SAMAMA⁽²⁾

(1) Centre de Pédologie Biologique du C.N.R.S., B.P. 5,
54501 Vandoeuvre-les-nancy Cedex, France

(2) Ecole Nationale Supérieure de Géologie Appliquée et de
Prospection Minière, B.P. 452, 54001 Nancy Cedex, France

(3) Université de Nancy I, Laboratoire des ensembles
Sédimentaires, B.P. 239, 54506 Vandoeuvre-les-nancy Cedex,
France.

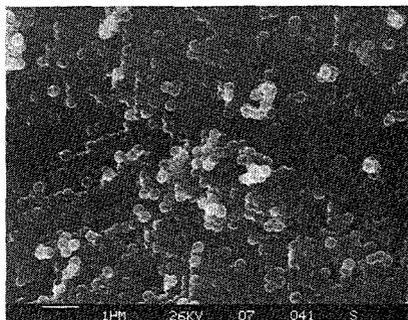
In the sixties, more than ninety-five per cent of the world's opal came from Australia. Since fifteen years similar opal sedimentary deposits were discovered and are mined in large open pits in Brazil (Pedro II, Piauí State, North-Eastern Brazil).

As Australian opals, Brazilian ones are poorly-ordered with a broad X-Ray band at near 4.1 Å characteristic of the opal A.

They also contain low amounts of water and their microscopic structure consists in regular cubic or hexagonal close-packed spheres of remarkable uniformity, mainly 2 000 to 3 000 Å diameter (photograph).

For the range of noble opals studied, color, crystallinity and surface properties are mainly controlled by

the isomorphous substitution of Al for Si in the tetrahedral network.



S.E.M. micrograph
of a Brazilian opal
after a 15 mn HF
vapors pretreatment

The less aluminous opals (0.8 to 1.4 % Al_2O_3), white-yellow to dark yellow are relatively better ordered. Correlatively, their close-packed spheres structure is more compact and their amounts in water lower (mainly 3 to 3.5 %). They have also lower amounts of Ca, Mg, Na (0.1 to 0.2 % $\text{MgO} + \text{CaO} + \text{Na}_2\text{O}$), probably associated with water, and of metals (0.02 to 0.05 % $\text{Co} + \text{Ni} + \text{Cu}$), probably specifically adsorbed.

Their silanol groups, mainly of isolated SiOH type, are characterized by a low aluminous environment, lower surface acidities and thermal stabilities.

On the opposite, the most aluminous opals studied (1.5 to 1.8 % Al_2O_3) are white with blue irrisations and are relatively more poorly-ordered. Indeed, the half-way up width of the broad X-Ray 4.1 Å band which was used as a crystallinity index was mainly 8 to 8.4 against 7 to 8

for the less aluminous and relatively better ordered opals.

Correlatively, their amounts of water are higher (4 to 5 %) as well as their amounts of impurities.

For the whole range of noble opals studied the isomorphous substitution of Al for Si in the tetrahedral network is function of the amount of Al_2O_3 and can be seen in the infra-red spectra.

As the Al_2O_3 content increases, the stretching and bending silanol Si-O bands become wider and shift towards lower wavenumbers (3620 to 3570 and 940 to 910 cm^{-1} respectively).

In the X-Ray diffraction patterns, as the Al_2O_3 and Al-Si substitution increases, the band becomes broader (crystallinity index = 7 to 8.4) and shifts towards higher 2θ values.

Correlatively, thermal stabilities of both silanol groups and water become higher.

On one hand, as the Al_2O_3 content increases, the deshydroxylation endothermic peak which was at 500-510°C for lesser aluminous and Al-Si substituted opals, become broader and shifts towards higher temperatures, up to 600°C.

On another hand and similarly, as the Al_2O_3 content increases, the water release endothermic peak which was at 160-170°C for lesser aluminous opals shifts towards higher temperatures, up to 280°C.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE ROLE OF POORLY-ORDERED HYDROUS OXIDES OF Al AND Fe IN
THE AGGREGATION OF SOILS

F. BARTOLI⁽¹⁾, R. PHILIPPY⁽¹⁾, G. BURTIN⁽¹⁾, J.J. DEMAI⁽²⁾,
E. JEANROY⁽¹⁾ and E. PATERSON⁽³⁾

(1) Centre de Pédologie Biologique du C.N.R.S., B.P. 5,
54501 Vandoeuvre-les-Nancy Cedex, France

(2) Université de Nancy I, Service Commun de Microscopie
Electronique à Transmission, B.P. 239, 54506 Vandoeuvre-
les-Nancy Cedex, France

(3) Macaulay Institute For Soil Research, Craigiebuckler,
Aberdeen AB9 2QJ, U.K.

Aggregation in a series of free of allophanes soils from tropical, mediterranean and temperate zones has been studied using a multivariable statistical approach which has demonstrated the importance of poorly-ordered Al and Fe hydrous oxides in the process (1).

The objectives of the present study concern both the nature of non-crystalline Al and Fe oxyhydroxides involved in the aggregation process and on the relationship between amount and nature of these poorly-ordered inorganic soil components and stability of soil aggregates measured by differential disaggregations.

Oxalate was used to quantify both non-crystalline Al and Fe oxyhydroxides (2).

0.1 M Na-pyrophosphate dispersed poorly-ordered hydrous iron oxides coated by organic matter (e.g. 3, 4,). For the nine A horizons studied, we confirm these previous results.

After a first 33 000 g centrifugation, the 100 000 g residues were mainly ferrihydrite (Fig. 1) (and often goethite traces) associated with organic materials rich in peptides (IR data).

100 000 g supernatants were dispersed colloidal Al and Fe pyrophosphates (dialysis, IR and DTA data) which replace Al and Fe organic chelates.

When both concentration of organics and non-crystalline Al and Fe oxyhydroxides increase the ratio Fe 100 000 g pyrophosphate supernatant/Fe oxalate increases from 0.33 to 0.69 (Fig. 2)

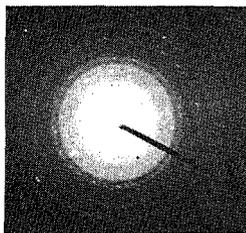


fig. 1 : electron diffraction pattern of a 100 000 g pyro. residue, mainly ferrihydrite : 2.55 Å (110), 2.15 Å (112 + 113), 1.7 Å (114), 1.5 Å (115 + 300).

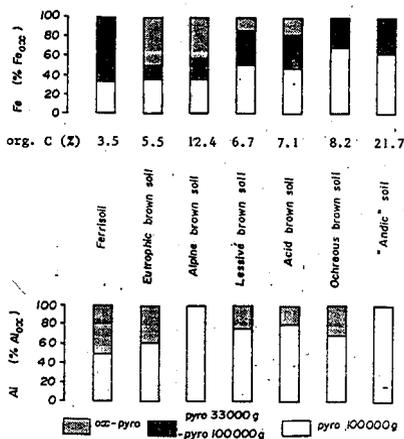


fig. 2 : poorly-ordered hydrous Al and Fe oxides forms in the soils studied.

The exception is the alpine brown soil on serpentine where presence of maghemite partly solubilized by oxalate (5) underestimates the amount of poorly-ordered Fe oxyhydroxides.

We will demonstrate that the nature and therefore the reactivity of poorly-ordered Al and Fe oxyhydroxides better explain the Na resin soil disaggregation process than their quantity.

Finally distribution of both soil organic matter and these poorly-ordered inorganic components into aggregates size compartments after 16 h. Na resin reverse shaking treatment (Fig. 3) demonstrated again the importance of poorly-ordered Al and Fe oxyhydroxides closely associated with organic matter in the soil aggregation process.

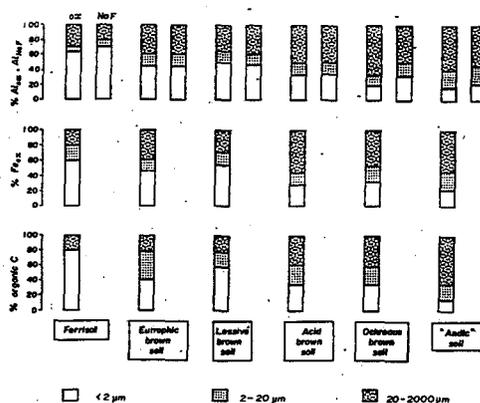


fig. 3 : distribution of poorly-ordered hydrous Al and Fe oxides into soils aggregate sizes after 16 hours reverse shaking Na resin treatment.

- (1) Bartoli F. et al., 1986. XII A.I.S.S. Symposium, Hambourg, 13-20 August 1986, III, 1049-1050.
- (2) Schwertmann, 1964. Zeitschf. Pflanzenern. u. Bodenkde, 105, 194-202.
- (3) Jeanroy & Guillet, 1981. Geoderma, 26, 95-105.
- (4) Kassim et al., 1984. Clay Minerals, 19, 99-106.
- (5) Baril & Bitton, 1969. Can. J. Soil Sci., 49, 1-9.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PARTICLE SIZE AND MINERALOGICAL COMPOSITION OF AEOLIAN DUSTS COLLECTED
IN SPAIN

J. BARRIOS*, V. BARRON, F. PEÑA AND J. TORRENT

Departamento de Ciencias y Recursos Agrícolas, Universidad de Córdoba,
E.T.S.I.A., Apdo 3048, 14080 Córdoba.

*Departamento de Química Inorgánica, Universidad de Córdoba, Facultad
de Ciencias, 14004 Córdoba.

The accretion of aeolian or aerosolic dust has influenced the genesis of a number of soils in the world. In the Mediterranean regions, for instance, it has been described in many soils of Italy, Greece and Israel where the aeolian dust carried by the Sirocco from Sahara constitutes an important part of the parent material. In the Iberian Peninsula the fall of "mud" or "red rains" (reddish dust carried by rain) is frequent and a marked impact on the genesis of some soils can be expected. The study of aeolian dusts can help to elucidate some facts that, at present, are of difficult interpretation such as textural balances, presence of some minerals not present in the underlying rocks (e.g. quartz in soils developed on basalts) or the unusual position of some mineralogical species in the soil profile (e.g. carbonates over argillic horizons).

We studied two aeolian dust samples collected in November 1984 (sample A) and February 1985 (sample B) from two zones in the Iberian Peninsula (Cataluña and Andalucía, respectively). The mineralogical composition of both samples was investigated by X-ray diffraction on powder and oriented aggregates and by chemical analysis.

Sample A contained 44% of clay (<2 μ m), 29% of fine silt (2-5 μ m), and 19% of coarse silt (5-20 μ m). Sample B contained 63% of clay, 11% of fine silt and 23% of coarse silt. The mineral assemblage of these size fractions is shown in Table 1. Quartz was the main component of the coarse textural fractions of both samples. In sample A the content of feldspar increased and the content calcite decreased with increasing particle size. Gypsum was detected in small amounts in the

Table 1 MINERALOGY OF THE AEOLIAN DUSTS

Sample	Size fraction (um)	Quartz	Feldspar	Mica	Kaolinite	Vermiculite	Smectite	Calcite	Gypsum	Iron oxides
A	2	X		XXX	XX	X		XX		X
	2-5	XX	X	X	X	X		XXX		X
	5-10	XXX	X	X	X			XX		
	10-20	XXX	XX	X	X			XX	X	
	20	XXX	XX	X				X	X	
B	2	X		XX	XXX		XXX			
	2-5	XXX			X			X		X
	5-10	XXX	X		X					
	10-20	XXX	X							
	20	XXX	X							

X: Present, XX: Abundant, XXX: Very abundant

coarse fractions. In the clay fraction mica was more abundant than kaolinite. In contrast kaolinite and smectite were more abundant than mica in the clay fraction of sample B. This sample contained also much less calcite and no gypsum.

The former data suggest that mineralogy of the aeolian dusts does not contrast markedly with the mineralogy of many soils of the Mediterranean region, which have calcite, quartz and a mixed clay mineralogy. Consequently identification of aeolian additions must be based on techniques other than common mineralogical analyses, such as oxygen isotopic ratio determination or geochemical balances. Some of these studies are presently underway.

REFERENCES

- Jackson, M.L., Gillete, D.A., Danielsen, E.F., Blifford, I.H., Bryson, R.A. and Syers, J.K., 1973. Global dustfall during the quaternary as related to environments. *Soil Science* 116, 135-145.
- Syers, J.K., Jackson, M.L., Berkheisen, V.E., Clayton, R.N. and Rex, R.W., 1969. Aeolian sediment influence on pedogenesis during the Quaternary. *Soil Science* 107, 421-427.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

KAOLINS OF HYDROTHERMAL ORIGIN OF PILONI DI TORNIELLA (TUSCANY, ITALY)

M. BERTOLANI, A.G. LOSCHI GHITTONI

Institute of Mineralogy and Petrology, University of Modena (Italy).

Rhyolitic volcanic rocks dating back to 2.3 m.y. crop out at Roccastrada in the province of Grosseto and are generally found to be resting on "Verrucano", which is a formation of the Middle Triassic.

One of the largest outcrops of the Roccastrada formation is that of Monte Alto. At its northernmost point, in the area of "Piloni di Torniella", widespread kaolinization has occurred, transforming the rhyolitic rock into a light, white, generally porous mass.

The products of this transformation have been studied at different times by Matteucci (1891), who identifies them as kaolins, by Panichi (1910), who affirms the presence of a large amount of alunite, by Rodolico (1938), who reports the findings of chemical analyses carried out on two samples. The last to concern himself with the kaolin of Piloni di Torniella was Mazzuoli (1967), who regards the kaolin as having been largely formed by lacustrine deposition.

There are a number of abandoned quarries in the outcrop, and it was here that both generalized and precise sampling was carried out.

Diffraction studies were performed on 35 samples, followed, in nineteen cases, by chemical analysis.

Two processes involving the deposition of kaolinic material were identified. One bed, of lacustrine origin, is restricted to the easternmost workings; it is of limited area and a few metres deep. Its main clay component is an illitic-muscovite mineral, accompanied by smaller amounts of kaolinite, quartz and k-feldspar; it does not

contain alunite. The second, in which the bulk of the kaolinized material is to be found, consists of volcanic rock still in place in the form of residual mineral. Illite is practically non-existent, while kaolinite is always present, albeit in widely-varying amounts. In a few samples, kaolinite is replaced by halloysite (7 A). Quartz is always present in abundance and, in one case only, is accompanied by cristobalite. K-feldspar is very variable, depending on the transformation processes. Alunite may be absent altogether or present only in small amounts, or again it may be the only mineral present together with quartz. Iron, in the form of Fe_2O_3 , accounts for about 2% of non-transformed rhyolitic rock and is present to the same degree in certain samples of kaolinite-alunite transformation products; however, it is usually so impoverished as a result of transformation that it hardly ever exceeds 1%. This impoverishment is particularly evident in alunite deposits, but virtually non-existent in kaolin deposited under lacustrine conditions.

It was noted that alunite is not distributed uniformly throughout the residual mass; there are whole areas in which alunite is absent or localized at concentrations that only precise sampling can detect and evaluate. The kaolin deposit of Piloni di Torriella can therefore in its existing state, be considered a source of supply for the ceramics industry, particularly that of wall and floor tiles, which can use the material as it is.

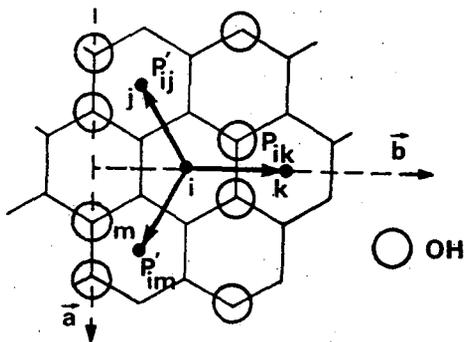
ORDER-DISORDER OF THE CATION DISTRIBUTION IN THE OCTAHEDRAL SHEET OF
 MICACEOUS MINERAL

G. BESSON, A. DECARREAU*, L.G. DAINYAK** and V.A. DRITS**

Laboratoire de Cristallographie, Université d'Orléans, 45067 Orleans
 Cédex, FRANCE. *Laboratoire de Géochimie des Roches Sédimentaires,
 91405. Orsay Cédex, FRANCE. **Geological Institute of Academy of
 Sciences, Moscow, U.S.S.R.

To study the cation distribution in the octahedral sheet of dioctahedral minerals, a collection embraced the whole compositional range from the Fe^{3+} end-members to the Al end-members with the minimum Al for Si substitutions was chosen. The samples were first studied by a number of methods, such as X-ray and electron diffraction, chemical analyses and thermogravimetry. The diffraction methods showed that the trans octahedra in the structure of all the samples were vacant. The chemical analyses showed that the interlamellar cation was potassium.

The octahedral sheets in these micas are occupied by Mg, Fe^{2+} , Fe^{3+} and Al cations designed here as A, B, C and D respectively. Probabilities of the occurrence W_A , W_B , W_C and W_D in cis-octahedra are equal to their content according to the crystal-chemical formula. If the nature of a cation to occur in one member of a pair of cis octahedra depend on the cation present in the other we shall name P_{ik} ($i, k = A, B, C, D$) the probability of the cation i occurring near cation k in the \vec{b} direction and P'_{ik} in the two other directions (see figure).



Fragment of the octahedral sheet of phyllosilicate with vacant trans-octahedra

It is known that the OH groups in the structure of dioctahedral mica are coordinated by two octahedral cations. The individual OH stretching frequencies depend on the type of the cations nearest to the OH group. The integrated optical density of each band is determined by the number of OH groups with the given cationic environment. The interpretation of each individual band is consistent with the mode of dependence of the OH stretching frequencies on the effective charges and masses of the nearest cations. The experimental values of the integrated optical densities for each IR band give the P_{ik} values, and has allowed revision of the crystallochemical formula of some samples (Slonimskaya et al., 1986).

But the analysis of one dimensional cation distribution does have its limitations. For the knowledge of the two dimensional cation distribution it's necessary to use another spectroscopic methods.

With Mössbauer spectroscopy we determine around Fe^{3+} how many R^{3+} (C and D) and R^{2+} (A and B) cations exist in the three directions (see figure). In order to interpret the doublets of the Mössbauer spectra of Fe^{3+} , an approach was developed based on possible variants of the immediate cation environment of these ions and a model of the character of the distortion of the iron containing octahedron together with calculations of the electric field gradients based on a model with formal point charges (Dainyak et al., 1984). The knowledge of the relative weight of each doublets allow to determine the values $P'_{Fe^{3+},j}$ ($j = R^{3+}, R^{2+}$). But it's not enough to determine the two dimensional cation distribution.

The oscillations of the X-ray absorption coefficient on the high energy side of an absorption edge (EXAFS) carry structural information about the nearest coordination shells surrounding the absorbing atom, i.e. interatomic distances, number and nature of the constituent atoms. The amplitude of the second peak is very sensitive to the atomic composition of the heavy ($L = B$ and C) and light ($l = A$ and D) atoms of the second shell surrounding heavy ions. The simulation of the second shell allows to determine the values $P'_{L,l}$ ($j=L,l$).

The comparison of these three methods with the help of the statistical analysis show for the minerals understudy that:

- 1. No sample contains Fe^{3+} and Al^{3+} pairs in the direction of the \vec{b} axis ($P_{Fe^{3+}Al^{3+}}=0$).
- 2. Cation distribution is never completely disordered.
- 3. The probability to find cation k near cation i in the direction \vec{b} (P_{ik}) is different of the probability P'_{ik} in the two other directions.
- 4. The maximum degree of short-ranges order in the octahedral cation distribution is observed in minerals having Al prevalent.

BESSON G., DRITS V.A., DAINYAK L.G. and SMOLIAR B.B. (1987). "Analysis of cation distribution in dioctahedral micaceous minerals on the basis of IR spectroscopy data". Clay Miner., (in press).

DAINYAK L.G., BUKIN A.S. and DRITS V.A. (1984). "Interpretation of Mössbauer spectra of dioctahedral Fe^{3+} containing layer silicates III Celadonite. Sov. Phys. Crystallogr., 29, 186-191.

SLONINSKAYA M.V., BESSON G., DAINYAK L.G., TCHOUBAR C. and DRITS V.A. (1986). "Interpretation of the IR spectra of celadonites and glauconites in the region of OH-stretching frequencies". Clay Miner., 21, 377-388.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SECONDARY IRON IN RED WEATHERED ROCKS AND SEDIMENTS
OF THE BOHEMIAN MASSIF

B. BEZVODOVA

Geological Survey, Malostranské nám. 19, Praha 1, Czechoslovakia

Red weathered rocks show various age and different genesis in the Bohemian Massif. Their common sign, at first sight very expressive, is red colour which depends on the content of secondary iron and its overall crystallinity. The aim of the present work is a comparison of secondary iron in red weathered rocks and sediments of various age and genesis.

THE STUDY AREAS

Four groups of red weathered rocks were studied: a/red weathered gneisses of the Krušné hory Mts. crystalline complex; parent rocks are of Precambrian age, the weathering process is of pre-Cretaceous age; b/clay sediments of Permian age from Central Bohemian region are the products of denudation and resedimentation of weathered rocks of the Upper Carboniferous /Westphalian-Staphanian/ latter affected by Jurassic and Lower Cretaceous climate; c/weathered volcanoclastic rocks of the North Bohemian Basin of Oligocene age; the period of weathering ranged from the Neogene to the Quaternary; d/paleosoils on fluviolacustrine sand and gravel sediments -terraces- of the river Vltava, Dyje and Morava; age of terraces spans from the Pliocene to Pleistocene; paleosoils originated in the periods of interglacials. For comparison, light-brown weathered rhyolite from the Krušné hory Mts. was studied; the age of the parent rock is Paleozoic, age of weathering is unknown, since weathered rocks are not covered by a younger system.

LABORATORY METHODS

Separation of particle fractions <0.01 mm was made by gravity sedimentation from suspension. Total iron (Fe_t) was determined after hydrofluoric acid attack. Dithionite soluble iron (Fe_d) was determined by the method of Mehra-Jackson /1960/ and oxalate extractable iron (Fe_o) by the method of Schwertmann /1964/. XRD patterns were obtained using $CoK\alpha$ radiation and Dron 3. Colour of dry samples was determined in daylight by the Munsell Color Charts /1975/.

RESULTS AND DISCUSSION

For evaluation of weathering intensity the ratio $(Fe_o + Fe_d) / Fe_t$ giving the whole amount of iron disengaged by the process of weathering is important. The ratio Fe_o / Fe_d evaluates the type of weathering and shows the amount of disengaged recrystallised and disengaged amorphous iron.

In all the studied samples the ratio $(Fe_o + Fe_d) / Fe_t$ is the lowest in the paleosoils on terraces /0.75-0.77/ and the highest in red weathered gneiss /0.83-0.87/. The ratio strongly oscillates in sediments of the Permian and in volcanoclastic rocks of Oligocene age. In light-brown fossil weathered rhyolite, the ratio $(Fe_o + Fe_d) / Fe_t$ is high and nearly the same as in red weathered gneiss.

The ratio Fe_o / Fe_d is very low in red weathered gneiss /0.009/ and corresponds to a mineral content of these samples - hematite and kaolinite only. Sediments of Permian age have a little higher ratio /0.03-0.04/ and are composed of hematite and kaolinite, sometimes with admixture of goethite. In weathered volcanoclastic rocks this ratio strongly varies /0.02-0.13/ and therefore the mineral content varies, too. In paleosoils on terraces the ratio Fe_o / Fe_d varies in dependence on age of the terraces /0.03-0.07/ and in all cases goethite is present only. Light-brown fossil weathered rhyolite shows extremely high ratio /0.20-0.38/ indicating no crystalline Fe-oxides.

CONCLUSION

The above mentioned ratios of various forms of iron and mineral content of clays were used to estimate the age of the weathering process. The results which have been obtained till now show that the used methods are suitable for short stratigraphical systems only /e.g. river terrace sequences/. When we correlate epochs with a great time span between them we have to consider the possibility that they might have been affected by many other events. These events comprise : erosion, re sedimentation, admixture of allocthonous material, heating close lava flows, influence of younger climate. After careful consideration of all these possibilities we can use the above mentioned methods.

REFERENCES

- Mehra O.P. - Jackson M.L. /1960/ : Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals, 7, : 317-328.
- Schwertmann U. /1964/ : Differenzierung der Eisenoxide in Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Zeitschr. Pflanzenarnähr. Düng., Bodenk., 105, :194-202.
- Munsell Soil Color Charts /1975/, Macbeth Division of Kollmorgen Corporation, Baltimore.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

IMPROVEMENT OF CLAY SOILS : A CASE STUDY

C. BINI¹, F. MATTEI SCARPACCINI², E. RASO², G.G. RISTORI³ and E. SPARVOLI³

1 - Dept. of Soil Science and Plant Nutrition, Univ. Florence, Italy.

2 - Dept. of Agriculture, University of Florence, Italy.

3 - Centro di Studio per i Colloidi del Suolo, CNR, Florence, Italy.

Laboratory and field experiments were carried out on an acid clay soil developed on alluvial terraces of the Mugello valley (Florence). According to the Soil Taxonomy, the studied soil is a fine clayey, mixed, mesic, Ultic Hapludalf.

The aim of the study was to contribute to the improvement of the soil structure and to increase the agricultural productivity of this kind of soils, which are spreaded over large areas in central Italy and abroad.

Laboratory studies on the role played by gypsum in determining the rearrangement of microstructure in agricultural acid soils were carried out recently by Guyot et al. (1984) and Delmas et al. (1985). Bini and Ristori (1986) found similar effects in natural soils developed on gypsum-clay rocks. A few field experiments are reported in recent literature on this subject.

Laboratory experiments. Samples of the Ap horizon were intensively mixed with water and subjected to a constant mechanical pressure, in order to have homogeneous prisms comparable with natural aggregates at field capacity (pF 2.5).

The effects of a treatment of these prisms with gypsum were observed both by physical and chemical analyses (pF, pH variations, water and exchangeable Ca²⁺ contents) and by S.E.M., in order to evaluate if there had been diffusion phenomena inside the clayey sticks, and a reorganization of the clay particles at submicroscopic level.

Field experiments. The experimental study in the field was carried out according to a split-plot scheme with four replies of the following theses :

Thesis A: distribution of four different amounts of gypsum (0, 20, 40, 60 qxha⁻¹);

Thesis B : distribution of two different amounts of phosphorus (100 and 200 Kgqha⁻¹ P₂O₅ respectively).

The soil was then sowed with maize and spray irrigated. The field experiments, carried out over two years, concerned totally thirtytwo

experimental plots randomly distributed over a 1000 m² surface.

At different periods of time (30 to 120 days; the time of maize growing), breaking load measures were taken in the field, and samples were collected to measure the soil pH and moisture in different plots. Moreover, undisturbed soil aggregates were taken for physical, micromorphological and submicroscopical analyses, in order to observe the modifications induced by the differential treatment both on the pore system geometry (by Hg porosimetry and light microscopy) and in the rearrangement of clay particles (light and electron microscopy).

Remarks. The following results have been obtained from the experimental work:

- The surface reactions at the gypsum-clay interface give rise to diffusion phenomena, as a function of the water content. The calcium diffusion, as measured by the extractable Ca²⁺ inside the clay sticks, shows differential accumulation of calcium from the top to the bottom and for long-term samples (90 days treatment) in comparison with mid-term samples (45 to 75 days), while the short-term samples (15 to 30 days) have a minimum increase with respect to the untreated samples.

- After gypsum application, the recorded pH proved to increase at the top of the sticks. The measured Δ pH between the top and the bottom, and among the different periods of time, suggests that there must have been a retro-diffusion process inside the sticks, which is responsible for lowering the pH at the bottom. In the same time, an increase of the soil pH in the field was recorded, as a function of the different amounts of gypsum fertilization, thus confirming the results from laboratory experiments.

- The fabric and the pore system geometry of the clay sticks, as observed by S.E.M., seem to be more stable, due to gypsum application, with regard to the untreated samples. An anisotropic arrangement, typical of the "non salt flocculated structure" (Lambe, 1953), is developed, with discrete domains disposed mainly EF and separated by intermicrodomain discontinuities.

- The S.E.M. observations carried out on undisturbed soil samples taken 30 to 90 days after the distribution of gypsum, show marked differences in the fabric. The test-plot has a rather isotropic structure made up of contiguous domains arranged mainly FF, with low porosity. The gypsum treated plots, at the beginning (20 qpha⁻¹) have an anisotropic structure, which develops first to an honey-combed one (40 qpha⁻¹) and then to discrete domains arranged mainly EE and FF, with decreasing porosity (60 qpha⁻¹). Thus, the best soil microstructure seems to be reached with a 40 qpha⁻¹ gypsum distribution.

- The pore size distribution, as observed by Hg porosimeter 30 to 90 days after the soil treatment, shows firstly (0 to 40 qpha⁻¹) an increase, then (60 qpha⁻¹) a decrease to the starting distribution of residual pores (0.1 µm e.c.r.). In the same time, the storage pores (0.1 - 10 µm e.c.r.) show an opposite distribution, while the transmission pores (10 - 100 µm e.c.r.) have a relatively constant pattern. Moreover, the total porosity measured by kerosene immersion doesn't show appreciable variations in different plots. It means that only the microporosity is influenced by gypsum application. This behaviour may be ascribed to the flocculation of clay particles in condensed microdomains, and is consistent with SEM observations.

- The agronomical results with maize over two years show that gypsum fertilization at the lower levels (20-40 qpha⁻¹) can increase corn yields by 10% and 5% respectively, while gypsing with higher amounts (60 qpha⁻¹) results in only 1.5% yield increases, suggesting that it needs more time for gypsum to penetrate the subsoil and to be effective. Appreciable corn yield increases (5%) are obtained with the higher phosphorus application too, while any negative interaction with gypsum is recorded. These results suggest that by-product gypsum from phosphate acid manufacture would be a feasible amendment for acid clay soils.

REFERENCES

- Bini C. and Ristori G.G. (1986) - Microstructure of soils developed on gypsic-clay rocks in Northern Apennines (Italy). Soil Microscopy, Proc. VIIth Int. Meeting on Soil Micromorphology, in press.
- Delmas A.B. et al. (1985) - The effect of gypsum on the poral system geometry in two clay soils. Min Petr. Acta, 29 A, pp. 499-509.
- Guyot J. et al. (1984) - Amélioration de la structure de sols non sales par le gypse. Trans Eur. Coll. "Fonctionnement hydrique et comportement des sols", Dijon.
- Lambe T.W. (1953) - The structure of inorganic soils. Proc. A.S.C.E., separate n. 315.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PROCESSING TRIALS ON KAOLIN-BEARING ROCKS FROM PUGU, TANZANIA,
USING CONVENTIONAL AND NEW HYDROCYCLONE BODIES

A. J. BLOODWORTH, D. A. BRIGGS AND D. J. MORGAN

British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

This paper will describe the results of laboratory beneficiation trials on kaolin-rich deltaic sandstones of Upper Cretaceous age from the Pugu Hills, W of Dar-es-Salaam, Tanzania. Two principal kaolin-bearing facies occur within the sandstones (Robertson *et al*, 1954), a proximal arkose which was probably kaolinized *in situ* ("Pugu soft"), and a more distal facies consisting of kaolin deposited along with fine quartz and feldspar ("Pugu hard").

Samples of both Pugu "soft" and "hard" were examined. After thorough dispersion, the slurry passing a 63 micron screen was pumped through a conventional 1.5 cm diameter glass hydrocyclone (Bain & Morgan, 1983) set to give >95% particles less than 10 microns in size. This fine product was used as the stock suspension for subsequent separation trials using a composite hydrocyclone body (Richard Mozley Ltd) comprising six injection-moulded hydrocyclones in an assembly with common feed and collection chambers. Spigots and vortex finders of three different diameters were available for the 10 mm cyclones, thus allowing a range of separation conditions.

Particle-size distributions of the products were determined with a Micromeritics X-ray Sedigraph. Kaolin particle morphology and average size were determined by TEM. BET surface areas of the dried products were measured using a Micromeritics FlowSorb model 2300. As fine-grained quartz was the only contaminant of the Mozley hydrocyclone products, amounts were determined by XRD using a computerized Phillips PW1730 system. Kaolin contents estimated as the difference between quartz content and 100% were found to be more reliable than kaolin contents determined by TG.

The original "hard" material contained 46% kaolin and screening at 63 microns gave a product containing 93% kaolin at virtually complete recovery. The glass hydrocyclone recovered 61% of the kaolin at a grade of 99%. Over 96% of particles in this product were <5 microns in size with 82% <2 microns. The Mozley hydrocyclone gave only a marginal gain in <2 micron particles. The fine-grained kaolin gave surface areas in the range 23.8-25.1 m²/g and XRD and TEM characteristics were identical with those of Pugu D (Robertson *et al*, 1954).

The original "soft" material contained 37% kaolin and screening at 63 microns gave a product containing 86% kaolin at a recovery of 85%. The glass hydrocyclone recovered 62% kaolin at a grade of 90%. 86% of particles in this product were <5 microns in size but only 55% <2 microns. The "best" product from the Mozley hydrocyclone, in terms of both kaolin grade and fineness, was obtained with the smallest diameter spigots and vortex finders. This product contained 97% kaolin, with 96% particles <5 microns and 86% <2 microns. The recovery of kaolin in this product, however, was only 14%. Surface areas of the various Mozley hydrocyclone products (all >90% kaolin) were found to be a sensitive indicator of the relative fineness. Fig. 1 shows the relationship between surface area and % <5 micron particles for both products and rejects from the "soft" material. The pure kaolin appears to have a surface area of ~11 m²/g. Its XRD and TEM characteristics were identical with those of Pugu K (Robertson *et al*, 1954).

REFERENCES

- BAIN J. A. & MORGAN D.J. (1983) Laboratory separation of clays by hydro-cycloning. *Clay Miner.* **18**, 33-47
- ROBERTSON R. H. S., BRINDLEY G. W. & MACKENZIE R. C. (1954) Mineralogy of kaolin clays from Pugu, Tanganyika. *Am. Miner.* **39**, 118-138.

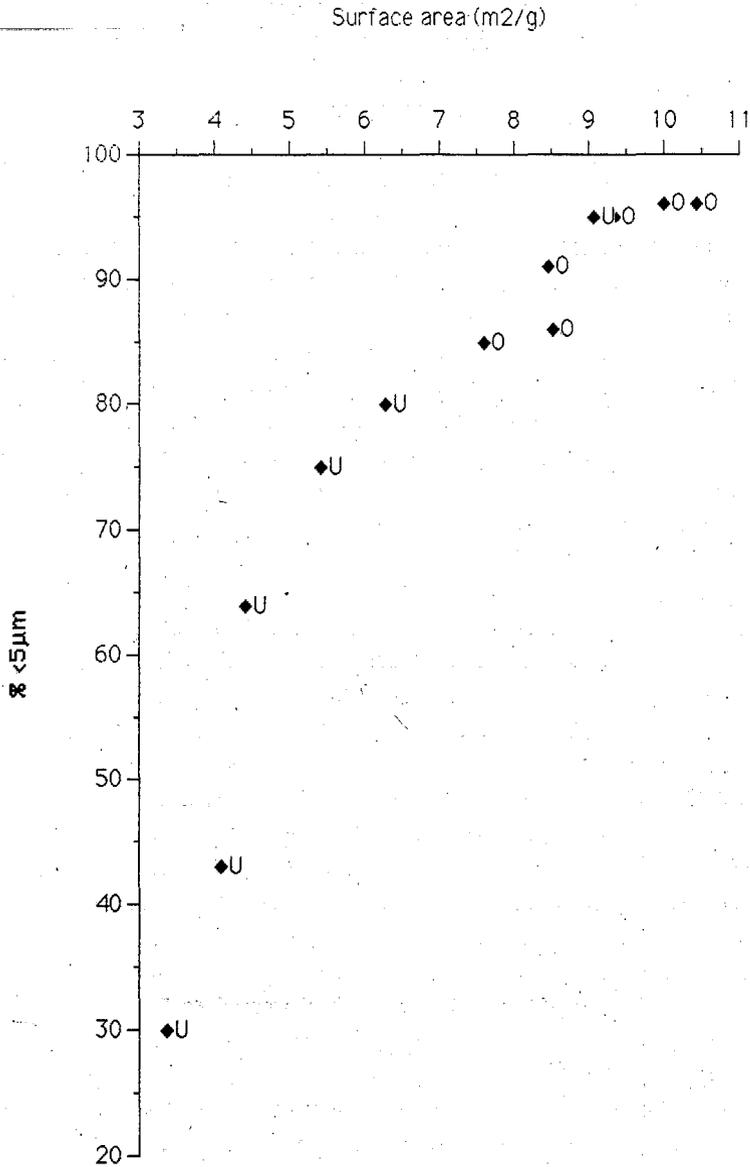


Fig. 1. Plot of surface area vs. % <5µm particles in Mozley hydrocyclone overflow (O) and underflow (U) reject products.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS OF CLAY-MINERAL ASSEMBLAGES IN THREE
PALEOZOIC MARINE EVAPORITE DEPOSITS IN THE UNITED STATES

M. W. BODINE, JR.

U.S. Geological Survey, MS 939, Box 25046, Denver, CO 80225, USA

Clay-mineral assemblages in marine evaporite rocks in the United States were studied from (1) the Upper Silurian Retsof salt bed in the Salina Group from the Appalachian Basin in western New York, (2) the Middle Pennsylvanian Paradox Member of the Hermosa Formation from the Paradox Basin in southeastern Utah, and (3) the Upper Permian Salado Formation from the Delaware Basin in southeastern New Mexico. All deposits have abundant halite; the Paradox salts contain thin beds with potash minerals, and the Salado salts constitute the nation's most important potash resource.

Clay mineralogy

Magnesium-rich trioctahedral clays dominate assemblages in these evaporite rocks rather than the kaolinite, dioctahedral smectites, illite, and mixed-layer clays that characterize most sediments. Chlorite (clinochlore), trioctahedral smectite (saponite), trioctahedral mixed-layer clinochlore-saponite (C/S) with varying fractions of expandable layers, talc, mixed-layer talc-saponite, and serpentine occur at one or more of the deposits. Discrete illite with little or no expandable interlayers is the only dioctahedral clay mineral and is ubiquitous at each deposit. Chemical compositions of insoluble <2- μ m fractions from the three deposits define clay-mineral assemblages with 15-30 weight percent MgO, 4-20 weight percent Al_2O_3 , 0.1-4.0 weight percent K_2O , and <3 weight percent total Fe expressed as Fe_2O_3 .

Clay-mineral distribution

In the Retsof salt bed (halite) the sole Mg-Al trioctahedral clay mineral is discrete chlorite; saponite and C/S are absent. Talc is abundant throughout the salt bed and serpentine occurs in some salts with low Br content (<85 ppm) toward the base of the unit.

In the Paradox salts discrete chlorite characterizes the dolomite beds, mixed-layer C/S with 10-50 percent smectite layers occurs in the anhydrite beds, and corrensite dominates the halite beds. Abundant talc coexists with corrensite in halite beds but serpentine is absent.

Mg-Al trioctahedral clays in the Salado Formation range from discrete chlorite, chlorite-rich to smectite-rich mixed-layer C/S, to discrete saponite. Talc is rare and serpentine is restricted to beds close to anhydrite-halite boundaries. Mixed-layer talc-saponite is associated with polyhalite beds and probably crystallized contemporaneously with the diagenetic polyhalite replacement of calcium sulfate salts.

Genesis of Mg-Al clay minerals

Magnesium enrichment of detrital clays most likely occurred during early diagenesis when the brine-sediment mass ratio was high and mass transfer between the clays and coexisting brine proceeded without significantly effecting brine composition. After burial and compaction, however, the brine-sediment mass ratio was substantially reduced and clay transformations were probably isochemical. This is because exchange between the clays and coexisting pore fluid would have been limited without drastically modifying pore fluid composition.

Early diagenesis effects transformation of detrital dioctahedral aluminous clays by Mg uptake at or slightly below the brine-sediment interface. B. F. Jones and coworkers have, for example, documented the transformation of aluminous detrital smectites into Mg-rich mixed layers with compositions midway between ideal dioctahedral and trioctahedral stoichiometry in continental evaporite environments of the western United States. The transformation of dioctahedral smectite (or, similarly, kaolinite) is illustrated by the simplified reaction



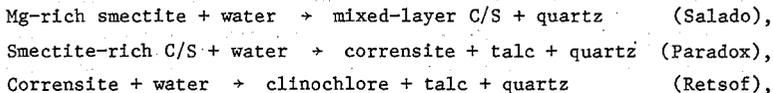
in which aluminum is conserved in the solids and the degree of Mg-enrichment in the clay is a function of the $(\text{Mg}^{2+})/(\text{H}^{+})^2$ activity ratio in the brine. The effect of increasing salinity (Mg concentration) on an authigenic smectite's composition explains the distribution of Mg-Al clays in the Paradox salts; their progressively increasing Mg/Al parallels the increasing salinities reflected in their host salts.

Some Mg-silicate minerals or their early diagenetic precursors,

such as kerolite, sepiolite, or stevensite, are neofomed during early diagenesis. The sequence quartz-talc-serpentine reflects increasing $(Mg^{2+})/(H^+)^2$ activity ratio and decreasing dissolved silica activity in the coexisting brine. Authigenic talc, for example, occurs in a small modern marine salina in the Caribbean, and kerolite, sepiolite, and stevensite have been reported by several workers from Quaternary terrestrial evaporites.

Late diagenesis over extended periods of geologic time allows isochemical recrystallization of the metastable phases such as the smectites with mixed di-trioctahedral stoichiometry. Thus, the compositions of early diagenetic smectites in the Paradox salts appear to be preserved in the chlorite through corrensite progression now observed.

Increased temperature accompanying burial also plays a role in late diagenesis. The succession of Mg-Al trioctahedral clays at the three localities is analagous to the well-known burial-metamorphic "illitization" of dioctahedral smectitic clays, and is similar to the burial progression in trioctahedral clays noted by F. A. Mackenzie and co-workers in a thick pile of weathered mafic detritus. The Salado clays (shallowest burial depth) consist of discrete smectite, chlorite, and the complete range of C/S compositions. The Paradox clays (intermediate burial depth) lack smectite-rich C/S but well-crystallized corrensite is abundant. The Retsof salts (deepest burial depth) contain only discrete chlorite. The generalized reactions,



illustrate the sequence of isochemical transformations with depth. Early diagenetic Mg-rich smectites are initially transformed to C/S whose compositions range from discrete saponite to discrete chlorite as observed in the Salado salts. With moderate burial, as in the Paradox salts, "chloritization" of the the smectite-rich C/S compositions produces corrensite and talc. Further burial, as with the Retsof salts, results in transformation of all smectite layers and produces a discrete chlorite-talc assemblage.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

IRON OXIDE MINERALOGY OF TERRA ROSSA

V. BOERO AND U. SCHWERTMANN*

Istituto di Chimica Agraria, Università di Torino, 15 v. Giuria, 10126 Torino, (Italy).

* Lehrstuhl für Bodenkunde Technische Universität München, 8050 Freising-Weißenstephan, West Germany.

Terra rossa (TR) forms a shallow and discontinuous cover on hard carbonatic rock and are especially common in areas of mediterranean climates. TR soils have been classified as Rhodoxeralfs or Xerochrepts (Soil Taxonomy), Luvisols or Cambisols (FAO-Unesco) as well as Sols rouges fersiallitiques (France).

The red color of TR is due to hematite and strongly contrasts with the white-gray color of the underlying rock, as well as with most of the brown soils in the same climatic environment, which are hematite free.

Although the TR material may no longer be found in its original position, its occurrence is usually restricted to hard, highly water permeable limestones which therefore must have been an essential part of the pedogenic environment under which the TR were formed.

The aim of our work was to characterize the iron oxide mineralogy of TR samples. The preliminary results of this characterization are presented here.

TR samples from Australia, France, Germany, Greece, Israel, Italy, Lebanon, Mexico and the USA were taken from profiles overlying the hard carbonatic rock or from cracks in the rock. The samples were free of particles $>2\text{mm}$ and contained only small quantities of particles $>20\mu\text{m}$ (see table). After dispersion in water with Na-hexametaphosphate and a mild ultrasonic treatment, the average clay content was 53%. The pH in water (1:10) was 7.7 (± 0.25). The

average total amount of iron oxide (Fed), (16h DCB treatment at RT), was 3.3%, of which 88% was in the clay fraction. The clays (separated after NaOH (pH=9) and ultrasonic dispersions) had an average Fed value of 5.5% with a narrow 95% P confidence interval (C.I. ± 0.35). The same was true for the Fed/Fet ratio (0.68 ± 0.03 ; n=39) which may serve as an index for the degree of weathering. The quantity of oxalate extractable iron (Feo), was low in B horizons (Feo/Fed 0.038 ± 0.006 ; n=32) but considerably higher (0.54 ± 0.02 ; n=5) in A horizons.

Al₂O₃ was separated into "amorphous Al-oxides" as dissolved by oxalate (Alo $0.43\% \pm 0.06$; n=37) and Al in Fe-oxides Ald-Alcb ($0.39\% \pm 0.07$; n=37).

Hematite (Hm) and goethite (Gt) were identified as the only iron oxides in the 19 samples so far examined. The Hm/(Hm+Gt) ratio (estimated from DXRD diffractograms) was not significantly correlated with Feo, Feo/Fed, Fed/Fet, Alo and Ald-Alcb. The mean crystallite dimension MCD111 (MCD perpendicular to the 111 plane) of Gt taken from DXRD peak broadening and MCDA (plate diameter) of Hm from 110 line, were both 29 nm. The plate thickness of hematite, MCDC (from WHH of 104 line), of 16 nm was estimated for a TR clay containing no Gt and having an MCDA of 38 nm. MCD and Al substitution in both Gt and Hm were not correlated with Ald-Alcb probably due to the simultaneous occurrence of Gt and Hm, but also because of the rather narrow range of values. This is also the case for the relationship between the Al substitution of Hm and that of Gt (average Al substitution ratio of 1:2), as well as between the Munsell color parameters (hue, value, chroma) and Hm and Gt properties (Al substitution and MCD).

In view of the wide geographic distribution of our TR samples, the rather limited variation of relevant Fe oxide characteristics (see 95% C.I. in the table) is noteworthy. It may indicate that their average values characterize a typical pedoenvironment for TR resulting from a combination of a mediterranean climate with a hard and permeable limestone.

The pedoenvironment would consist of a rather wet and cool winter period and a drier and warmer summer period and neutral pH conditions. Relatively high amounts of Fe would be released from

autochthonous or allochthonous primary Fe sources resulting in a rather high Fed/Fet ratio of ca 0.7 followed by preferential formation of hematite over that of goethite during the drier summer period (Torrent and Cabedo, 1986). Furthermore, the high Hm/(Hm+Gt) ratio and the medium level of Al substitution in both Gt and Hm are in accordance with the neutral pH conditions.

References

Torrent, J. and Cabedo, A., 1986. Sources of iron oxides in two reddish brown soil profiles from calcarenites in southern Spain. *Geoderma*, 37: 57-66.

TERRA ROSSA	x	n	CV%	0.95P C.I.
<2um (%)	53	25	35	45-61
2-20 um (%)	19	25	49	15-22
20-50 um (%)	8	25	73	5-10
50-200 um (%)	16	25	53	13-20
200-2000 um (%)	4	25	158	1-7
pH	7.7	39	11	7.4-8.0
Fed (%)	3.3	39	28	3.0-3.6

TERRA ROSSA CLAY

Fed (%)	5.5	39	19	5.1-5.8
Fet (%)	8.0	39	12	7.6-8.3
Fed/Fet	0.68	39	13	0.65-0.71
Feo (%)	0.21	37	41	0.18-0.24
Feo/Fed	0.040	37	45	0.034-0.046
Alo (%)	0.43	37	45	0.36-0.49
Alcb (%)	0.11	37	27	0.10-0.12
Ald (%)	0.50	37	42	0.43-0.57
Hm/(Hm+Gt)	0.64	20	29	0.55-0.72
MCDa of Hm (nm)	29	19	61	21-38
MCD111 of Gt (nm)	29	19	38	24-34
Al sub.Hm (mole%)	8	20	36	7-9
Al sub.Gt (mole%)	16	19	34	14-19
Hue (Munsell color) value	4.2	37	40	3.6-4.7
chroma	4.9	37	11	4.7-5.1
	5.6	37	18	5.2-5.9



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE CRYSTALLIZATION TEMPERATURE OF HYDROTHERMAL CLAY MINERALS :
THE DATA FROM FLUID INCLUSIONS AND CLAY GEOTHERMOMETERS

M.C. BOIRON¹, M. CATHELINEAU²

¹Laboratoire de Pétrologie de la Surface, Université de Poitiers, UA
CNRS 721, 40, Avenue du Recteur Pineau 86022 Poitiers Cédex France.

²CREGU, B.P. 23, 54501 Vandoeuvre-les-Nancy Cédex France.

Problems related to the temperature estimation of clay crystallization.

Temperature estimation is a necessary step in the understanding of the physical and chemical conditions of water-rock interactions. At medium-to-high temperature, geothermometric investigations of these natural processes use numerous techniques based on the mineral compositions, the fluid chemistry, the isotopic fractionation... Most of the available geothermometers are of no use in the case of studies dealing with water-rock interactions at temperatures ranging from 50°C to 350°C. This is mainly due to the lack of a characteristic mineral assemblage, and especially of theoretical or experimental values at these temperatures. As clay minerals are largely dominant in these systems, many authors attempt to use these minerals as thermal indicators, considering mostly the crystallographic features obtained by X.R.D., such as the expandable layer content, or the crystallinity of the material. Nevertheless, these thermal indicators are in general qualitative because of the difficulty of a precise thermal calibration. The combination of both the crystal chemistry of clays and a fluid inclusions study on coexisting minerals provides a satisfactory solution to this problem. As the use of clay geothermometers is still in its beginnings, comparison of the different geothermometric approaches on the same objects can give informative data, as described in the following section.

An example of thermal reconstitution : the fossil alteration of a volcanic series.

The above mentioned methodology was applied to the case of a fossil

hydrothermal system located in the northern part of the french Central Massif. The geological series consist of a pile of carboniferous volcanic sediments, acidic tuffs and rhyolites. They are affected by a strong multistage alteration due to a relatively complex tardi-hercynian hydrothermal activity. Two stages can be distinguished :

1) An early pervasive fluid circulation occurred first and is assumed to be related to the cooling of the volcanic system. Fluid-rock interaction provoked the alteration of the Fe-Mg bearing phases (biotites) into chlorites (brunsvigites). These chlorites are characterized by a relatively high Si substitution by aluminium in the tetrahedral site, which ranges from 1.15 to 1.3. This indicates, using the chlorite geothermometer of CATHELINÉAU et NIEVA (1985) and new data concerning the geothermometer calibration above 250°C (CATHELINÉAU, 1987), that the chlorite crystallized at temperatures above 300°C.

Temperatures are estimated to have been around $300 \pm 15^\circ\text{C}$, using the average Al_{IV} values obtained from the statistical treatment of the chemical variables.

Fluids in the chlorite zone were studied in the microcracks located in the magmatic quartz. These secondary fluid inclusions are assumed to give the P,T,X conditions of the dominant alteration of the rocks. Fluid inclusion data indicate that the minimum trapping conditions were around or slightly above 300°C (pressure correction about 30°C-50°C). Thus, there is a good agreement between the different estimations.

2) Later fluid circulation was more restricted to faulted areas. Fluid rock interaction in the vicinity of veins and microcracks provoked the retromorphosis of the first alteration assemblage into K-micas, ankerite and quartz. Two stages are distinguished according to the K-mica composition.

a) The first K-micas are phengites with an interlayer occupancy of between 0.80 to 0.90 (mean value = 0.87), a celadonite content of around 30 % and a very low paragonite content.

b) The second K-micas are illites without any expanding phase contribution, as demonstrated by the X.R.D. study. They are an interlayer charge ranging from 0.65 to 0.75. Fluid inclusions analysed in coexisting quartz (primary inclusions) show a minimum trapping temperature of $180 \pm 20^\circ\text{C}$.

A comparison of these data concerning the illite composition with the data from geothermal systems (MAC DOWELL and ELDERS, 1980 ; CATHELINEAU, 1987) suggests that the cristallization temperatures of the phengites and the illites were in the ranges of 250-270°C and 170-210°C respectively. The application of the illite geothermometer from CATHELINEAU et IZQUIERDO (1987) gives similar estimations.

In all three cases there is considerable agreement between the interpreted data obtained from the fluid inclusion studies and those deduced from the application of clay geothermometers.

CATHELINEAU M., NIEVA D. (1985). A chlorite solid solution geothermometer. The Los Azufres (Mexico) geothermal system. *Contrib. Mineral. Petrol.*, 91, 235-244.

CATHELINEAU M. (1987). Les interactions entre fluides et roches : thermométrie et modélisation. Exemple d'un système géothermique actif (Los Azufres, Mexique) et d'altérations fossiles dans la chaîne varisque. *Doct. Thesis. Nancy Univ.*, 515 p.

CATHELINEAU M., IZQUIERDO G. (1987). Temperature-composition relationship of authigenic clay minerals in the Los Azufres geothermal system. *Soumis à Contrib. Mineral. Petrol.*

MAC DOWELL S.D., ELDERS W.A. (1980). Authigenic layer silicate Minerals in Borehole Elmore 1, Salton sea Geothermal Field, California, USA. *Contrib. Mineral. Petrol.*, 74, 293-310.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

POLARIZED X-RAY ABSORPTION SPECTRA OF BIOTITE: APPLICATION TO THE STUDY OF FE-MG DISTRIBUTION IN THE PHLOGOPITE-ANNITE SERIES.

D. BONNIN¹, A. MANCEAU², C. FRETIGNY¹ AND P. KAISER¹

1-Laboratoire de Physique Quantique, Ecole Supérieure de Physique et de Chimie,
10 rue Vauquelin, 75231 Paris Cedex 05.

2-Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et 7 et CNRS
UA09, Tour 16, 4 place Jussieu, Paris 75252, France.

The x-ray absorption spectroscopy (XAS) is a method of choice to study the reality of octahedral solid solutions in phyllosilicates^{1,2}. This arises from the fact that EXAFS spectra provide information about the local structure around the x-ray absorbing atom. Typically, three nearest neighbour bond lengths, *nature* and number of atoms surrounding the central x-ray absorber can be determined. One of the main interest of EXAFS for clay mineralogy is its capability for distinguishing 3d elements from Mg and Al in the octahedral sheet. But this distinction necessitates a *careful* analysis of EXAFS data because phyllosilicates possess a complex structure.

Photoelectron waves backscattered by 3d elements and by Mg or Al atoms are out of phase making them easily distinguishable from each other. Unfortunately Si atoms are located in the vicinity of the first cation coordination sphere surrounding the x-ray absorber. As a consequence the resulting backscattered wave, which interfer with the outgoing wave in the EXAFS process, is the composition of elementary waves backscattered by octahedral cations and Si atoms. The precise analysis of EXAFS data necessitates to understand how these waves interfere. The structurally well known phlogopite-annite series offer a unique way to decipher x-ray absorption spectra. Data reported here have been obtained on the samples studied elsewhere by Sanz and Stone by Mössbauer and NMR³.

POLARIZED EXAFS SPECTRA OF BIOTITE

The unique method to separate Fe-Mg and Si contributions to EXAFS is to use the plane polarized nature of synchrotron radiation. The angular dependence of EXAFS, χ , is given by

$$\chi_{\text{pol}} = 3(\chi_{\text{iso}} \cos^2 \theta)$$

where χ_{pol} is the polarized EXAFS, χ_{iso} is the isotropic EXAFS and θ the angle between the polarization vector and the absorber-scatterer vector.

EXAFS spectra have been collected between 0° and 60° by steps of 10° . At each energy of row spectra, a linear regression analysis of the absorption for these different incidence angles permits obtention of the limiting case spectrum for which the polarization vector should be perpendicular to the ab plane^{4,5}. In that geometry, the beam direction should be parallel to this plane. At this angle the contribution of octahedral cations to EXAFS is canceled and it is then possible to extract the amplitude and phase functions of the Fe-Si atomic pair.

EXAFS SPECTRA OF FE-MICAS

A complete series of samples belonging to the phlogopite-annite series have been studied at the Fe K-edge to firstly examine the influence of the Fe/Fe+Mg ratio on EXAFS spectra. Then, the contribution of the Si atomic shell, which is *independent* of the chemical composition of biotites, has been subtracted to the row spectrum of each sample. It is shown that the photoelectron waves backscattered by Fe in annite and Mg in phlogopite are almost out of phase. This wave phase shift *continuously* increases along the series in agreement with the random distribution of Fe atoms within the octahedral sheet. For every sample the number of Fe and Mg second nearest neighbours surrounding Fe atoms has been determined fitting EXAFS spectra.

REFERENCES

- 1- Manceau A. and Calas G. (1985) Heterogeneous distribution of nickel in hydrous silicates from New Caledonia ore deposits. *Am. Miner.* 70, 549-558.
- 2- Manceau A. and Calas G. (1986) Ni-bearing clay minerals. 2. X-ray absorption study of Ni-Mg distribution. *Clay Minerals*, 21, 341-360.
- 3- Sanz J. and Stone E. E. (1983) NMR applied to minerals: IV. Local order in the octahedral sheet of micas: Fe-F avoidance. *Clay Minerals*, 18, 187-192.
- 4- Bonnin D., Bouat J., Kaiser P., Frétygny C. and Béguin F. (1986) Bond angle determination by angular EXAFS study and Debye-Waller anisotropy in 2D graphite intercalation compounds. *Journal de Physique*, C8, 47, 865-868.
- 5- Frétygny C., Bonnin D. and Cortès R. (1986) Polarization effects in XANES of layered materials: alkali-graphite intercalation compounds study. *Journal de Physique*, C8, 47, 869-873.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ADSORPTION OF COBALT BY SOIL IRON OXIDES AT LOW AND HIGH
EQUILIBRIUM SOLUTION CONCENTRATIONS

O.K. Borggaard

Chemistry Department, Royal Veterinary and Agricultural
University, Thorvaldsensvej 40, DK-1871 Frederiksberg C,
Denmark.

Eleven selected soils from Denmark and Tanzania were extracted with ammonium acetate (controls), EDTA, and dithionite-EDTA to fractionate iron (and manganese) oxides. EDTA-extractable Fe corresponds to what was earlier called amorphous Fe oxides, while the difference between dithionite-EDTA-extractable Fe and EDTA-extractable Fe corresponds to crystalline Fe oxides. The amount of cobalt adsorbed from 3 μM equilibrium Co solution, corresponding to the Co level in soil solution, and from 0.85 mM Co in 0.2 M NaNO_3 were determined for the extracted soils and for two synthetic Fe oxides. To investigate the stoichiometry of the adsorption process the amounts of acidity desorbed from the samples due to Co adsorption from 0.85 mM solution were also measured.

No significant correlations were found between Co adsorption and the content of organic matter and extractable Mn but they were low in the soils investigated. Close correlations were, however, found between Co adsorption and the Fe oxide contents.

The amount of Co adsorbed by the dithionite-EDTA treated soils, free of Fe and Mn oxides, were attributed to the clay silicates. The difference between Co adsorbed by acetate-extracted and dithionite-EDTA-extracted samples was attributed to the Fe oxides. This portion of adsorbed Co was well described by considering soil Fe oxides composed of only two fractions, an EDTA-extractable fraction of high reactivity and a less reactive fraction corresponding to the remaining Fe oxides.

Cobalt adsorption by the clay silicates was associated with a release of c. one H^+ per adsorbed Co, whereas about 1.7 H^+ were desorbed per Co adsorbed by the two Fe oxide

fractions in soils and by the synthetic Fe oxides.

The amount of Co adsorbed by the soil Fe oxides at both concentration levels were well predicted from the contents and specific surfaces of the two Fe oxide fractions together with the amount of Co adsorbed per m^2 of synthetic Fe oxides.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ADSORPTION OF NONIONIC POLYACRYLAMIDE ON Na MONTMORILLONITE: RELATION BETWEEN ADSORPTION, ZETA POTENTIAL, TURBIDITY, ENTHALPY OF DISPLACEMENT DATA AND DYNAMICS OF THE ADSORBED PHASE BY ^{13}C NMR IN AQUEOUS SOLUTION.

J. Y. BOTTERO*, M. BRUANT*, J. M. CASES*, D. CANET**

*Centre de Recherche sur la Valorisation des Minerais de l'ENSG et UA 235 du CNRS-BP 40-54501 Vandoeuvre Cédex France.

**Laboratoire de Méthodologie RMN-Université de Nancy I-BP 239-54506 Vandoeuvre Cédex France.

The aim of this work concerns the interactions between nonionic polyacrylamide (PAM) with different molecular weights (Mw), the monomer represented by isobutyramide with a homoionic Na montmorillonite (2g/l). Flocculation and adsorption mechanisms were interpreted by means of X-ray scattering, electrophoretic mobility, enthalpy of displacement and ^{13}C NMR of the adsorbed polymers in aqueous solvent.

RESULTS and DISCUSSION

At saturation in the interlamellar space one adsorbed isobutyramide molecule occupies two hexagonal sites. During the adsorption on the exposed basal plane surfaces the electrokinetic potential is constant. This means i) the NH_2 function is not protonated at the surface contact ii) Na ions are not displaced iii) the isobutyramide molecular size (0.56nm) is lower than the interface-shear plane surface length (0.8 to 1.5nm).

To understand precisely the mechanism of interactions one have to analyze the phenomenon at local and semi-local order. The adsorption isotherms ($Q_a\text{-Ca(g/l)}$) also show a $Q_a\text{-Mw}$ dependence. The higher the Mw the higher the adsorbed amount. At the plateau, Q_a increases from $\sim 20\text{g}\cdot 100\text{g}^{-1}$ to $68\text{g}\cdot 100\text{g}^{-1}$ while Mw increases from $4.4 \cdot 10^4$ to $3 \cdot 10^5$. The increasing of the adsorbed amount for a same Mw is accompanied by a small variation of the particle size in the range of 0.5-2 μm , corresponding to a limited aggregation and a decrease of the

electrokinetic potential absolute value. It means that the electrokinetic thickness d_e is larger than the interface shear-plane surface length. d_e remains lower than the diffuse layer thickness for $M_w < 3.7 \cdot 10^5$.

It may be asked whether the initial tactoid structure is conserved as adsorption proceeds. The evolution of d_{001} (nm) of dried state particles shows that the polymers have entered into the interlamellar space. The variation of d_{001} versus C_e also depends on M_w . For PAM $4.4 \cdot 10^4$ and $1.2 \cdot 10^5$ the highest limit is 1.7nm, whereas for PAM $3.7 \cdot 10^5$ and $3 \cdot 10^6$ d_{001} goes up to 2nm. Due to the macromolecule size ($16\text{nm} < R_g < 130\text{nm}$), which is one or two orders of magnitude larger than the interlamellar porosity (1 to 2nm), the adsorption of PAM into the interlayer space is expected to increase the particle size by means through the destruction of the regular stacking of the silicates sheets. Along the isotherms, the accessible surface increases and the tactoid structure changes.

The isotherms present, whatever M_w a change of the slope for $Q_a > 20\text{g}_a \cdot 100\text{g}_s^{-1}$. Beyond this value the slope decreases to attain the plateau of the isotherm. Such a curve has been previously obtained. It can be due to an aggregate break-up or macromolecule polydispersity. Both hypothesis can be considered. It is assumed that the beginning of the isotherms is related to a continuous tactoid break-up; from $Q_a > 20\text{g}_a \cdot 100\text{g}_s^{-1}$ the accessible surface area is invariant.

The NMR linewidth $\Delta\nu_{1/2}$ measurements of the adsorbed macromolecules ($-^{13}\text{C}=\text{O}$), larger than in water, allow to check this hypothesis. This broadening has been shown to arise from a chemical shift dispersion. This is due to a more rigid structure of the adsorbed molecules and consequently to the lack of averaging by rotational isomerism or to the surface heterogeneity. $\Delta\nu_{1/2}$ continuously decreases as Q_a increases indicating a narrower distribution of the chemical shifts. In other words the environment tends to the one encountered in solution. $\Delta\nu_{1/2}$ decreases from 430Hz and 390Hz to 180Hz and 106Hz respectively for $M_w = 3.7 \cdot 10^5$ and $3 \cdot 10^6$. Consequently loops and tails are more and more extended towards the bulk. The larger linewidths correspond to $Q_a < 20\text{g}_a \cdot 100\text{g}_s^{-1}$.

The heat of displacement values $-\Delta_{dep}H$ versus C_e shows a deep decrease, indicating that $-\Delta_{dep}H$ are only high at smallest Q_a values. Beyond $-\Delta_{dep}H$ is negligible, indicating a non thermic adsorption. Notwithstanding the lack of accuracy of the data it appears that the large values of $-\Delta_{dep}H$ correspond to the adsorption with a flat conformation of the macromolecules. The decrease of $-\Delta_{dep}H$ corresponds to the tactoids break-up and the formation of large loops towards the bulk, the number of segments anchored to the surface keeps constant.

From the different methods (isotherms of adsorption, microcalorimetry, ^{13}C NMR) it is possible to calculate the bound fraction P , which corresponds to the ratio between the segments number in the trains over the total segments number, as a function of Q_a .

From NMR, the parameter P can be defined as follows:

$$P = \frac{(\Delta\nu_{1/2})_{exp} - (\Delta\nu_{1/2})_{sol}}{(\Delta\nu_{1/2})_{ref} - (\Delta\nu_{1/2})_{sol}} \quad (1)$$

The validity of the formula (1) rest on the hypothesis of fast exchange between trains and loops. $(\Delta\nu_{1/2})_{ref}$ corresponds to the linewidth for $Q_a < 20g_a \cdot 100g_s^{-1}$ and $(\Delta\nu_{1/2})_{sol}$ corresponds to the linewidth in solution ($\sim 8Hz$).

From isotherms data $P \sim 1$ for $Q_a < 20g_a \cdot 100g_s^{-1}$. For highest Q_a values:

$$P = \frac{20}{Q_a} \quad (2)$$

From microcalorimetric experiments, P is evaluated as follows: the maximum of $-\Delta_{dep}H$ value is obtained from the maximum isobutyramide adsorbed amount: $23g_a \cdot 100g_s^{-1}$. This value corresponds to $-\Delta_{dep}H = 46J/100g_s$.

This value is also relative to the macromolecules adsorbed amount: $Q_a \sim 20g_a \cdot 100g_s^{-1}$ corresponding to $-\Delta_{dep}H = 46/20 = 2.3J_g$. This last value is the reference $(\Delta_{dep}H)_{ref}$. In this case:

$$P = \frac{(\Delta_{dep}H)_{exp}}{(\Delta_{dep}H)_{ref}} \quad (3)$$

P decreases from ~ 1 to 0.25 as Q_a increases. There a high degree of consistency between P values calculated from NMR and isotherms data.

On the other hand it exists a discrepancy between the P values from isotherms and microcalorimetric data.

CONCLUSION

Isobutyramide adsorbs firstly on the edges, secondly on exposed basal plane surfaces of the tactoids and ultimately between the interlamellar space without modifying the particle texture. At saturation, the molecular area is that of two hexagonal oxygen cavities.

At equilibrium the PAM macromolecules do not flocculate the clay particles, but the adsorption is strong and shows a Mw dependence. The turbidity evolution and size distribution versus Q_a corresponds to the destruction of the clay sheets stacking. The increase of d001 is due to the presence of PAM on the internal basal space. ^{13}C NMR data show that for $Q_a < 20\text{g}_a \cdot 100\text{g}_c^{-1}$, the adsorbed macromolecule conformation is rather flat. For higher Q_a values, the adsorbed macromolecules have larger and larger loops and tails towards the bulk. The heat of displacement $-\Delta_{\text{des}}H$ quickly decreases to zero. At low surface coverage, the adsorbed polymer conformation is flat and the heat of displacement is large. The heat of displacement is near zero from $Q_a > 20\text{g}_a \cdot 100\text{g}_c^{-1}$ where loops and tails are largely extended towards the bulk.

The calculation of the bound fraction P from NMR and adsorption isotherms are correlated.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE CLAYS OF THE PIEDMONTESE TERTIARY BASIN: GENETIC ASPECTS AND
TECHNOLOGICAL CHARACTERISTICS.

BOTTINO G.*; GRASSI G.*; STAFFERI L.**

* Dipartimento Georisorse e Territorio - Politecnico di Torino

** Dipartimento di Scienza dei materiali e Ingegneria Chimica - Politecnico di Torino.

A thick sequence of miocenic sediments extensively outcrops in the Tertiary Piedmont Basin.

These sediments mainly consist of deep sea argillaceous - marly deposits, in which several sandy lenticular bodies, mostly of turbiditi origin, are enclosed; as a response to tectonic movements of the alpine inland.

The recent deposits of the pliocenic transgression are in superposition on this sequence. These deposits are predominantly deep sea clays, followed by the quaternary sediments in transition and continental facies.

A systematic study of the argillaceous - marly sediments was carried out with the aim of highlighting firstly possible interconnections between the sedimentological and mineralogical aspects and secondly of defining the principal technological parameters of these materials, especially of those which are being excavated.

The mineralogical study, carried out principally by means of x-ray diffractometry, highlighted some differences of composition which can be correlated with the genesis of the deposits themselves.

The quaternary clays, in transition facies, show a clear predominance of illite compared with the other clay minerals. Among these kaolinite and smectite are present, but in small quantities, quartz is always present as well, whereas calcite and feldspars are absent.

Red clays, which are a residue of limestone solution, show a completely different composition. They are composed of amorphous substances as well as of quartz.

Pliocenic and miocenic marine clays are characterized by a combination of illite and kaolinite, in practically equal amounts in miocenic clays and with a predominance of illite in pliocenic clays. Smectite is always in very limited quantities.

Among non-clay minerals quartz is always present and plentiful with combined calcite, whereas feldspars are found predominantly in miocenic clays. These differences underline the dominant role of the deposit environment on the provenance of material connected to the direction of the paleocurrents.

Technological characterization was carried out by the definition of the granulometry, of the dilatometric, greification and drying curves, the study of the thermal transformations through the heating microscope and observation through the scanning electron microscope.

Quaternary clays, with illite predominant, at firing show rather marked dilatation (about 1%) around 800 °C, with shrinkage in the order of 15% at a temperature above 1100 °C. Effective porosity (measured as the water absorption %) ranges from values of about 30% at temperatures of 900 °C to values below 5% for temperatures around 1100 °C, while the drying shows shrinkage of up to 3% for weight loss values of about 10%.

Pliocenic clays with illite-kaolinite predominant show somewhat variable characteristics with absorption between 35% and 15% at 1150 °C, expansion around 800 °C in the order of 1,2% and modest shrinkage values at drying (0,2 ÷ 1%).

Miocenic clays, predominantly illitic-kaolinitic with abundant quartz and calcite present are characterized by rather variable values as regards the water absorption % (25-35 at 1100 °C). The maximum dilatation is found in the range 650-800 °C and has values of 0,1 ÷ 1,4%. Finally, the shrinkage at drying is between 4 and 0,2%.

We can affirm that the technological characteristics of the clays examined also highlight the dominant role played by the granulometric composition compared with mineralogical composition.

The analysis performed showed that the Piemontese Tertiary Basin clays are in general suitable only for the manufacture of bricks because of their mineralogical

and granulometric characteristics. Only in a few cases, (above all in quaternary clays) were technological characteristics found of a kind which might permit their use in the field of ceramic tiles in general and of stoneware in particular since they have an acceptable level of greification in the temperature range between 1070 and 1130 °C.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CHEMISTRY AND STRUCTURAL ORDER IN HYDROTHERMAL
AND SEDIMENTARY KAOLINITES

M. F. BRIGATTI

*Istituto di Mineralogia e Petrologia dell'Università, Via S. Eufemia 19 - 41100
Modena (Italy)*

Chemical, thermal, X-ray analyses and crystallinity tests were made on kaolinite samples of hydrothermal and sedimentary origin (from Sardinia quarries, Italy), to explore correlations among structural order, unit cell parameters, chemistry and geological setting.

The structural formulae indicate the nature and extent of ionic substitution (prevalently Fe^{3+} for Al in octahedral sites); it is interesting to note the low Al for Si tetrahedral substitution, thus the overall layer charge, although low, is only linked to octahedral substitutions.

According to Weaver and Pollard (1974), the lowest Ti content in sedimentary samples demonstrates that kaolinite is a residual weathering product of a leucogranite; feldspar is the major source mineral and its degree of alteration is complete as confirmed by the low K content (Tsolis-Katagas, 1983).

The interpretation of crystallinity tests, on the whole, emphasizes a higher structural order in sedimentary than in hydrothermal samples, the former were characterized by: (i) lowest 002 X-ray line broadening, that is a function not only of clay plate thickness, but also of stacking faults, i.e. structural disorder along *c* direction (Williams and Garey, 1974); (ii) lowest d_{001} values due to the scarcity of multiple phases (Tchoubar *et al.*, 1982); (iii) lowest percentage of layer expansion after hydrazine treatment: the expansion is particularly linked to "geometric" faults, i.e. layer distortion as suggested by Tchoubar *et al.* (1982); (iv) lowest random structural faults in *ab* plane as suggested by R_2 -test (Cases *et al.*, 1982).

The dehydroxilation endothermic effect ranges between 555 and 575°C in sedimentary kaolinites and between 530 and 555°C in hydrothermal ones broadening asymmetrically in the latter; the exothermic effect shows a different behaviour for hydrothermal and sedimentary samples ($T > 1000^\circ\text{C}$ and

$T < 1000^{\circ}\text{C}$ respectively): this underlines that symmetry and temperatures of thermal reactions are affected by structural order of the mineral (Mackenzie, 1970).

Results of a statistical test (*Factor Analysis*) emphasize that kaolinite crystallinity is particularly affected by whole octahedral chemical composition; a dimension decreases linearly with the increase in kaolinite disorder and/or Fe octahedral content, whereas other cell dimensions are linked to yttrium and copper content.

The different behaviour of sedimentary and hydrothermal kaolinite, confirmed also by statistical analysis, cannot be considered as a proof of the existence of a direct cause-effect relationships between chemistry, structural order and genesis. Certainly a lot of factors controlling both the composition and structural order of the mineral is considerable inside the two genetic environments.

REFERENCES

- CASES, J.M., LIÉTARD, O., YVON, Y., DELON, J.F. (1982): Étude des propriétés cristallographiques, morphologiques, superficielles de kaolinites désordonnées. - *Bull. Mineral.* **105**, 439-455.
- MACKENZIE, R. C. (1970): *Differential Thermal Analysis 1*. Academic Press, London, 775pp.
- TCHOUBAR, C., PLANÇON, A., BEN BRAHIM, J., CLINARD, C., and SOW, C. (1982): Caractéristiques structurales des kaolinites désordonnées. - *Bull. Minéral.*, **105**, 477-491.
- TSOLI - KATAGAS, P. (1983): Investigation of kaolin deposits associated with extrusive rocks in Lesvos island, Greece. - *Neues. Jahrbuch. Miner. Abh.*, **146**, 182-196.
- WEAVER, C., POLLARD, L.P. (1973): The chemistry of Clay Minerals. - *Development in sedimentology*, **15**, Elsevier, Amsterdam.
- WILLIAMS, D.G. and GAREY, C.L. (1974): Crystal imperfections with regard to direction in kaolinite mineral. - *Clays and Clay Minerals* **22**, 117-125.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ASYMMETRY OF THE THICK ORDOVICIAN POTASSIUM BENTONITE BED
(B-BED) AT KINNEKULLE, SWEDEN.

ANN MARIE BRUSEWITZ

Geological Survey of Sweden, Box 670, S-75128 Uppsala,
(Sweden)

In a recent paper on potassium bentonites at Kinnekulle, Sweden, the thickest bed (nearly 2 m) was studied in its upper 110 cm only (Brusewitz, 1986). The main clay mineral was shown to be illite/smectite (I/S) with increasing proportions of illite layers towards the upper boundary. This is well reflected by a change in K_2O , successively increasing from 2.4% at the centre of the bed to .4% at the top, as well as in X-ray powder diffractograms. In the present paper results from a study of samples from the lower part of the B-bed, earlier not available, will be presented.

The $< 0.5 \mu m$ fraction was used for chemical analysis, cation-exchange capacity and X-ray powder diffraction. Structural formulae were calculated on the basis of $O_{10}(OH)_2$. The ratios of K:Rb and K:Sr were used as indicators of changes within the B-bed.

The results indicate that there is no similar increase in potassium and in consequence of illite layers in I/S towards the lower boundary as was found for the upper part of the bed. This is in contrast to what was described by Altner et al. (1984) for a bentonite bed of comparable thickness in Montana. This bed showed potassium to increase towards both the upper and the lower boundary in a symmetrical way. The increase was reflected in higher proportions of illite in I/S towards both boundaries.

An explanation of this difference may be the geologic positions of the two beds. The Kinnekulle bed is flat-lying whereas the Montana bed is tilted through thrusting (Mudge, M.R., 1972). At Kinnekulle the sediment below the bentonite is silicified, a fact which may have reduced circulation of reactive solutions. The upper part of the bed could have been in contact with sea water for a longer period increasing the availability of potassium.

REFERENCES

- Altaner, S.P., Hower, J., Whitney, G., and Aronson, J.L.
(1984) *Geology* 12, 412-415.
- Brusewitz, A.M. (1986) *Clays & Clay Minerals* 34, 442-454.
- Mudge, M.R. (1972) U.S. Geol. Surv. Prof. Pap. 663-A, 142 pp



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGICAL VARIATIONS IN A TONSTEIN DOUBLET OF THE SOUTHERN MOLTEÑO FORMATION, KAROO SEQUENCE, TRANSKEI

D. BOHMANN AND M. HEINEMANN*

Department of Geology and Mineralogy, University of Natal,
P.O. Box 375, Pietermaritzburg, 3200, (R.S.A).

*Transkei Mining Corporation, P.O. Box 903, Umtata, (Transkei).

Coal occurrences of the southern Molteno Formation (Upper Triassic) in Transkei, southern Africa, were recently re-evaluated. Two special bands from composite coal seams noted by Schwarz (1902) proved to be tonsteins. The vertical distance between the two tonsteins ranges from 40 to 60 cm. The tonstein doublet is traceable over a distance of 250 km. In the most northeastern coalfield the upper and lower tonsteins have a thickness up to 6 and 8 cm respectively, whereas in the most southeastern Guba coalfield their thickness increases to 10 and 12 cm respectively. These tonsteins are distinguished in the field by their usually slightly yellowish to grey colour from the black surrounding sediments which, in most cases, consist of coal and/or carbonaceous shale. The coal rank varies from low to high volatile bituminous coal to anthracite.

X-ray diffraction analyses revealed that the mineralogy of the tonsteins is considerably different from that of the enclosing rock. The quartz content of each tonstein was always found to be much lower than that of the enclosing sediment. In some tonsteins no quartz could be detected by means of XRD.

The clay minerals identified in the claystones were most frequently rectorite (a regular mica/smectite interstratification) or an ordered mica/smectite interstratification (mica < 40% or > 60%). Additional to this interstratification frequently chlorite, less frequently kaolinite, seldom mica and only in a few cases traces of pyrophyllite or talc were found. Accessory minerals include feldspars as well as goethite in some surface samples.

The following regional clay mineral variations were recognized: kaolinite seems to be restricted to the most northern part of the Maluti coal field where it is the dominant clay mineral and the most southwestern parts of the Guba coalfield where it is a minor constituent. The kaolinite content decreases mainly in favour of regular (rectorite) or ordered mica/smectite interstratifications southwards in the Maluti coalfield and east and northeastwards in the Guba coalfield. These interstratifications are the dominant clay minerals in between the extreme NE and SW sample localities. The presence of chlorite was observed in a number of samples.

The sediments other than claystones are composed of a significant amount of quartz beside mica and/or chlorite as the most frequent phyllosilicates and small amounts of a random interstratification. Furthermore plagioclase is a common constituent of these sediments.

Microscopic investigation of the tonsteins revealed that kaolinite occurs as both cryptocrystalline matrix and euhedral to subeuhedral crystals. Bent or coiled kaolinite vermiforms up to 1.5 mm in length are observed. Wisps of mica occur along the boundaries of vermiforms or as individuals floating in a kaolinite matrix. Some parcels of kaolinite crystals that fill nearly square or rectangular outlines are regarded as pseudomorphs after feldspar. Few remnants of sanidine are optically detectable, especially by their splintery and wedge-shaped forms. Rectorite displays a micaceous habit, high birefringence and a texture inherited from volcanic tuff or ash. Glass shards could not be identified in any of the Upper Triassic tonsteins.

Two of the three main tonstein types distinguished by Mackowsky (1982), are found in the southern Molteno Formation: (1) the kaolinite coal tonstein and (2) the mixed layer coal tonstein (mica/smectite). Though no glass shards could be identified in the tonsteins, because they did not undergo early carbonate or silica cementation which prevents glass shards from alteration to clay minerals (Jeans, Marrinau and Mitchell, 1977), the following criteria warrant the term tonstein: (a) presence of sanidine; (b) nearly monomineralic composition (kaolinite or rectorite); (c) lateral passage from one clay mineral dominance to the other; (d) large lateral extent (250 km) and (e) sharp contacts to the adjacent sediments.

Volcanic glass is extremely sensitive to weathering in an aqueous environment and its alteration products vary according to the properties of that environment (Millot, 1970). The airborne ash was deposited in a palaeoenvironment with marked primary differences. Kaolinite formed under "freshwater" or limnic-fluviatile conditions which prevailed only in the extreme NE and SW of the study area, whereas smectite formed in a marine-influenced water and rectorite as well as other mica/smectite interstratifications developed from smectite during diagenesis.

The tonstein doublet described here improved stratigraphic correlation of various coalfields in the southern Molteno Formation.

REFERENCES

- Jeans, C.V., Marrinau, R.J. and Mitchell, J.G. (1977). Origin of Middle Jurassic and Lower Cretaceous Fuller's Earth in England, Clay Miner. 12, p. 11-144.
- Mackowsky, M.-T. (1982). Minerals and trace elements occurring in coal. In: Stach's Textbook of Coal Petrology, Gebrüder Bornträger, Berlin.
- Millot, G. (1970). Geology of Clays, Masson et Cie, Paris, 429 pp.
- Schwarz, E. (1902). Geological Survey of parts of the Matatiele Division, Griqualand East, Cape of Good Hope, Annual Report.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

INFLUENCE OF TANNIC ACID ON THE FORMATION OF HYDROXY-AL-MONTMORILLONITE COMPLEXES.

A. BUONDONNO, D. FELLECA AND A. VIOLANTE

Institute of Agricultural Chemistry, University of Naples
(Italy).

The nature of hydroxy-Al-clay complexes is affected by many factors, as the amount of Al saturating the clay, the pH, the type of expansible phyllosilicates, and the presence of foreign ligands. The influence of some organic acids (citric, oxalic, tannic or humic acid) on the formation and the stability of Al-interlayers in montmorillonite has been studied particularly during the last ten years.

Aim of this work was to study the influence of the order of addition of montmorillonite, Al and tannic acid on the mineralogical and chemical properties of complexes formed at pH 4.5.

In this paper, for the sake of clearness, montmorillonite (a suspension of 312.5 ml containing 5 grams of Uri montmorillonite), aluminum (300 ml of $AlCl_3$ 0.1 M) and tannic acid (5 grams) are indicated as <M>, <A>, and <T> respectively. Chlorite-like complexes were prepared, as described below:

i- The complexes MT, AM and AMT were obtained by mixing respectively $\langle M \rangle + \langle T \rangle$, $\langle A \rangle + \langle M \rangle$, and $\langle A \rangle + \langle M \rangle + \langle T \rangle$ and slowly adding NaOH 0.1 N up to pH 4.5.

ii- The complexes A+MT, AM+T, AT+M and MT+A were prepared by slowly adding to the components on the left of "+" NaOH 0.1 N up to pH 4.5. The other components were then added, and the pH of each suspension was brought again to 4.5. The final volume of all the suspensions was adjusted to 2000 ml, in order to have an Al concentration of 15 mM (18 meq Al per g of clay and a tannic acid/Al molar ratio of 0.1). The samples, aged 2 months at 20 °C, were filtered through membrane filters (0.45 μm), washed and then freeze-dried.

It has been found that, in the absence of $\langle T \rangle$, 70% of Al was retained by montmorillonite (complex AM), whereas, in the presence of $\langle T \rangle$, more than 90% of Al was adsorbed by montmorillonite, or precipitated as separate phase oxydes.

In the AM complex, the fixation of hydroxy-Al ions increased the X-ray basal spacing (d_{001}) of montmorillonite from 11.87 Å to 15.55 Å. This sample, when preheated at 110, 300, and 550 °C, only gradually collapsed up to 14.06 Å (9.65 Å for montmorillonite), and, after ethylen-glycol (EG) solvation, expanded at 16.04 Å (17.10 Å for montmorillonite) showing a good interlayering. In the complex MT there were also evidences for the retention of some tannic acid in the interlamellar spaces of montmorillonite (d_{001} =13.16 Å at room

temperature).

The hydroxy-Al-tannate-montmorillonite complexes (AMT, A+MT, AM+T, AT+M and MT+A) showed broad and asymmetric peaks, with maxima ranging from 15.55 Å (AMT, MT+A) to 19.18 Å (A+MT). After EG solvation, the peaks showed maxima ranging from 16.29 Å (AMT) to 19.00 Å (A+MT). These complexes also showed different behaviour to preheating. For example, the complex AMT showed at 300 or 550 °C small and broad peaks with maxima at d-spacings similar to those ones ascertained for the complex AM, whereas the complexes AT+M, MT+A, and A+MT showed absence of distinct collapse of d-001 spacing upon heating at 300 or 550 °C. Probably, in the latter samples, the continuous removal of tannic acid upon heating leaved hydroxy-Al pillars randomly distributed.

Chemical and thermal analyses, potentiometric titrations, Al-selective extractions, IR spectroscopy gave important informations on the hydroxy-Al-tannate-montmorillonite complexes. It was ascertained that the order of addition of clay, Al and tannic acid widely affected the nature and the stability of the chlorite-like complexes which showed characteristic mineralogical, thermal (DTA), and chemical properties. The titratable and exchangeable acidity and CEC of the samples as well as the amounts of Al and C removed by chemical treatments (oxalate, pyrophosphate, hydrogen peroxyde and Na₂CO₃) often differed significantly from sample to sample.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SYNTHETIC AND NATURAL EARLY STAGES SMECTITES

E. CABALLERO, E. REYES, F. HUERTAS AND J. LINARES

Estación Experimental del Zaidin, C.S.I.C., Prof. Albareda, 1, 18008-Granada (Spain).

In the genetic study of bentonites from the volcanic region of Cabo de Gata (Almería, Spain) it has been observed that the smectites varie in composition depending on the alteration degree of parent rocks. So, the smectites are less rich in irons as the alteration goes on. In the region, however, we have not found examples of early stages of alteration, because normally the alteration affects more than 50% of the parent rock. Thus, experimental alteration is needed to obtain these first stages.

The alteration was carried out in a Soxhlet equipment permitting continuous cycles of leaching. Three typical rocks were selected for the experiment: sample VR (amphibolic andesite), sample J (amphibolic dacite) and sample RSP (pyroxenic andesite). The sample VR is a vitrophide (>80% of vitreous matrix), while samples J and RSP have a porphidic texture (52 and 56% of vitreous matrix). The rocks were crushed and sieved to <0.63 mm, and the <2 nm fraction was separated to remove fines. The samples (ten grams of the 2 - 630 nm fraction) were introduced into dialysis bags, so that the hydrolyzed elements can react between themselves prior to their passing to the bottom flask. By this mean the neoformation of smectite in the bags is favoured. The time of hydrolytic reaction was of 1457 hours with a temperature of 82±5°C. The total amount of percolated water was 394, 243 and 302 liters for the samples VR, J and RSP, respectively.

The amount of neoformed smectites ranged from 11 to 12%, with matter losses depending on the texture of the parent rock, so that, the sample VI underwent a higher loss.

The products obtained in every case were: a) altered residue and smectite remaining in the alteration bags, and b) the hydrolyzed elements that passed to the reception flask. The last ones can be

considered as "partial losses", which added to the elements included in the neoformed smectites will give the "total losses". From these data the mobility of each element can be obtained. So, for the "partial loss" the sequence is: Ca>Na>K>Si>Mg>Al>Fe, and for the "total loss": Ca>Mg>Na>Si>K>Fe>Al. It must be pointed out that Mg is an immobile element in the first sequence, indicating that this element is retained by the smectite, as it is also the case for Fe and Al.

From the normative minerals present in the fresh and altered rocks a mineralogical balance was calculated, and the following sequence of mineral susceptibility to hydrolysis was deduced: Biotite>Amphibole>Pyroxene>Plagioclase>Sanidine>Quartz. Therefore, the chemical environment during the alteration reaction will change from a system dominated by the hydrolysis of ferromagnesian minerals, in the first stages of alteration, to another controlled by the hydrolysis of feldspars, at the final of the reaction. In this way, the neoformed smectites will change, accordingly, from iron to aluminium rich composition.

Actually, the structural formulae deduced for the synthetic smectites are:

Sample	Si ^{iv}	Al ^{iv}	Al ^{vi}	Fe ^{vi}	Mg ^{vi}	X ⁺
VR	7.566	0.434	2.244	0.660	1.468	0.783
J	7.215	0.785	2.481	0.988	0.793	0.793
RSP	7.413	0.587	2.527	0.983	0.730	0.844
Region average	7.784	0.214	2.894	0.215	1.008	0.875

It can be observed that the smectites are richer in iron than the average of natural smectites of the Cabo de Gata region. Other fact to be emphasized is the high tetrahedral substitution in these early stages smectites. A similar tendency can be also observed in the natural smectites of the zone.

Although these results are in accordance with the general trends observed in natural bentonites, there are, however, some noticeable differences. First, the amount of leaching water is considerably higher in the laboratory experiments than in natural environment, this promoting and increase in the rate of transformation. Second, the temperature regime is also higher (82°C in laboratory and 40-70°C in nature), what will increase also the smectite formation rate. Finally, the diminution in permeability, in the natural system, produced by the gradual transformation of pyroclastic materials into smectite, and the contribution of elements by the hydrothermal solution, can modify the rate of alteration in nature.

In conclusion, the differences between the process of smectite formation from volcanic rocks in natural and artificial systems are strictly kinetical and should not affect neither the mechanism of the reaction nor the composition of neoformed smectites.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ORDER-DISORDER IN TWO LAYER Mg-VERMICULITE

C. de la CALLE, H. SUQUET and C.H. PONS^{**}

Laboratoire de Réactivité de Surface et Structure. Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05 (France)

^{**}Université d'Orléans, Laboratoire de Cristallographie (U.A. 810), B.P. 6759, 45067 Orléans Cedex 2 (France).

The present paper reports the results about the crystal structure of two-layer Mg-vermiculite obtained by a new approach to the study of semi-random structures (de la Calle et al, 1984).

The Y-axis projection of the structure of a Mg-vermiculite from Sta. Olalla (Spain) is ordered. It is obtained by classical two-dimensional Fourier analysis (Fig.1). The resultant electron-density contour map provides accurate parameters for the atoms of the silicate layer and locates the water molecules at $x = 0.142$, $z = 0.42$ and probably $x = 0.45$, $z = 0.35$ (water in hexagonal hole) and the exchangeable cations at $x = 0.5$, $z = 0.5$. The final reliability factor for $h0\ell$ reflections was 14.6% (70 reflections).

By contrast reciprocal lattices rows parallel to c^* , with indices hK , become diffused when $K \neq 3n$.

The Llano vermiculite described by Shirozu and Bailey (1966) is considered to have the stacking sequence s (Mathieson and Walker, 1954). In the terminology of Bailey and Brown (1962) for chlorites, the s structure is an alternation of $Ia-4$ and $Ia-6$ layers with an L type shift within each talc sheet of $-\frac{1}{3}$ parallel to the symmetry plane. This sequence incorporates shifts of alternate layers relative to another by $+\frac{b}{3}$ and $-\frac{b}{3}$ along the Y-axis.

Calculation of the diffusion intensities along the rows of the $|0K\ell|^*$ and $|1K\ell|^*$ planes allows a single model to be derived (de la Calle et al, 1984).

It is proved that the layer displacements are not regular. The disorder is created by the random distribution of two translations parallel to Y-axis : $+\frac{b}{3}$ and $-\frac{b}{3}$. In other words, the layers do not have a regular succession of displacements $+\frac{b}{3}, -\frac{b}{3}, +\frac{b}{3}, \dots$, but there

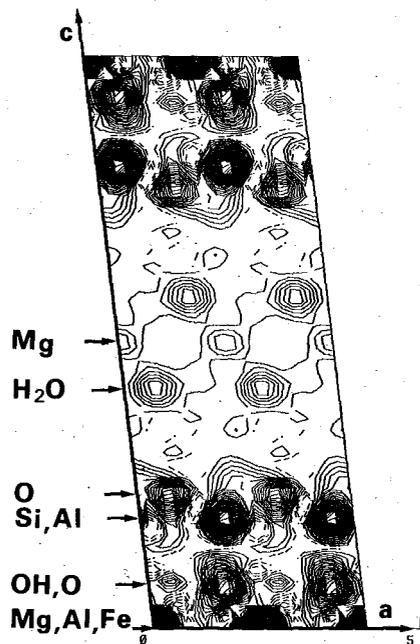


Fig 1

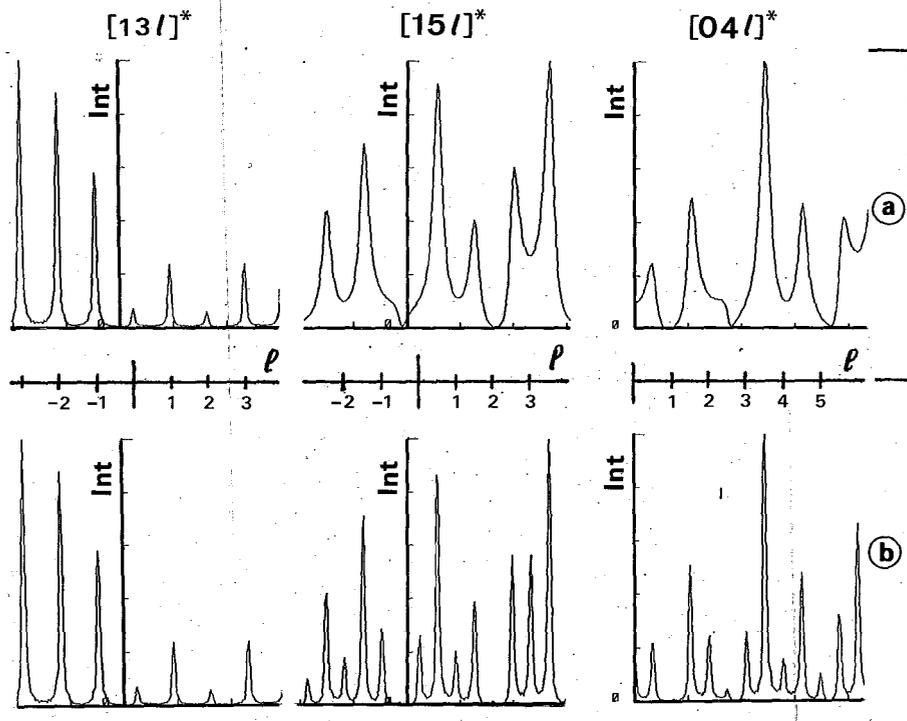


Fig 2

are "mistakes" in the sequence.

Figure 2 shows a comparison of calculated profiles of (1.3), (1.5) and (0.4) bands : a) model with random translations $+\frac{b}{3}$ and $-\frac{b}{3}$; b) model with ordered translations $+\frac{b}{3}$ and $-\frac{b}{3}$ (two-layer polytype).

The general agreement, the experimental intensities of the $K = 3n$ reflections and of the $K \neq 3n$ bands with those of a) model prove that the layer stacking in Sta Olalla vermiculite is disordered.

The Weissenbergs films of Sta Olalla vermiculite resemble most natural vermiculite (Llano, Malawi, Prayssac, Benahavis, Ampandradana..) and it is possible to believe that most natural vermiculite exhibit layer stacking disorders.

REFERENCES

- BAILEY S.W. and BROWN B.E. (1962). "Chlorite polytypism. I. Regular and semirandom one-layer structures". Am. Miner., 47, 819.
- DE LA CALLE C., PLANCON A., PONS C.H., DUBERNAT J., SUQUET H. et PEZERAT H. (1984). "Mode d'empilement des feuillets dans la vermiculite sodique hydratée à une couche (phase A 11.85 Å)". Clay Minerals, 19, 563.
- MATHIESON A.M. and WALKER G.F. (1954). "Crystal structure of magnesium-vermiculite". Am. Miner., 39, 372.
- SHIROZU H. and BAILEY S.W. (1966). "Crystal structure of a two-layers Mg-vermiculite". Am. Miner., 51, 1124.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**GENERAL FLOW-SHEET OF THE STUDY OF INDUSTRIAL APPLICATIONS OF KAOLINS
OF GALICIA (NW SPAIN)**

G. CAMPILLO, R. CONDE-PUMPIDO*, J. FERRON*, C. R. BALTAR, A. VARELA

Instituto de Minerales de Sargadelos, Cervo-Lugo (Spain)

*Departamento de Edafología y Química Agrícola, Universidad de Santiago de Compostela (Spain)

The results obtained in an investigation project performed by the Instituto de Minerales de Sargadelos (Galicia - Spain) can be summarized as presented below. The project consisted of the study of 14 galician kaolin samples with the aim of establishing their possible industrial applications in ceramic and paper fields.

The difficulty of a reliable industrial evaluation of a kaolin by means of several simple tests is clear. Kaolins with similar chemical, mineralogical and granulometric composition, even in neighbour samples are of dissimilar technical capabilities.

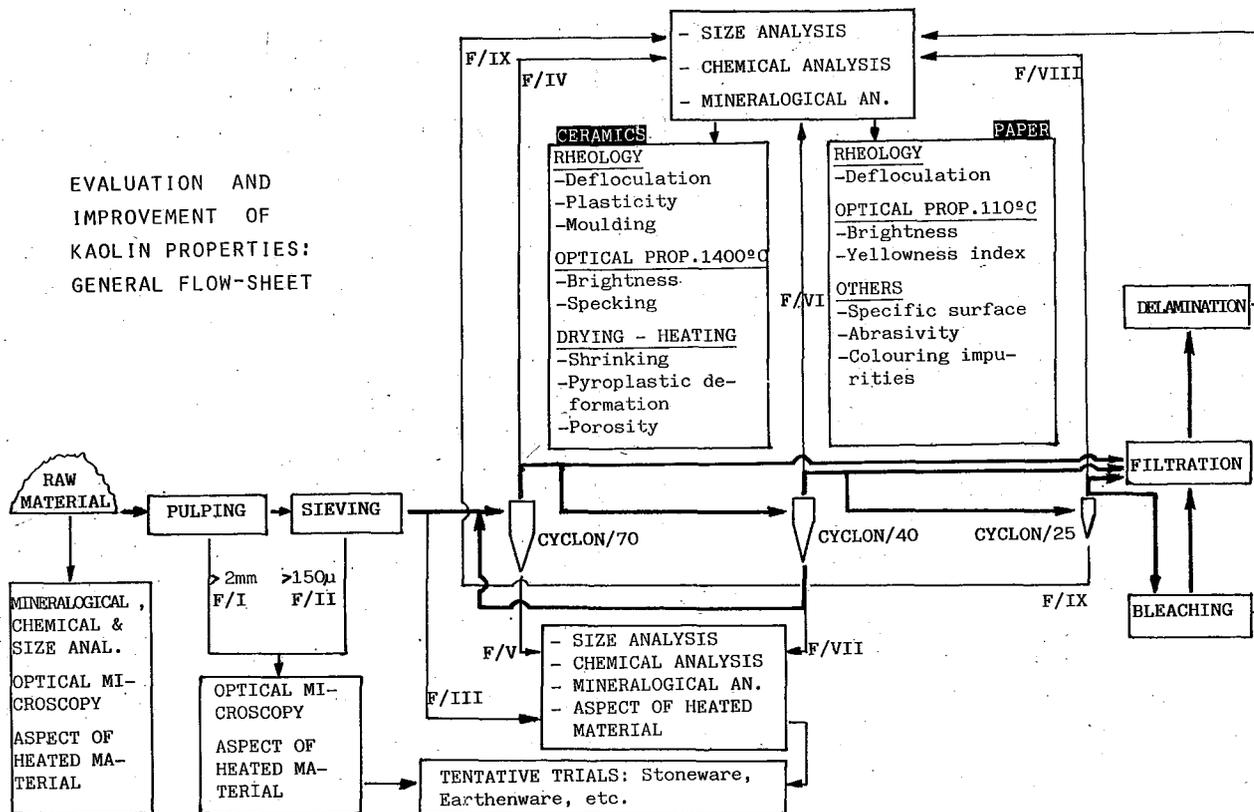
The evaluation diagram presented here is complex and includes a great variety of essays which must be performed with sophisticated and expensive techniques which, in many cases, are not easily accessible to industry.

As a simplification of it, a series of rejection-aimed trials to be performed in the first stage of an investigation can be established:

- general appearance of raw material as received, dried to 110 °C and heated to 1400 °C.
- loss on ignition to 1000 °C
- granulometric distribution
- brightness of minus 75 microns fraction dried to 110 °C and heated to 1400 °C
- deflocculation behaviour of this fraction.

These trials allow an estimation of the general behaviour and establishing the minimal requirements for it.

EVALUATION AND
IMPROVEMENT OF
KAOLIN PROPERTIES:
GENERAL FLOW-SHEET



Several pilot plants, with capacities for the treatment of 10 kg, 100 kg and 500 kg/h (continuous) of raw material, were designed and constructed. Such plants are based on screening coarse fractions off the pulped material and on hydrocycloning it in order to obtain fractions of different granulometric distribution.

The study of bleaching methods and their technical equipment has served to demonstrate that the designed device is effective for elimination of plus 10 microns particles. Chemical bleaching, for which a new fluid bed device based on "BALTAR" pulsator was designed, was more applicable in most cases.

Bleaching efficiency can be predicted by means of the previous study of kaolin impurities or of its yellowness index, which is clearly related to the quantity of iron oxides extracted by chemical methods.

An improvement of the rheological properties of the kaolin is achieved by changing, in a proper manner, the granulometric distribution. Among the usual methods, attrition grinding was rejected because of its undesirable changes on surface properties, which are exerted in virtue of its grinding action.

Delamination of kaolinite empilements by pug-milling or kneading has proved to be the more suitable method, especially in kaolins having a considerable quantity of minus 10 plus 2 microns fraction.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE EFFECT OF CO₂ ON THE FORMATION OF GOETHITE VERSUS
LEPIDOCROCITE FROM OXIDATION OF FeII SOLUTIONS

L. CARLSON*) AND U. SCHWERTMANN

Lehrstuhl für Bodenkunde, Technische Universität München,
8050 Freising-Weißenstephan, F.R.G.

* Geology Department, University of Helsinki, SF-00171
Helsinki, Finland

The common occurrence in close association of goethite and its metastable polymorph lepidocrocite in many soils has not been satisfactorily explained. A detailed study of Fe oxide accumulations around root channels (so-called pipestems) revealed that within a zone of a few mm from the root goethite dominated in the immediate contact with the root whereas further away lepidocrocite was the main oxide (Schwertmann & Fitzpatrick, 1977). This could be due to the existence of special chemical environments within the rhizosphere. A factor which may vary across the rhizosphere will be P_{CO₂} which, because of respiration, should decrease with increasing distance from the root.

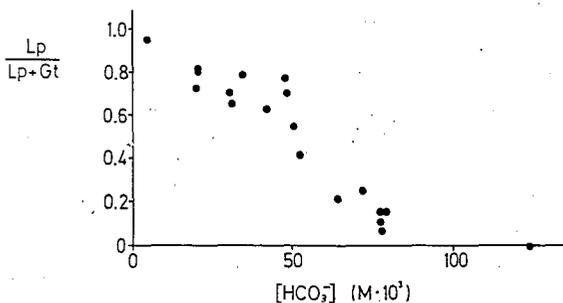
Experiments were therefore conducted in which 0.1 M FeCl₂ solutions were oxidized at room temperature under controlled conditions with respect to pH and flow of

air and CO₂. The gas flow was accurately monitored with a gas mixture apparatus (Fa. Walz) in the range of 8-215 ml min⁻¹ of air and 0-88 ml min⁻¹ of CO₂, resulting in a range of P_{CO2} of 0 to 0.84 · 10² kPa.

The rate of oxidation depended strongly on the P_{CO2}. At pH 7 intermediate products, so-called green rusts, were formed, but hardly any at pH 6. X-ray diffraction showed these green rusts to be either the choride form (d₀₀₃ = 7.74 Å) or the carbonate form (d₀₀₃ = 7.50 Å, Taylor & McKenzie, 1980).

The product of complete oxidation was lepidocrocite only if air was used as purge gas. As P_{CO2} increased, more and more goethite was formed, and at pH 7 goethite was the sole product at P_{CO2} > 0.5 · 10² kPa. At the same P_{CO2} relatively more goethite was formed at pH 6 as compared to pH 7. With increasing goethite formation, the crystallinity of the lepidocrocite increased. The proportion of oxalate-soluble Fe paralleled the proportion of lepidocrocite in the mixture.

Assuming that the HCO₃⁻ anion may be involved in the formation of the two oxyhydroxides, [HCO₃⁻] was also determined (by titration). A significant relationship was found between [HCO₃⁻] in solution and the lepidocrocite:goethite ratio (figure)



The way HCO_3^- may favor the formation of goethite relative to lepidocrocite is not clear, but may be linked to the different structures. The structures of both minerals consist of rows of double bands of $(\text{FeO}_3\text{OH}_2)$ octahedra. In lepidocrocite the double bands share edges, whereas in goethite they share corners. It is assumed that in the first step of crystal formation, double bands form by linking $[\text{Fe}_2(\text{OH})_4]^{2+}$ dimers together. The second decisive step then consists of connecting the double bands via edges or corners depending on the type of anion neutralizing the positive charge of the double bands. Because HCO_3^- favors goethite, it is suggested that HCO_3^- inhibits the edge-sharing necessary to built up the lepidocrocite structure, whereas the chloride anion does not. The stronger effect of the HCO_3^- at pH 6 as compared to pH 7 would then be due to a stronger preference of the double bands for HCO_3^- at this lower pH, where the positive charge will be higher than at pH 7.

REFERENCES

- Schwertmann, U. and Fitzpatrick, R.W. (1977). Occurrence of lepidocrocite and its association with goethite in Natal soils. Soil Sci. Soc. Am. J. 41, 1013-1018.
- Taylor, R.M. and McKenzie, R.M. (1980). The influence of aluminium on iron oxides. VI. The formation of Fe(II)-Al(III) hydroxychlorides, -sulfates, and -carbonates as new members of the pyroaurite group and their significance in soils. Clays Clay Min. 28, 178-187.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CHARACTERIZATION OF THE PLYGORSKITE-SEPIOLITE DEPOSIT OF
EL CUERVO

J. CASAS, C. BALLESTEROS, A. ALVAREZ and J.L. SASTRE

Research and Development Department, TOLSA S.A.
P.O. Box 38.017, 28080 Madrid (SPAIN).

Near the town of "El Cuervo", located in the South-West Spain, between the Seville and Cádiz Provinces, there is a sedimentary deposit of lacustrine continental origin, from which materials commonly catalogued as "special clays" are mined and commercialized, after a suitable treatment, as high capacity absorbents.

From a geological point of view, it is located in a marginal area relating to the folding of the Betic Mountains. In this area, from the Middle Miocene Period, an autochthonous and marine sedimentation took place in a shallow sea that gradually receded due to the continuous lifting of the continent. Around the Pliocene Period the coast line was situated to the West of El Cuervo, but some isolated basins remained in the emerging zones where a lacustrine sedimentation, that still continues at present, started and produced a near circular shape deposit of 2.5 Km in diameter and 57 m of maximum thickness.

In the stratigraphic series of the basin, 3 depositional units are clearly separated by sedimentary discontinuities.

A) Lower unit. It is located by an erosive contact, on the marine Pliocene sandstone. From the bottom to the top, this unit is composed of limestone and marl-limestone mixed with narrow layers of a marly clay, with high sepiolite content, commonly named "Tierra del vino". Moving upwards, the sedimentation is increasingly

argillic, forming a brownish marl with several sepiolite and palygorskite-rich layers that are currently being mined.

B) Intermediate unit. It is composed of sand and clayey sand. This unit is located in the North-West part of the deposit. A strong marine influence is detected in its origin, that also occurs in the other places of the region, due to the effects of the sea regression.

C) Upper unit. Once more, it is a unit of clearly lacustrine origin. It is composed of alternating layers of a white marl-limestone and greenish palygorskite marl that were mined in the past.

In the study, samples of the different beds of the deposit have been examined by X-Ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis, atomic absorption chemical analysis, surface area and absorption measurements.

This study has shown that the upper zone of the lower unit consists of calcite and a clayey fraction, mainly comprising poorly crystallized palygorskite. By electron microscopy this material shows palygorskite and calcite crystals cemented by an amorphous, gel-like mass that provides the material with high porosity and mechanical strength, when dried.

Moving downwards, the sepiolite content continuously increases, while palygorskite decreases, being this clay very scarce in the lower layers of the deposit. These clays of the bottom are presented in compact sheets, with low porosity and barely joined to the limestone crystals. By X-Ray diffraction, it has been confirmed that this mineral has a higher crystallinity and a lower amorphous content. This arrangement produces a material with less mechanical strength and absorbent capacity than in the

upper zone. For this reason, it must be industrially processed to improve these properties before being commercialized.

Nowadays, an intensive opencast mining of the deposit is being carried out. The mineral is worked from the layers richest in sepiolite and palygorskite, and after the industrial processing, a product with exceptional absorbent properties is obtained. Among others, the main uses of this product are absorbent granular, cat litter, pesticide carrier, semirreinforcing filler for rubber, etc.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

IMPROVEMENTS IN FRC PROCESSABILITY BY USING WET
MICRONIZED SEPIOLITE

R.P. CASTELLS, J. SANTAREN AND A. ALVAREZ BERENGUER

Research and Development Department, TOLSA S.A.
P.O. Box 38.017, 28080 Madrid (Spain).

Fibre reinforced cement is a fairly new term to describe asbestos-free cement products which are proposed as replacements for asbestos-cement products (a/c).

Asbestos has unique properties for the manufacturing of a/c products. The compatibility between these fibers and cement is perfect so, water suspension of asbestos and cement is homogeneous, without lumps. These slurries produce sheets with adequate plasticity and green strength for molding.

Due to environmental problems asbestos replacement is being carried out in many final products. In a/c products, the replacement of mechanical and processability properties of asbestos by any other synthetic fibre is not possible. So it is necessary to use more complicated formulations to get both. The new formulations are composed of a cement system and a fibre system.

The cement system is composed of Portland cement, fly ash, and fillers. The fibre system consists of reinforcing (PVA, PAN, PP...) and retention fibres (cellulose pulp).

Fillers play very different roles. Fine fillers are used to close particle size distribution, this improves plasticity and mechanical strength slightly. Active fillers can react with cement to improve mechanical

strength. Rheological or colloidal fillers control the fine particle loss in cement.

Replacing asbestos causes many problems, for example the compatibility between cement and reinforcing fibers; low retention of fine particles, etc. All of these problems cause the heterogeneity of the sheet's structure, decreasing its plasticity and the formation of lumps which produce green sheets that are very difficult to handle.

Fine particle retention can be improved by using flocculants. However these products decrease the mechanical strength because they help form filtration channels.

Wet Micronized Sepiolite (WM-Sepiolite) is able to give stable suspensions of high viscosity in relatively low concentrations. The process in obtaining WM-Sepiolite, involves the disentangling of the clay's needle-like particles, which appear as large bundles of fibre in its natural form. Thus, WM-Sepiolite is easily dispersed in water forming a random lattice of fibre that entraps the liquid. These suspensions of sepiolite have a pseudoplastic behaviour.

WM-Sepiolite has proved to be a good colloidal filler which improves fine particle retention, increases sediment volume and compatibility between cement and PAN, PVA and PA fibers; although WM-Sepiolite decreases drainage. It is possible to obtain convenient drainage without disturbing retention nor compatibility by an appropriate selection of the quantity and type of organic flocculant. The results of fine particle loss, settling volume, drainage and homogeneity are shown in Table 1. WM-Sepiolite decreases fine particle losses up to 63.5% when it is added in a quantity of 3%. Settling volume increases as WM-Sepiolite's

content increases. The same happens with homogeneity, but drainage decreases sharply when WM-Sepiolite is used.

Different types of flocculants were used to increase drainage. The results are shown in Table 2. Using 0.10% of anionic polyacrylamide of high molecular weight, drainage is recovered without a significant increase of fine particle loss, decrease in homogeneity and in settling volume.

TABLE 1: Colloidal filler effect on FRC slurry properties

WM-Sepiolite	-	1	3	-	-	-	-
Microsilica	-	-	-	3	6	-	-
Natural silica	-	-	-	-	-	3	6
Fine particle losses (%)	5,2	4,3	1,9	6,7	6,9	5,5	5,2
Settling volume (%)	55	80	94	78	76	63	73
Drainage (seg for 500 cm ³)	37	39	113	46	79	34	43
Homogeneity (a)	3	2	1	2	2	3	3

(a) 1)- Smooth, no lumps 2) Small lumps 3) Large lumps

Basic formula: Portland cement 100; PAN-fibre 1.5;
 $Al_2(SO_4)_3$, 1.8; Anionic polyacrylamide, 0.008; Cellulose pulp (50 μ SR short fibre), 3.0
 Slurry's solid concentration 9%.

TABLE 2: Flocculant effect on FRC pulp properties

WM-Sepiolite	-	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8
Tetrasodiumpiro phosphate	-	-	0.0024	0.0048	-	-	-	-	-
High molecular weight anionic polyacrylamide	-	-	-	-	0.0048	-	-	-	-
Low molecular weight anionic polyacrylamide	-	-	-	-	-	0.0024	0.0048	-	-
Medium molecular weight anionic polyacrylamide	-	-	-	-	-	-	-	0.0024	0.0048
Settling volume (%)	84.2	100	98.4	98.4	94	97.6	96.0	95.2	93.6
Drainage (seg for 500 cm ³)	31	231	100	160	45	142	115	126	103
Fine particle losses (%)	3.68	1.03	1.02	1.60	1.70	2.02	1.70	2.02	2.08
Homogeneity	2	1	1	1	1	1	1	1	1

Basic formulacion: Portland cement, 8.70; Chrysotile, 13.0;
Slurry's solid concentration 9.0%.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE Si-Al SUBSTITUTION IN THE TETRAHEDRAL SITE OF CHLORITES AND ILLITES : THERMODYNAMICAL AND GEOTHERMOMETRIC INDICATIONS

M. CATHELINÉAU

Department "Water rock interactions", CREGU and GS CNRS-CREGU, BP 23, 54501 Vandoeuvre-Lès-Nancy Cedex (France).

Clay minerals (illite, chlorite) are the most abundant authigenic minerals in active geothermal systems for temperatures ranging from 150 to 300°C. In such geological environments, a great number of thermodynamical variables controlling clay crystallization may be known precisely : temperature, pressure, fluid density and compositions,... Thus, the variations in mineralogy and composition of clays in a given zone of the geothermal system may be related to the main P-T-V-X changes of the fluids, or to lithological changes. Such study was made in the Los Azufres geothermal system (Mexico) which was considered as a satisfactory natural analogue to the experimental conditions of clay synthesis or water-rock interaction. As temperature and rock lithology (rhyolites on andesites) are the main changing parameters in the considered field, geothermometers based on clay mineral composition were mainly investigated. This needed to express quantitatively solid solutions in clay minerals (mainly illite and chlorite) and to check the quality of the temperature estimates used for the geothermometer calibration.

The temperature estimation was done considering direct present day measurements and the different calculated downhole temperatures using chemical geothermometers and the chemical composition of the produced fluids. Crystallization temperature of clay minerals was also estimated from microthermometric studies on fluids trapped in coexisting transparent minerals (quartz, calcite, anhydrite).

QUANTITATIVE DESCRIPTION OF SOLID SOLUTIONS

For each individual set of analyses of a given mineral in a sample, and the complete set of analyses for a given geothermal field, correlation coefficients among chemical variables were calculated. This was useful for selection of appropriate end-members and dominant substitutions.

Simultaneous intersite substitutions were described in a vectorial space using an arbitrary reference composition and substitution vectors selected after consideration of the results from the statistical analysis. For instance, illites from Los Azufres are perfectly described 1) by the coefficient x_1 of the following substitutions vectors $K_{-1}(Si_{+1}Al_{-1})_{IV}$, $K_{-1}Na_{+1}$, $K_{-1}Ca_{\frac{1}{2}}(Si_{+1}Al_{-1})(Al_{-1}R^{2+}_{+1})_{VI}$ and $Mg_{-1}Fe$ or alternatively 2) by molar fractions (X_i) of major components such as muscovite, paragonite, Ca-paragonite, Fe-celadonite, Mg-celadonite and pyrophyllite. In both cases, values of substitution coefficients (molar fraction of theoretical end members) on molar fractions of minerals were calculated solving systems of simultaneous linear equations (n equations, p unknowns) using minimization methods.

VARIATIONS OF THE (Si/Al)_{IV} RATIO WITH TEMPERATURE

Data from the Los Azufres system show that the $Al_{(IV)}$ content of the tetrahedral site increases with temperature considering either chlorite or illite. These variations were proposed as geothermometers (CATHELINÉAU et NIEVA, 1985 ; CATHELINÉAU et al., 1987) and are consistent with data from other geothermal fields.

Electric deficit caused by the Si replacement by Al is balanced by an increase of the interlayer occupancy (K) in illites, and by a Fe-Al substitution in the octahedral site of chlorites. This explains : 1) the strong correlation $K-Al_{(IV)}$ in illites expressed by the vector $K_{-1}(Si_{+1}Al_{-1})_{IV}$ 2) the strong correlations $Si_{IV}-Al_{VI}$ and Si_{IV} -octahedral vacancy, and the anticorrelation $Si_{IV}-Fe$, in chlorites, which are expressed by the dominant substitution : $(Si_{-1}Al_{+1})_{IV}(Al_{-1}Fe_{2-1})_{VI}$. The increasing $Al_{(IV)}$ content with temperature is also described by the spectacular decrease of the molar fractions of kaolinite in chlorite, and pyrophyllite in illite, from 150 to 300°C where they become

negligible. (The choice of pyrophyllite for the algebraic calculation of the contribution of a $(\text{Si}_{\text{IV}})(\text{Al}_{\text{VI}})$ rich end member in the illites, and kaolinite (pyrophyllite-2 gibbsite) for chlorites respects only the stoichiometry of the di- and trioctahedral series, and does not involve any consideration respecting the relative stability of pyrophyllite or kaolinite with temperature).

The decrease of the molar fraction of the $(\text{Si}_{\text{IV}})(\text{Al}_{\text{VI}})$ rich end member may be compared to the behaviour of kaolinite as mineral. Thus, the saturation rate ($Q = [\text{Al}^{3+}]^2 \text{H}_4\text{SiO}_4]^2 [\text{H}_2\text{O}][\text{H}^+]^{-6}$) of kaolinite decreases with temperature (FRITZ, 1981). This is in agreement with the observed decrease of the activity of kaolinite as a theoretical major component in chlorites or illites which corresponds to a low Q_j in solution, e.g. to an increasing stability of the end member in solution with temperature. Agreement between data concerning the behaviour of a mineral in solution, and the behaviour of the same mineral considered as a major component of a complex clay particle is very important for thermodynamics of clay. This justifies the use of ideal solid solution models for calculating solubilities of clay minerals as those proposed by TARDY and FRITZ (1981). Alternatively, the data from natural cases may help greatly in refining the calculation of the Gibbs free energies of clay minerals used in such models.

CATHELINÉAU M. and NIEVA D. (1985) - A chlorite solid solution geothermometer. The Los Azufres geothermal system. *Contrib. Mineral. Petrol.*, 91, 235-244.

CATHELINÉAU M. and IZQUIERDO G. (1987) - Temperature-composition relationships of authigenic clay minerals, in the Los Azufres geothermal system. *Contrib. Mineral. Petrol.* (in press).

FRITZ B. (1981) - Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques. *Sci. Geol. Mem.*, 65, 197 p.

TARDY Y. et FRITZ B. (1981) - An ideal solid solution model for calculating solubility of clay minerals. *Clay minerals*, 16, 361-373.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SPECTROSCOPY OF METHYLENE BLUE ADSORBED ON CLAYS.

J. CENENS AND R.A. SCHOONHEYDT.

Laboratorium voor Oppervlaktechemie, K.U. Leuven, Kard. Mercierlaan 92,
B-3030 Leuven (Heverlee), Belgium.

Introduction.

The study of the organisation of organic molecules on clays in colloidal suspension and at low loadings is now being done by luminescence spectroscopy. The advantage is the extremely high sensitivity and that dynamic processes can be studied. The disadvantage is that only luminescent molecules can be studied on clays which are essentially free of Fe^{3+} (ref.1). Our aim is to obtain similar information with classical absorption spectroscopy using Methylene Blue (MB) as a probe molecule. Here we report our results for static measurements.

Experimental.

The clays are Hectorite (HEC) and Barasym SSM-100 (BS) both from the "Clay Minerals Society", and Laponite B (LAP) from Laporte Industries. Dye-clay suspensions suitable for spectroscopic studies are prepared in polyethylene vessels by shaking 10 cm³ of an aqueous 10⁻⁵ molar solution of MB with various amounts of clay suspension (fraction <0.3 μm) to obtain the desired loading, and simultaneous dilution to 40 cm³. Absorption spectra are taken with a Cary 17 instrument. Pure MB spectra are obtained after subtraction of the clay background.

Results and discussion.

Typical spectra are shown in figure 1 and a summary of the species involved is given in table 1.

When MB is brought into contact with clay minerals 4 reactions occur: ion exchange, protonation, dimerisation and trimerisation. These reactions are dependent on the available surface, the loading and the

type of exchangeable cation. HEC and LAP are swelling clays with a readily available interlamellar surface. BS has a interlamellar surface which is difficult to access for exchange because of the high charge density neutralised by K^+ and NH_4^+ (ref.2): partial layer collapse is the result (ref.3).

The absorption maximum of the MB monomer is different from its position in H_2O (664 nm). The maximum is at 673 nm with a shoulder at 653 nm (BS at all loadings, LAP at low loadings) or at 653 nm with a shoulder at 673 nm (HEC at all loadings, LAP at higher loadings). Exchange on the external surface leads to a red shift (673 nm), interlamellar exchange to a blue shift (653 nm).

Dimer formation (610 nm) takes place on all the clay surfaces down to loadings of 0.1%. Interlamellar dimerisation (HEC) leads to an extra absorption at 720 nm. This band is predicted theoretically (ref.4) and its intensity is dependent on the dimer configuration.

Trimerisation (580 nm) does not occur on all the clays; it is only clear with BS and LAP. HEC shows a broadening of the dimer band and a shift to shorter wavelenghts (600 nm). Trimerisation is only possible on the external surface; between the layers only 2 MB monomers can aggregate.

The protonated MB absorbs at 750 nm and the spectra are similar to those of an acid dye solution ($pH < 1$). Protonation of MB is most pronounced on BS. For HEC and LAP the extent of protonation depends on the exchangeable cation: with K^+ , Cs^+ or NH_4^+ a clear increase of protonation is observed. Because of their low hydration K^+ , Cs^+ and NH_4^+ form aggregates in suspension. It seems that at the external surface (edge sites) acid sites are present. These sites are exchanged with MB when the interlamellar sites are not (BS) or not so easily (K^+ , Cs^+ and NH_4^+ -HEC,LAP) available.

Table 1. Spectroscopy of adsorbed Methylene Blue.

monomer	673 and 653 nm
protonated monomer	750 nm
dimer	720 and 610 nm
trimer	580 nm

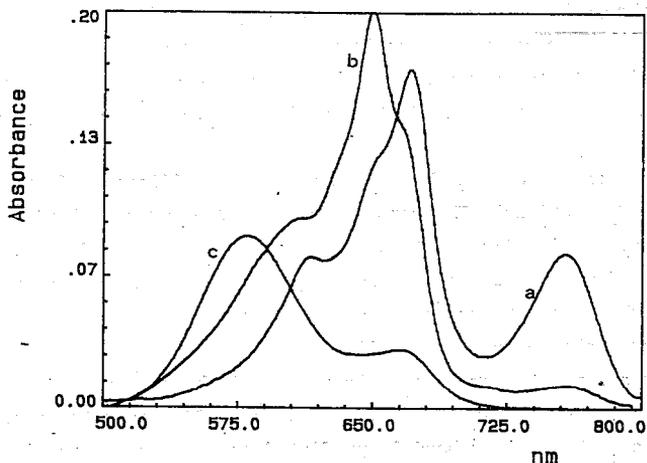


Figure 1. Spectra of adsorbed Methylene Blue.

a) K^+ -LAP 0.2% (of the CEC), b) Na^+ -HEC 0.2%, c) Na^+ -LAP 20%.

Conclusions.

MB is a sensitive probe for claysurface properties. The exchange initially takes place at the external surface but very quickly the interlamellar surface is available. The extent of aggregation reactions is dependent on the nature of the surfaces. Protonation takes place at the external surface.

References.

1. a) J. Cenens, D.P. Vliers, R.A. Schoonheydt and F.C. De Schryver; Proc. Inter. Clay Conf., Denver 1985, in press.
- b) R.A. Schoonheydt, P. De Pauw, D. Vliers and F.C. De Schryver; J. Phys. Chem., 1984, 88, 5113-5118.
2. H. Van Olphen and J.J. Fripiat; Data handbook for clay minerals and other non-metallic minerals: Pergamon Press, New York, 346 p.
3. B.L. Sawhney; Clays and Clay Minerals, 1970, Vol. 18, 47-52.
4. Cantor and Schimmel; Biophysical Chemistry (Part II), W.H. Freeman and Company, 1980, 391-398.



THE EFFECT OF COMPOSITION OF DIOCTAHEDRAL Na-SMECTITES ON THEIR SWELLING

B. ČIČEL, P. KOMADEL, D. GYEPESOVÁ and L. NOVÁKOVÁ

Institute of Inorganic Chemistry, Centre Chem. Res., Slovak Acad. Sci., 842 36 Bratislava (Czechoslovakia).

The effect of composition and layer charge on the swelling of dioctahedral Na-smectites was studied by Foster (1953). She concluded that

- octahedral Fe^{3+} appeared to have about the same depressing effect on swelling as Mg^{2+} ,

- the swelling of Na-montmorillonites decreases with the increase of octahedral substitution,

- the degree of swelling showed no correlation with CEC or with tetrahedral charge. Her results are considered as valid for dioctahedral smectites generally though they were determined only within narrow concentration limits of their components. The aim of the present study is to verify the validity of Foster's (1953) conclusions if applied to more extensive concentration limits of tetrahedral and octahedral substitutions in dioctahedral smectites.

11 smectites separated from bentonites from Clay Spur (Wyo. USA), Jelšový Potok, Jelšový Potok-Sever, Krásny Dvoreček, Blšany, Veľký Rybník, Kadaň-Rokle, Otovice and Vinné (Czechoslovakia) were studied.

Na-smectites were prepared by repeated treatment of Ca-smectites with 1M solution of NaCl and following washing, drying at 60 °C and crushing until the material passed through the 0.2 mm sieve.

To determine the swelling ability of samples 500 mg of dried material was added in divided portions to 25 ml graduate with 25 ml distilled water. Two hours after the first portion was added a reading of the volume of gel was taken

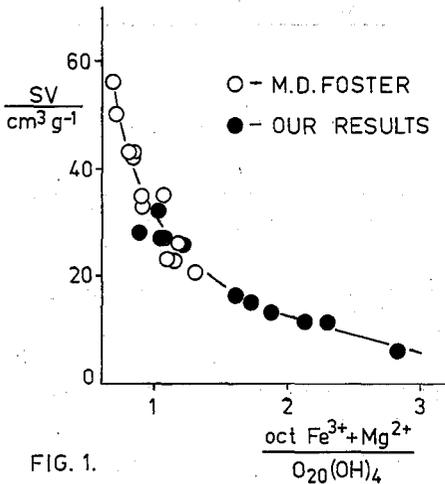


FIG. 1.

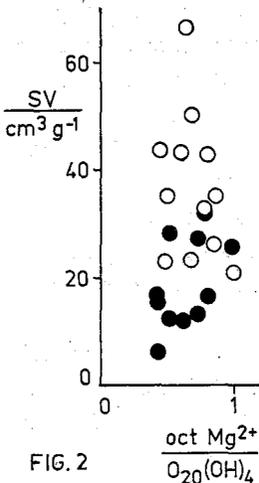


FIG. 2.

using the graduate scale.

Concentrations cited in abstract were calculated per $O_{20}(OH)_4$

Fig. 1 shows the swelling volume of the samples studied plotted against the octahedral substitution expressed as the sum of octahedral Fe^{3+} and Mg^{2+} contents [$\Sigma(Me)VI$]. For

$\Sigma(Me)VI$ between 0.68 and 2.84 the swelling decreases as the $\Sigma(Me)VI$ increases.

The relation between the swelling and the $(Fe^{3+})VI$ content is similar to the above mentioned correlation curve. For $(Fe^{3+})VI$ between 0.0 and 2.41 the SV measured decreases as the $(Fe^{3+})VI$ content increases.

The points in the diagram (Fig. 2) show no correlation between the $(Mg^{2+})VI$ content and the swelling of dioctahedral smectites in concentration limits from 0.41 to 1. The nonstoichiometric substitution of Mg^{2+} in octahedra does not show the expected depressing effect on swelling though similar substitution, described by Foster (1953), $(Fe^{3+})VI \rightarrow (Fe^{2+})VI$ does.

If the swelling volume is plotted against the negative charge of the smectite layer, within the limits from 0.78 to 1.24 of negative charge the swelling decreases as the negative layer charge increases. The data presented by Foster (1953) do not show such a decrease of the swelling ability in smectites.

Stoichiometric substitution of $(\text{Fe}^{3+})\text{VI}$ for $(\text{Al}^{3+})\text{VI}$ causes the SV-decrease. In the same way the swelling is influenced by an increase of negative layer charge. Some relationship between both the $(\text{Fe}^{3+})\text{VI}$ content and negative layer charge is suggested.

The plotting of the tetrahedral $(\text{Al}^{3+})\text{IV}$ against the $(\text{Fe}^{3+})\text{VI}$ showed that the increase of $(\text{Fe}^{3+})\text{VI}$ content from 0.0 to 2.41 results in the increase of tetrahedral substitution from 0.02 to 0.97. It can be expected that the swelling is in some way correlated with tetrahedral substitution. A general tendency of SV-decrease with increasing tetrahedral $(\text{Al}^{3+})\text{IV}$ content was thus established.

The results presented show the validity of Foster's (1953) conclusions that increasing octahedral substitution $[\Sigma(\text{Fe}^{3+})\text{VI}+(\text{Mg}^{2+})\text{VI}]$ within the range $\langle 0.68; 2.84 \rangle$ and increasing content of $(\text{Fe}^{3+})\text{VI}$ within the range $\langle 0.0; 2.41 \rangle$ results in a decrease of the swelling of dioctahedral smectites as well.

The role of $(\text{Mg}^{2+})\text{VI}$ substitution, negative layer charge and tetrahedral substitution in relation to the swelling of smectites differ from that presented by Foster (1953). The $(\text{Mg}^{2+})\text{VI}$ substitution is the source of part of total negative layer charge but no correlation with swelling of dioctahedral smectites has been established. With the increasing negative layer charge within the range $\langle 0.68; 1.24 \rangle$ the swelling of dioctahedral smectites decreases. Increasing tetrahedral substitution also results in a decrease of the swelling of dioctahedral smectites.

Foster, M.D. (1953): Geochemical Studies of Clay Minerals., Am. Mineral., 38, 994-1006.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**TRANSFORMATION OF FERRIHYDRITE TO HEMATITE:
A TOPOLOGICAL APPROACH BY EXAFS**

Jean-Marie COMBES, Alain MANCEAU and Georges CALAS

Laboratoire de Minéralogie-Cristallographie, 4 place Jussieu, Universités Paris VI et VII,
75252 PARIS cedex 05, FRANCE.

Although numerous works have outlined the determining role of poorly-crystalline precursors in hematite formation, the actual structural mechanisms involved during the evolution of poorly-ordered iron oxy-hydroxides towards hematite remain still obscure. In particular, X-ray diffraction patterns of ferric oxide hydrated gels (commonly called "protoferrihydrites"), precipitated from aqueous solutions containing trivalent iron, show only two hk broad reflections at 2.55Å and 1.5Å: this does not allow a precise structural study of these precursors. EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy is very useful to provide structural and chemical informations around a chosen element, whatever the crystallinity of the system. It is thus possible to determine parameters such as coordination number, metal-ligand and metal-metal bondlengths, as well as the nature of these neighbouring atoms. The nature of the linkages between the constituting Fe (O,OH)₆ octahedra, relying on the measured Fe-first nearest Fe and Fe-second nearest Fe distances, can be determined in the initial gel. It can be also followed during the transformation of these precursors into well-crystallized hematite at 92°C during 20-40h.

In the initial products, Fe-Fe interatomic distances are characteristic of edge- and vertice-sharing octahedra (3,06Å and 3,46Å). Then, after 1h30, the most important feature of the further structural rearrangements is the appearance of a Fe-Fe distance at 2.89Å characteristic of face-sharing octahedra. This material is built up by octahedra which share faces (d[Fe-Fe]=2,89Å), edges (d[Fe-Fe]=3,06Å) and vertices (d[Fe-Fe]=3,46Å). The presence of hematite nuclei is excluded as it would have given a Fe-Fe distance of 2,94Å. At 6 hours of ageing, the 2,89Å Fe-Fe bond length disappears in favour of the 2,94Å one. At this stage, the presence of hematite crystals begins to be detected through X-ray diffraction. EXAFS shows that the contribution of hematite tends further to increase at the expense of that of ferrihydrite.

Three structural stages have been recognized during this transformation process:

- until 1h30; the ferrihydrite framework is build up by octahedra sharing edges and vertices.

- between 1h30 and 6 hours; octahedra sharing faces appear, coexisting with octahedra sharing edges and vertices, without hematite clusters.

- at 6 hours; apparition of hematite clusters in the host ferrihydrite.

This study has revealed the existence of a *transitional phase* which precedes the nucleation of hematite. The existence of this phase, intermediate between the non-aged ferrihydrite and hematite, shed direct light on the heterogeneous nucleation process of hematite. The presence of face-sharing octahedra is assumed to represent the actual nucleation stage, before the further growth of hematite. Its role is very important in reducing the free energy of the reactions, and can thus be assimilated to an equivalent of a catalytic process.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

COMPARATIVE STRUCTURES OF HYDROUS FERRIC OXIDES THROUGH EXAFS

Jean-Marie COMBES¹, Alain MANCEAU¹, Jean-Yves BOTTERO² and Georges CALAS¹

1- Laboratoire de Minéralogie-Cristallographie, 4 place Jussieu, Universités Paris VI et VII, 75252 PARIS cedex 05, FRANCE

2- Centre de Recherche et Valorisation des Minerais de L'E.N.S.G, B.P.40-54501 Vandoeuvre cedex, FRANCE

During the past few years there has been a considerable amount of work showing the importance of poorly-ordered phases in iron soil geochemistry. The main physico-chemical parameters governing the future evolution of these precursors are relatively well-known. A better understanding of transformation processes involves a good knowledge of the structure of these hydrous ferric oxides which can not be completely elucidated by conventional X-ray diffraction techniques.

EXAFS (Extended X-ray Absorption Fine Structure) is entirely appropriated for analyzing the local atomic structure of such highly-disordered compounds. A fruitful approach for probing the short-range order of these materials consists in using the Fe-Fe interatomic distances, as measured by EXAFS, in order to characterize the linkage type (faces, edges or vertices) of the constituting $\text{Fe}(\text{O},\text{OH})_6$ octahedra.

This work is based on the comparison of synthetic and natural materials.

Structure of colloidal particles that are the first to form by partial hydrolysis of trivalent iron solutions is strongly dependent on hydroxyls groups availability. For increasing OH/Fe ratios, the progress of the polymerization has been followed until the formation of polynuclear complexes. EXAFS studies evidence that their structure is characterized by the presence of edges- and vertices-sharing Fe octahedra with Fe-Fe interatomic bondlengths of 3.05Å and 3.47Å, respectively.

Ferric gels freshly precipitated total hydrolysis of trivalent iron solutions or by oxidation of divalent iron solutions reveal different local organizations, similar respectively to that of goethite and lepidocrocite. Nevertheless, both products exhibit the same X-ray diffraction pattern, characteristic of the hexagonal close-packed system, with only two hk broad reflections at 2.55 and 1.5Å.

In contrast, synthetic and natural six-lines ferrihydrites, are likely to possess an analogous topological agencement to that of feroxyhyte. The only difference lies in the grade of the structural disorder. These three compounds were found to present faces, edges and vertices-sharing octahedra with Fe-Fe distances of from 2.89Å, 3.08Å and 3.43Å, respectively. EXAFS allows us to understand the inhibition of the crystal growth towards oxyhydroxides phases. Indeed, the presence of face-sharing octahedra prevents the *direct formation* of oxyhydroxide minerals, because they are only constituted by edge- and vertice-sharing octahedra. This strongly supports the dissolution-reprecipitation mechanism generally invoked for the goethite formation from ferrihydrite. The inhibition role of silica in natural ferrihydrites will also be discussed.

In spite of their highly-disordered character through X-ray diffraction, these hydrous ferric oxides present distinct local organizations allowing not only to provide information about the physico-chemical conditions occuring during their precipitation, but also to foresee the nature of the well-crystalline compound which could be formed in the future.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

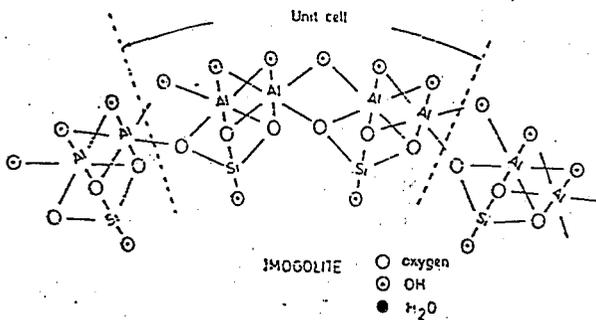
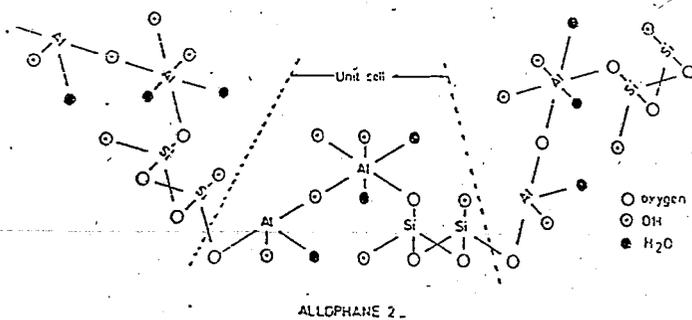
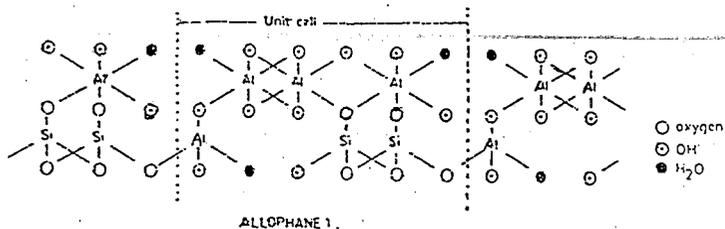
PROPERTIES OF SOILS ON VOLCANIC MATERIAL FROM JAVA AND CAMEROON

F. DE CONINCK, R. SUTANTO, M. DOUBE and ABDIMAJID M. JAMA

Laboratory of Soil Science, Geological Institute, State University Ghent, Krijgslaan 281, 9000 Ghent, Belgium.

Soils developed on volcanic material in a humid climate may contain high amounts of ill-defined minerals, like allophane, imogolite, allophane-like constituents. For allophane and imogolite, tentative chemical compositions have been proposed. Allophanes have a structure comparable to 1/1 clay minerals. The difference, however, is that in both the tetrahedral and the octahedral sheet, some cations are missing (see fig.). This feature causes many $-OH$ or $-OH_2$ groups to be bound on one cation only, e.g. $Al-OH_2$; $-Al-OH$; $-SiOH$. Through acid-base reactions, these "reactive" groups are able to develop a large variable charge ; $Al-OH$ and $Al-OH_2$ groups may be responsible for complexation of anorganic and organic ligands : phosphates and organic matter. Another property is reactivity with F^- , i.e. alkalinity released in contact with a NaF solution. Variable charge properties, phosphorus fixation and alkalinity produced by F^- reactivity have been studied in soils on volcanic material from Java and Cameroon. Exchange capacity as determined by classical methods can give an overestimation with a factor of 10 or more, when compared with the sum of the cations including Al^{+3} . Equilibration with a 0.002 mol $CaCl_2$ solution without washing (compulsative method of Gillman) gives values of exchange capacity which are more consistent with the sum of the exchangeable cations. The latter sum, however, may show rather strong variations depending on the method used. In soils with typical "acid" properties the sum of the exchangeable cations is very low, in many cases less than 2 meq/100 g soil. In the latter soils,

phosphorous fixation may reach almost 100%. Alkalinity produced by F^- reactivity at constant pH 7 is closely related to charge properties. In soils with high variable charge, alkalinity released may exceed 500 meq/100 g soil.





Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

"TRAMOS ROJOS" DEPOSIT CONDITIONS. A CLAY MINERALS STUDY

M.A. CÓRDOBA*, E.M. SEBASTIAN and A. ACOSTA****

* Laboratorio de Edafología y Mineralogía. Universidad de Castilla-La Mancha (Ciudad Real - España).

** Departamento de Mineralogía y Petrología e Instituto Andaluz de Geología Mediterránea. Universidad de Granada. CSIC (España).

Clay minerals composition may be useful to characterize sedimentary deposits. We have studied, from this point of view, Betic Zone Serravallian "Tramos Rojos". Trying to establish deposit conditions, extreme that, to the date, remain quite obscure.

These materials are found in scattered outcrops of limited dimensions. They are made up of different lithologies, although in the most of cases they are conglomerates of an intense red colour, with stones and blocks immersed in a sometimes sandy or clay matrix.

They are assumed to be of an Upper Serravallian-Basal Tortonian age, and their deposition coincide with an important fall in the level of the oceans, producing in these areas a regression that gives rise to very irregular sedimentation. The strong influence tectonics has exercised in this zone prevents the correct characterization of the environment.

In this study the results obtained from twelve outcrops of these "Tramos Rojos" are being analyzed: All of them are situated in the province of Granada (Spain).

The mineralogy is composed of calcite, dolomite, quartz and clay minerals. The proportions vary notably, although, in general, the last ones prevail. More over, in some isolated samples feldspars and ankerite have been identified.

The fractions in the size of the clay and lime (2-20 μ) have similar mineralogical compositions.

These are formed of illite, smectites, chlorite, kaolinite and goethite, in all cases and in the same order of abundance.

In three zones, more over, palygorskite and talc have been found. At other points, paragonite.

From qualitative analysis of the phyllosilicates, together with the calculation of distinct crystallographic parameters of the illites (bo, crystallinity, rate of intensities of the basal reflections...) chlorites, smectites, together with the dates of the chemical analysis, it has been possible to deduce the following reasons.

The sediments were brought by source areas very near to the place of deposit. These must have been formed fundamentally by rocks of the "Complejo Alpujáríde" that contain, on the other hand, in some very concrete points, high levels of magnesium.

The deposition was produced in an environment of shallow water, restricted environment with high ionic concentration, principally of magnesium, iron, silica.. and alkaline pH.

One may be dealing with a perimarine environment divided into small sub-basins in which the genesis of the palygorskite would be possible by neof ormation or transformation of other clastic phyllosilicates (especially mica and smectites).

The climatic conditions were characterized by high temperatures and important precipitations, concomitant with a so active although pulsating tectonics.

This work is included in the project: "Análisis sedimentológico, mineralógico y evolución tectosedimentaria de las Depresiones Béticas Orientales", financed by C.A.I.C.Y.T. - C.S.I.C.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ALTERATION OF SEPIOLITE BY DRY GRINDING

J. CORNEJO and M. C. HERMOSIN

Instituto de Recursos Naturales y Agrobiología de Sevilla. C.S.I.C.
Apartado 1052. Sevilla. Spain.

The study of the grinding effects on clay minerals is a subject of great interest because it is a very common process in the industry and research laboratory. Very little is known of the effects of dry grinding on sepiolite, which is widely used in the industry. In this study, Vallecas sepiolite was subjected to dry grinding in a ball mill for various periods of time. Changes induced during the comminution process were examined by X-ray powder diffraction (XRD), specific surface area measurements, DTA-TG and IR-spectroscopy.

The X-ray diffraction patterns of ground samples showed a great resistance of the sepiolite structure to be destroyed before 4 h grinding. Even the samples ground for 8 h and 14 h showed the characteristic sepiolite reflections quite well defined. The width at half-height of the diffraction peaks and integral intensity (I) of the 110, 060 and 131 reflections were calculated. The I_{110} decreased more rapidly than I_{060} and I_{131} for short times of grinding. This seems to indicate that the first effect of grinding is to disturb the parallel array of the structural units in the sepiolite fibers. After 4 h grinding, the decreases of I for these three reflections were similar, probably because the atomic structure begins to break up.

The specific surface area evolution of the ground samples indicated an initial increase until 15 min grinding and a subsequent decrease which was very rapid from 8 h to 24 h (Table 1). This latter decrease of the surface area indicated that the line broadening in the X-ray reflections from 4 h was due to structural lattice deformation induced by dry grinding rather than to particle size diminution.

The DTA of sepiolite shows three endothermic effects due to free moisture and zeolitic water (110°C), bound or structural water (330°C

TABLE 1. Specific surface areas and DTA-TG data of ground samples.

Grinding time h	Surface area $\text{m}^2 \text{g}^{-1}$	DTA peak-temperature $^{\circ}\text{C}$				Weight-losses from TG-curves %			
		20-200	200-400	400-700	700-1000	20-200	200-400	400-700	700-1000
0	283.6	105	334	500	843	10.78	3.19	3.05	2.63
0.25	304.7	-	-	-	-	-	-	-	-
0.50	284.1	-	-	-	-	-	-	-	-
1	260.1	110	350	515	838	10.65	2.94	2.85	2.42
4	216.3	110	355	nm*	830	10.17	3.05	3.18	2.45
8	159.8	110	355	nm	825	10.37	3.52	3.48	1.78
14	59.4	114	nm	nm	820	10.42	4.68	3.70	1.82
24	27.2	113	nm	nm	816	9.57	5.38	3.23	1.21

* not measurable

and 500°C) and an endo-exothermic effect at 845°C which is characteristic of the development of high temperature phase by structural dehydroxylation. The peak-temperature of these endothermic effects increased and broadened upon grinding, and the 14 h samples only showed the first endothermic at 110°C (Table 1). The weight losses from TG-curves corresponding to three steps defined by the DTA effects (Nagata et al., 1974) are summarized on Table 1. The weight losses at $200-400^{\circ}\text{C}$ and $400-700^{\circ}\text{C}$ increased upon grinding from 4 h, while those at $20-200^{\circ}\text{C}$ and $700-1000^{\circ}\text{C}$ decreased. This indicated that the weight losses between 200°C and 700°C for ground (4 h or more) samples should correspond not only to bound water but also to new, weakly bound hydroxyl groups produced by sepiolite lattice disruption. For this reason the TG-loss and the peak-temperature of the dehydroxylation exothermic effect decreased upon grinding. The peak-temperature increase and broadening of the first endothermic on DTA could suggest that some extremely weakly bound hydroxyl groups of an amorphous phase are being lost in the $20-200^{\circ}\text{C}$ range.

The IR spectra changes of sepiolite upon grinding were monitored by the stretching absorption bands of bound (3540 cm^{-1}) and zeolitic (3400 cm^{-1}) water and the bending absorption band at 1650 cm^{-1} , the O-H vibrations of Mg_3OH at 3680 and 655 cm^{-1} and the Si-O vibration at 1210 cm^{-1} (Ahlrichs et al., 1974; Serna and VanScoyoc, 1978). Spectral changes were only perceptible for grinding times higher than 1 h. The

1210 cm^{-1} band decreased and broadened at 4 h grinding and almost disappeared at 8 h grinding. However, the Mg_3OH vibration bands remained unchanged after 4 h of grinding, decreasing after 8 h and disappearing after 18 h grinding. A decrease in the bound water band (3540 cm^{-1}) with a large broadening at 3400 cm^{-1} and a decrease, broadening and frequency lowering of the 1650 cm^{-1} band were observed. The spectral changes observed at $3500\text{--}3300 \text{ cm}^{-1}$ and 1600 cm^{-1} on samples ground for more than 4 h suggest a transformation of the initial zeolitic and bound water of sepiolite to weakly bound water groups on degraded surface.

All these results indicated that the structural framework of sepiolite is mechanically more stable than those of other clay minerals. The alteration upon grinding seems to proceed in three steps:

- 1) For short grinding times (<15 min) there are a thinning and shortening of fibrous particles producing a slight increase of the specific surface area without structural alteration.
- 2) From 1 to 8 h of grinding a distortion of the parallel units on the particles surface with destruction of surface channels affecting tetrahedral (SiO_4) sheets is suggested, producing a surface area decrease.
- 3) From 14 to 24 h of grinding an inner disruption of the lattice affecting octahedral units is produced and an amorphous phase with certain residual order at inner particles is observed by XRD analysis.

REFERENCES

- AHLRICH, J.L.; SERNA, C. and SERRATOSA, J.M. 1975. Structural hydroxyls in sepiolites. *Clays and Clay Minerals* 23, 119-124.
- NAGATA, H.; SHIMODA, S. and SUDO, T. 1974. On dehydration of bound water of sepiolite. *Clays and Clay Minerals* 22, 285-293.
- SERNA, C.J. and VanSCOYOC, G.E. 1978. Infrared study of sepiolite and palygorskite surfaces. *Proc. Int. Clay Conf., Oxford 1978. In Developments in Sedimentology 27 (M.M. Mortland and V.C. Farmer, eds.) pp. 197-206.*



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

TRANSFORMATION OF CLAY MINERALS BY HYDROTHERMAL ALTERATION, IN ORDOVICIAN ROCKS, GASPE PENINSULA, QUEBEC, CANADA.

A. CHAGNON AND M. DESJARDINS

Institut national de la Recherche scientifique, Géoressources, C.P.
7500, Sainte-Foy, Québec, (Canada) G1V 4C7.

The clay mineralogy and the crystallinity index of micaceous minerals are used in order to evaluate the diagenetic evolution of an Ordovician and Lower Silurian rock sequence, and to detect and define alteration zones related to acid and mafic dykes and locally to mineral showings of Sb, Pb, Zn. In some cases, no intrusion is observed within or in the vicinity of an altered zone.

The studied rocks are mainly mudstones and shales from the Pabos Formation, and limestones from the White Head Formation, both forming the Matapedia Group.

Most of the samples contain well crystallized micas and chlorites and the crystallinity index of the micas as well as the organic matter reflectance indicate that the thermal maturation is high (supramature). It ranges from the dry gas zone to the green schist facies of regional metamorphism.

From the good correlation between the age, the stratigraphic position and the thermal maturation, it is concluded that burial is the main cause controlling that maturation.

Circulations of fluids probably associated with the intrusive phase in the Upper Devonian have produced clay minerals and clay assemblages that are inconsistent with the general thermal maturation and also with the clay mineralogy of the general background. Four assemblages based on index minerals have been defined: kaolinite, smectite, illite (mica), and chlorite.

A method using X-Ray diffraction, chemical analysis on particles by electron microscopy and energy dispersive analysis, and calculation of diffraction patterns is used to determine the composition and the proportion of the clay minerals. Thus, it is possible to define more precisely the altered zones and understand the clay minerals paragenesis better.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GEOTECHNICAL AND MINERALOGICAL CHARACTERISTICS OF RED SOILS IN THE PROVINCE OF BARI

C. CHERUBINI*, A. GRECO**, M. LUPO**, F.P. RAMUNNI*, F. VENIALE***.

* Institute of Applied Geology and Geotechnics, University of Bari, Italy.

** Professional Geologist, Bari, Italy.

*** Departement of Soil Sciences, University of Pavia, Italy.

It is a well-known fact the territory of the province of Bari (Italy) is mainly covered by outcroppings of calcareous, calcareous-dolomitic and dolomitic rocks of the Mesozoic.

Karst phenomena are highly developed both on the surface and at depth and are accompanied by concentrations of red soil which are extensive in some areas but circumscribed and isolated in others; this is a particular type of clay that can be irregularly found as material for filling cavities or structural discontinuities and/or interbedded layers on the surface or at depth.

The possibilities of finding red soils connected with the calcareous complex of the Murgie thus vary in terms of size and importance.

In some places there are merely small deposits of interbedded layers or fractures, while in others there may even be large deposits in karst cavities at different evolutionary stages, varying in both shape and size. The red soil of Apulia, as far as is known to date, is the outcome of polycyclical karst phenomena conditioned by the relative movements that have occurred from the Cretaceous epoch to present day between the sea and the continent.

The red soil deposits of Apulia, and of Murgian hills in particular, can be differentiated both in terms of position and of composition in relation to the degree of evolution and maturity of the deposits themselves.

The origin, position, disposition and geographical distribution of the red soil have not been established in detail so far, although there have been excellent attempts at classification made, such as that of Grassi, Romanazzi, Spilotro (1975).

In this present paper the geologico-technical and applicational characteristics have been examined of a group of such terrigenous material which can be ascribed to post-Calabrian deposits, and more specifically to the red soils of epigean and hypogean deposits and to the red soils caused by the flowing and filling of karst and morphostructural depressions of the central part of the Murgia Barese, defined as Group A in the classification made by Grassi et alii (1975). A precise identification of the above-mentioned soil deposits may be of vital importance both in terms of predicting the future mechanical behaviour of the deposits and also as regard possible applications of an industrial kind as natural impermeable materials that can substitute the grey-blue pliocenic clays which are only marginally present in the Murgian territory.

At the moment the only reference point as regards the characterization of the mineralogical and petrographic features is to be found in the numerous works by L. Dell'Anna who has carried out research on mineralogical bases on the red soils both in outcroppings and at depth. The results of this research show that the red soils are constituted predominantly of kaolinite, while goethite is also present in quantities that are sometimes modest and at other times considerable, and ferrous oxides (hematite and

magnetite) and anatase (in very small quantities) and secondary minerals are also present. Quartz, bohemite and gibbsite are often completely absent but are occasionally present in abundance; illite is almost always absent, and when it is present it is either to be found in minimal quantities or else in amounts so small that can hardly be detected at all.

As far as we have been able to ascertain so far, from the mineralogical viewpoint, samples of red soil from Group A present, in order of abundance, the following minerals that can be considered as significant: quartz, illite, feldspar and vermiculite.

The geotechnical characterization, which is currently being completed, carried out on the same samples of red soil, characterized mineralogically, present the following values: natural density varies from a minimum value of 1.64 to a maximum of 1.82 g/cm³; natural water content varies from 7.90% to 36.60%; the real weight of the granules goes from 2.72 to 2.82 g/cm³; the liquid limit is situated between 37.50% and 82.10%, while the plasticity limit varies between 17.60% and 23.60%. Permeability tests and tests for characterizing the mechanical behaviour of the soil have also been carried out.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
 Seville, Spain, 1987. Sociedad Española de Arcillas

TEXTURE INFLUENCE ON SULPHUR DEPOSITION ON SEPIOLITE

L. Daza, S. Mendioroz and J.A. Pajares

Instituto de Catálisis y Petroleoquímica, CSIC, Serrano 119, 28006 Madrid, (Spain).

The influence of texture in the deposition of sulphur via hydrogen sulphide oxidation on three different types of sepiolite has been studied. Sulphur incorporation is clearly related to the textural parameters of the samples increasing with macropore volume.

Materials were supplied by TOLSA, S.A. under the tradenames BURRUS (SB), PANGEL (SPG) and PANSIL (SPS). BURRUS is a natural mineral 95% sepiolite with particle size range, 0.2-0.4 mm. The materials PANGEL and PANSIL were obtained from subsequent treatment of BURRUS by wet (SPG) or dry (SPS) micronization treatment, respectively.

The sulphur incorporation was achieved through catalytic oxidation of hydrogen sulphide by oxygen at low temperatures, <200 °C, the material to be sulphurized acting as a catalyst of the reaction. Samples were prepared with sulphur content ranging between 5 and 30% (Table 1).

TABLE 1
Sulphur content

	% S	t (h)		% S	t (h)		% S	t (h)
SB1	5.72	2	SPG1	11.43	3	SPS1	11.63	1
SB2	11.45	6	SPG2	17.64	5	SPS2	13.76	2
SB3	16.42	10	SPG3	23.88	7	SPS3	18.10	4
SB4	20.68	14	SPG4	25.77	10	SPS4	22.41	6
SB5	23.28	18	SPG5	25.86	14	SPS5	26.60	9

The textural evolution of the sulphurized material was followed by scanning electron microscopy (ISI-DS130), nitrogen adsorption-desorption isotherms at 77 K (MICROMERITICS DIGISORB 2500) and mercury intrusion porosimetry (MICROMERITICS 9305).

Nitrogen adsorption-desorption isotherms are all alike but minor shifts of the hysteresis loop closure points towards the high relative pressures and lower total nitrogen uptakes denote losses in mesoporosity as sulphur deposition increases. The loops in SPG4 and SPG5 samples are slightly different with an almost asymptotic adsorption at high pressures. As mentioned previously [1], this can not be ascribed to sulphur's own texture development but must be produced by sulphur deposition inside the throats and macropores of the samples.

Textural parameters have been calculated following conventional methods [2,3]; values are gathered in Tables 2-4. A large decrease in surface area is seen in all three series after the first sulphur deposition. Afterwards, only linear changes are produced as S content increases. This denotes that only morphological effects are present during the sulphur deposition. Also the C_{BE+} constant suffers a drastic falldown from the natural to the sulphurized samples, and attains a

limiting value (around 90) as S deposition progresses. Since C_{NET} is related to adsorbate-adsorbent interaction, that change clearly arises from the different chemical nature of the solid surface as it is covered by sulphur monolayer. The changes on PANGEL are slower but finally they reach the same values than in the two other series.

TABLE 2
BURRUS Textural parameters

	SB	SB1	SB2	SB3	SB4	SB5
$S_{\text{NET}} (\text{m}^2/\text{g})$	337	127	81	73	60	53
C_{NET}	233	65	79	90	96	92
$V_{\text{P}098} (\text{cm}^3/\text{g})$	0,546	0,449	0,308	0,357	0,299	0,277
$r_{\text{P}098} (\text{Å})$	33	71	94	98	99	105
$V_{\text{MP}} (\text{mm}^3/\text{g})$	70	18	18	9	5	14
$V_{\text{M}} (\text{cm}^3/\text{g})$	0,138	0,106	0,094	0,080	0,076	0,014
$R_{\text{M}} (\text{Å})$	719	644	608	649	583	555

TABLE 3
PANGEL Textural parameters

	SPG	SPG1	SPG2	SPG3	SPG4	SPG5
$S_{\text{NET}} (\text{m}^2/\text{g})$	364	78	59	51	55	40
C_{NET}	151	112	121	106	85	90
$V_{\text{P}098} (\text{cm}^3/\text{g})$	0,640	0,305	0,254	0,222	0,230	0,176
$r_{\text{P}098} (\text{Å})$	35	79	86	87	84	88
$V_{\text{MP}} (\text{mm}^3/\text{g})$	60	2	1	6	2	7
$V_{\text{M}} (\text{cm}^3/\text{g})$	1,240	0,101	0,093	0,047	0,061	0,060
$R_{\text{M}} (\text{Å})$	1727	776	762	863	709	707

TABLE 4
PANSIL Textural parameters

	SPS	SPS1	SPS2	SPS3	SPS4	SPS5
$S_{\text{NET}} (\text{m}^2/\text{g})$	298	80	75	68	49	37
C_{NET}	180	81	89	99	97	96
$V_{\text{P}098} (\text{cm}^3/\text{g})$	0,602	0,314	0,290	0,273	0,197	0,165
$r_{\text{P}098} (\text{Å})$	40	78	77	80	80	89
$V_{\text{MP}} (\text{mm}^3/\text{g})$	61	14	8	3	3	3
$V_{\text{M}} (\text{cm}^3/\text{g})$	1,796	0,043	0,049	0,024	0,030	0,025
$R_{\text{M}} (\text{Å})$	1574	603	622	531	557	538

The quantitative analysis of the isotherms corroborates the loss in microporosity suspected from the surface area decrease. However, this loss does not affect the mean micropore radius which remains unchanged along each series. In addition mesoporosity diminishes parallelly in all samples with the mean pore radius shifting towards larger sizes once the first deposition is surpassed. In summary, at first, a narrower distribution in pore size is produced, always preserving the more

frequent pore size. Afterwards, a progressive decrease in all sizes but more important in the smaller ones becomes apparent.

The main differences among samples are revealed by mercury penetration porosimetry. For the SPG and SPS series, a large loss of macroporosity is observed with the first deposition. This is not observed with the SB series. These changes are related to the morphology of the samples, their particle size, and aggregation state. On one hand, the wet micronization procedure, results in finer particles on SPG than on SB. On the other hand, the dry micronization procedure, SPS, causes the breakdown (and consequent fringe and edge formation) of the original fibers. Both samples are therefore liable to form crosslinked networks, on which sulphur deposition is easier and results in a large decrease in interparticular voids.

From the preceding study, completed by TEM, a mechanism for sulphur deposition has been abstracted. At the very beginning, sulphur is deposited on the surface active sites, acidic centers, corners, edges and tips of the fibers [4]. From these points, it spreads along the fibers until a monolayer is produced. Afterwards, filling of the pores proceeds from smaller to larger sizes following the Kelvin equation. Care must be taken in order to insure that external conditions do not influence the deposition process: hydrogen sulphide oxidation is a quite exothermic process [5] which, along with the insulating character of sepiolite can produce hot spots or temperature rises when changes in reaction rates are produced. Then, sulphur redistribution can occur in the porous system of the samples resulting in final textural characteristics quite different from those expected from the original pore distribution and the sequential character of the pore filling.

Sepiolite has been shown to be a suitable material for use as a sulphur seizer. Its mesopore network, but especially its interparticular voids resulting from its fibrous character provide the proper textural conditions for sulphur retention. As much as 25% weight S has been retained by these samples before a plateau in sulphur concentration was reached. There exist kinetic differences among samples but they all have similar overall retention capacities. Thus, sepiolite can be used as an alternative material for hydrogen sulphide removal from stack gasses [6,7].

BIBLIOGRAFY

1. L. Daza, S. Mendioroz and J.A. Pajares, "Sulphurized diatomites as potential demercuriating agent". Reactivity of Solids, in press.
2. S. Brunauer, J. Skalny and I. Older, Proc. Inter. Symposium RYLEM/IUPAC, Prel. Report, Part 1, Akad. Praga, 1973 (C-3).
3. A. Lecloux and J.P. Pirard, J. Colloid Interface Sci., 70, 265 (1979).
4. L. Daza, Ph.D.Thesis, Universidad Complutense, Madrid, 1986.
5. A.R. Chatterjee, N.B. Bhatthacharya and S.P. Sen, Technology, 8, 48 (1971).
6. S. Miner, Air pollution aspects of hydrogen sulfide, Litton System Inc., Bethesda, Maryland, USA (1969).
7. R.J. Sullivan, Air pollution aspects of odorous compounds, Litton System Inc., Bethesda, Maryland, USA (1969).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CRISTALLINITY VALUES OF SOME SPANISH KAOLINS

Delgado Calvo-Flores, R.; Gámiz Martín, E. and Martín de Vidales, J.L.*

Departamento de Geología Aplicada. Facultad de Farmacia. Universidad de Granada. 18001 Granada. Spain.

* Departamento de Química Agrícola, Geología y Geoquímica. Facultad de Ciencias. Universidad Autónoma de Madrid. Cantoblanco. 28049 Madrid. Spain.

The 1:1 phyllosilicates cristallinity of the kaolinite subgroup has been empirically studied by several authors (3,4,5 and 7); cuantitative theoretical studies have been also made (6 and 8). The cristallinity of these phases is important not only from a cristallochemical point of view, but also from their genetic and technological applications.

The purpose of this study, is the cristallinity determination of some Spanish kaolins from several empirics measurements: expansibility test with formamide (X.R.D.), cristallinity indexes (X.R.D.) and mean size of particles (S.E.M.).

MATERIALS AND METHODS

The silt (2-20 μm) and clay (< 2 μm) fractions, have been studied on six industrial kaolins characterized by (2), as also ceramic and other paper kaolin (Table I). The relative proportion of phase 7Å swelling with formamide, was determinated from oriented specimens on glass slides; solvation was carried out by inmediate contact (30' to 1 hour) by the (1) and (9) method. Due to the presence of micas it was employed the following formulae:

$$P(\%) = 100 \times \frac{I(10\text{Å})_{\text{form.}} - I(10\text{Å})_{\text{untreated}} * 0.8}{I(7\text{Å})_{\text{form.}} + I(10\text{Å})_{\text{form.}} - I(10\text{Å})_{\text{untreated}} * 0.8}$$

The 0.8 factor was calculated by the decrease of intensities in the 9.4Å to 10.0Å stretch from untreated and formamide-solvated orientated diagrams, from pure mica and talc measurements. The intensities were measured as peaks height and areas.

Several cristallinity empirical index (3,4,5 and 7) were determinated from random powder diffractograms with a speed of 0'5--/min. Mean sizes of silt and clay were determinated by S.E.M.

RESULTS AND DISCUSSION

The results have been collected in Table I. The relative reflections width in the major part of the diagrams after the treatment with formamide method (1), advises to select the proportion of the swelling phase from areas. Silt generally shows a proportion of swelling components higher than clay.

There is some disparity between cristallinities determined by different methods: the Hinckley, Lietard and Range et al. indexes show middle to high values but the Hughes and Brown index shows middle to low ones. except in the C-1 kaolin, the Hinckley index is slightly lower in clay than in silt fraction.

The statistics studies of the degree of relation between the whole of variables against the swelling degree, point out that there is no correlation with size particle, although there is some negative correlation degree with the Lietard, Hughes and Brown, and Hinckley indexes (except C-3 and C-5 silt and ceramic kaolin, which are very expandible). Finally, there is an important correlation ($r=0'88$; $p>0'995$) between the Hinckley and Lietard indexes.

CONCLUSION

The formamide test, could be a new method of cristallinity determination in the minerals of the kaolin subgroup.

In the studied Spanish kaolin, the swelling degree oscillates between zero and 76'4%; the Hinckley index from 0'55 to 1'03; the Range et al. index from 0'31 to 0'57; the Lietard index from 0'59 to 1'07 and the Hughes and Brown index from 12'1 to 25'0.

REFERENCES

- (1) Churchman, G.J.; Whitton, J.S.; Claridge, G.G.C. and Theng, B.K.G. (1984) Clays and Clay Minerals, 32, 241-248.
- (2) Gámiz Martín, E. (1987). Tesis Doctoral. Univ. Granada (in press).
- (3) Hinckley, D.M. (1963). Clays and Clay Minerals Proc. 11th 299-235.
- (4) Hughes, J.C. and Brown G. (1979). J. Soil Sci. 30, 557-563.
- (5) Lietard, O. (1977). These Doc. Sci. Phys. Nancy, 345 p.

(6) Plancon, a. and Tchoubar, C. (1977). Clays and Clay Minerals 25, 436-450.

(7) Range, K.J., Range, A. Weiss, A. (1982). Cit. by Cases, J. Lietaud, O. Yvon, J. Delon, J. Bull. Min. 105, 439-455.

(8) Tchoubar, C.; Plancon, A.; Ben, J. Clinard, C. and Sow, C. (1982) Bull. Min. 105, 477-491.

(9) Theng, B.K.G.; Churchman, G.J.; Whitton, J.S. and Claridge, G.G.C. (1984). Clays and Clay Minerals. 32, 249-258.

Sample	Site	Type	Fract.	%Swell (I)	%Swell (A)	H.I.	R.I.	L.I.	HB.I.	Size(μm)
C-1	CU	Light	Silt	0.0	2.3	0.90	0.39	1.05	19.2	6.4
C-1	CU	Light	Clay	3.8	9.4	1.03	0.33	0.89	19.0	0.7
C-3	LU	Raw	Silt	78.8	76.4	0.88	0.46	10.7	12.1	7.5
C-3	LU	Raw	Clay	1.1	11.9	0.73	0.42	0.84	18.5	1.0
C-4	PO	Light	Silt	17.4	19.5	0.66	0.54	0.81	9.8	5.6
C-4	PO	Light	Clay	-	1.0	-	0.57	0.59	15.7	0.7
C-5	OV	Raw	Silt	71.0	70.8	1.02	0.31	0.86	25.5	3.6
C-5	OV	Raw	Clay	9.5	0.0	1.02	0.33	1.05	23.5	1.3
C-6A	LU	Light	Silt	35.6	31.7	0.72	0.41	0.73	15.5	3.6
C-6A	LU	Light	Clay	13.1	22.0	0.55	0.48	0.59	22.3	0.8
C-6B	LU	Light	Silt	23.7	29.7	0.77	0.46	0.89	15.3	6.3
C-6B	LU	Light	Clay	2.4	7.3	0.65	0.42	0.75	25.5	0.7
Pap.	-	Light	Total	26.8	16.9	-	0.37	1.03	25.5	-
Cer.	-	Raw	Total	73.0	75.0	-	0.39	1.08	17.6	-

TABLE I.- Sites: CU= Cuenca; LU= Lugo; PO= Pontevedra; OV= Oviedo.

Fractions: Silt= 2-20 μm; Clay=<2 μm; (I)= height peak. (A)= area peak. H.I.= Hinckley index; R.I.= Range et al. index. L.I.= Lietaud index. HB.I.= Hughes and Brown index.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

RELATIONSHIPS BETWEEN CLAY MINERALOGY AND K^+ SELECTIVITY IN A SOIL CHRONOSEQUENCE ON BASALTIC ASH DEPOSITS FROM CAMEROON

B. DELVAUX*, A.J. HERBILLON**, J. DUFEY** and L. VIELVOYE*****

- * IRFA (CIRAD), Unité de Chimie des Interfaces, Univ. Cath. de Louvain, Belgium
- ** Unité de Pédologie, Univ. Catholique de Louvain, Belgium
- *** Section de Physico-chimie Minérale du Musée Royal de l'Afrique Centrale
- **** Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium
C.P.B., C.N.R.S., Vandoeuvres-lez-Nancy, France

The chronosequence under study is made of the following soil types : Andepts, Tropepts, Udalfs and Udults. To each of these soil types corresponds a different clay mineralogy : allophanic materials progressively disappear while halloysite (10A) and eventually kaolinite become the dominant clays.

At the halloysitic stage correspond a high CEC (~30-40 meq/100g clay) as well as the maximal K^+ selectivity (as measured by K^+ - Ca^{2+} exchange equilibria).

Mineralogical investigations (X-ray diffraction, IR, TEM, DTA-TGA, etc..) show that the high CEC and the high K^+ affinity observed in halloysitic soils are likely due to smectitic 2:1 clays impurities that are associated with the halloysite (10A). These 2:1 clays are probably iron-rich beidellites. On the other hand, the K^+ selectivity appears to be well related to the weathering stage of the halloysitic soils.

The results suggest that in these situations at least and in agreement with previous findings, halloysite (10A) per se is not a high charge clay mineral.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

A PICTURE OF CLAY SEDIMENTATION IN THE BASIN OF THE CRATI RIVER (CALABRIA, SOUTHERN ITALY).

L. DELL'ANNA AND R. LAVIANO

Dipartimento Geomineralogico, University of Bari - (Italy)

A mineralogical, chemical and grain size study of the clays from deposits outcropping in the basin of the Crati River shows a clay sedimentation picture which can be related to source and environment.

The Tortonian clays are made up mainly of clay minerals (illite, smectite, mixed layer illite-smectite, chlorite, kaolinite and mixed layer hydrobiotite-vermiculite), muscovite, biotite, quartz, feldspars, calcite and dolomite, and of scarce micaschists, chlorite-rich schists, Na-amphiboles, actinolite and hornblende amphiboles, almandine garnet, tourmaline, sillimanite, chloritoid, phlogopite, apatite, strengite, vivianite, rutile, ilmenite, Fe-hydroxide, glauconite and gypsum. The Messinian clays differ from the Tortonian clays because they are richer in phosphates, sulphates, and dolomite; and also contain chlorides, such as halite and carnallite; and clay minerals: such as palygorskite and mixed layer chlorite-smectite, chlorite-vermiculite and illite-vermiculite. The Pliocene clays consist mainly of clay minerals (smectite, illite, chlorite, kaolinite, and mixed layer illite-smectite, smectite-chlorite, and smectite-vermiculite), carbonates (calcite and dolomite), quartz and feldspars. Compared with those of Pliocene the Pleistocene clays contain more illi-

te and clay minerals and are poorer in smectite, mixed layer (illite-smectite, chlorite-smectite, smectite-vermiculite) and subordinate (micas, biotite, garnet, amphiboles, sillimanite, rutile, ilmenite) minerals.

The clastic materials of the basin derive essentially from the metamorphites and magmatites of the Calabrian Alpine overthrust rocks; the clay minerals are the products of various areas of diagenesis in a continental environment during weathering of the parent rocks. The sulphates and chlorides and most of the clay minerals and carbonates (dolomite) of the Messinian sedimentation were formed authigenically in a marine hypersaline environment.

The grain size, mineralogical and chemical analyses of the clay sedimentary sequences indicate that: a) during the Tortonian period a neritic sedimentation took place; b) while in the Lower Messinian small sedimentary basins were activated within which a marine clastic sedimentation and a coexisting chemical deposition took place; c) a further neritic sedimentation occurred during the Pliocene and also during the Pleistocene when the basin of the Crati River became deeper and attained its present form.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PEDOGENIC IRON OXIDE FORMATION IN THE SOILS OF TWO RIVER TERRACE SEQUENCES OF CENTRAL SPAIN.

MARIA C. DIAZ¹ AND JOSE TORRENT²

¹Departamento de Edafología, E.T.S.I.A., Universidad Politécnica de Madrid, Ciudad Universitaria, 28040 Madrid (Spain).

²Departamento de Ciencias y Recursos Agrícolas, E.T.S.I.A., Universidad de Córdoba, Apdo. 3048, 14080 Córdoba (Spain).

Soil chronosequences, such as those found in many river terrace systems, are useful to investigate the nature and intensity of pedogenic processes. In this work we examine the geochemical evolution of Fe in the soils of the terraces of the River Henares and the River Jarama, in Central Spain. The present climate of these areas is mediterranean; mean annual temperature is about 13°C; mean annual rainfall is 440 mm for the River Henares area and 515 mm for the River Jarama area.

The soils of the alluvial plains and eight (River Henares) and five (River Jarama) terrace levels have been studied. The ages of the upper levels studied in both sequences are similar (Lower Pleistocene). Except for the recent alluvial areas the soils are, in both sequences, Alfisols. In the River Henares the soils are Haploxeralfs (second and third terrace levels) and Rhodoxeralfs (levels 4 to 8). In the River Jarama the soils are Haploxeralfs (first terrace level) and Palexeralfs (levels 2 to 5). In both sequences the clay content of the argillic horizon increases with terrace height (age) and pH decreases although the soils of the Jarama sequence have pH values markedly lower than those of the Henares because they have developed on less base-rich parent alluvia.

The degree of weathering increases with age. This is supported by several data such as the decrease in the (staurolite + garnet) / (tourmaline + zircon) ratio in the heavy 50-200 μm fraction or the decrease in the Si/Al and the Mg/Al ratios in the clay fraction. The dithionite extractable Fe (Fe_d)/total Fe (Fe_t) ratio of the soils

increases also with age, suggesting that the Fe-bearing silicates have been gradually weathered to supply Fe oxides.

The Fe oxides present in the clay fraction have been quantified by differential X-ray diffraction (Schulze, 1981). In the Henares sequence both goethite and hematite are present in measurable amount in all terrace levels; the hematite/goethite ratio increases up to the levels 5-6 and then decreases. In the Jarama sequence much less hematite is found. Two factors seem to be responsible for this difference: a) the higher pH of the Henares soils may favour hematite over goethite (Schwertmann and Murad, 1983) and b) the pedoclimate is different for the two sequences. The Jarama soils are stony and have, consequently, less water holding capacity. They moisten quickly in autumn and remain moister than the Henares soils during the rainy winter months. This moister (and cooler) pedoclimate favours goethite over hematite (Schwertmann and Taylor, 1977). Similarly, the soils of the high terraces of the Henares are more clayey and moister in winter than those of the low terraces: this probably explains their higher goethite content.

REFERENCES

- Schulze, D.G., 1981. Identification of soil oxide minerals by differential X-ray diffraction. *Soil Sci. Soc. Am. J.*, 45: 437-440.
- Schwertmann, U. and Taylor, R.M., 1977. Iron oxides. In: J.B. Dixon and S.B. Weed (Editors), *Minerals in Soil Environments*. *Soil Sci. Soc. Am.*, Madison, Wisc., pp. 145-180.
- Schwertmann, U. and Murad, E., 1983. Effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays Clay Miner.*, 31: 277-284.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CRISTALCHEMISTRY OF "PINK CLAYS" FROM THE TERTIARY MADRID
BASIN. ITS RELATIONSHIP WITH THE SEPIOLITE OCCURENCE.

M. DOVAL, M. RAUTUREAU*, J.M. BRELL AND C. FONTAINE*

Faculty of Geology, University Complutense of Madrid (Spain)

*Laboratoire de Cristallographie, Université d'Orleans (France)

The greenish clays unit, of the Miocene sediments of Madrid basin, about 40 m. thick, is made up of green clays with some tongues of micaceous sands in its lower middle part and carbonates towards the top;

This unit forms as a fringe cropping in the Western part of the basin, more than 100 kms. long from N. to S. It is mainly composed of trioctahedral smectite, specially saponite with lesser amounts of illite, quartz and feldspars.

In the northern part of the basin, these clays are covered paraconformably by the arkosic levels of the Upper Unit. Near the contact, and between the arkosic materials sepiolite deposits of economic importance are found. These are, now mined. Towards the south and east, these materials pass gradually to carbonates better developed southwards. This unit lies on the gypsum central units of the basin.

A very significant feature of these clays is the presence of some pinkish clay levels, very porous, intercalated between them, often showing alternances made up of green-pink clay couplets and dolomite levels.

Composition and properties of these pink clays have been studied by X-Ray diffraction, chemical analysis, DTA, infrared spectroscopy and electron microscopy.

The data indicate that the dominant mineral present is a very high-magnesium smectite, probably stevensite, with minor amounts of illite and sepiolite. X-Ray diagrams as well as DTA and infrared data show some interesting features of this material.

Nevertheless, the poor or absent resolution of the higher order reflexions of sepiolite as well as of smectite, due to small particle size and structural disorder make the detailed characterization very difficult.

On the other hand scanning electron microscopy shows some apparent genetic relationship between smectite and sepiolite, because fibers probably of the second mineral, seem to grow from the jagged limits of the smectite platelets.

Because of that a more detailed study using high resolution transmission electron microscopy has been carried out, to establish chemical and mineralogical particle composition, and the structural and genetic relationships between illite, stevensite and sepiolite.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**LAYER SILICATES IN THE CONTACT ZONE BETWEEN GRANITE AND SERPENTINITE
(JORDANÓW, LOWER SILESIA, POLAND)**

E. DUBIŃSKA, A. WIEWIÓRA*

Institute of Geochemistry, Mineralogy and Petrography, Warsaw University, al. Zwirki i Węgury 93, 02-089 Warsaw (Poland)

*Institute of Geological Sciences, Polish Academy of Sciences, al. Zwirki i Węgury 93, 02-089 Warsaw (Poland)

Materials coming from Jordanów (eastern part of Jordanów-Gogolów serpentinite massif, Lower Silesia, Poland) have been extensively studied for last 100 years. Attention of scientists was focused on the nephrite and calcareous-silicate rocks and minerals, whereas layer silicates were thought to be of rather secondary use for genetic considerations since they were regarded as alteration products of the amphiboles.

Layer silicates form veins filling the fissures in highly tectonized leucogranites. These veins extend up to the contact zone between calcareous silicate rocks (rodingite-like) and serpentinite. The composition of veins changes gradually. In parts from granite layer silicates prevail, whereas in parts close to the serpentinite an amphibole become major and even the only mineral.

Three layer silicates were recognized by means of polarising microscope: a micaceous mineral (1) intergrown with a clinocllore (2), both strongly deformed, talc (3) developed after a tectonic event and showing milder symptoms of deformation. A second tectonic episode separated talc and monoclinic amphibole formation. A fine-grained talc replacing the chlorite represents the latest generation of minerals formed after a third tectonic episode.

SEM observations disclosed very fresh appearance of the amphibole contrasting with layer silicates showing numerous symptoms of alteration.

An extensive preliminary examination of various rocks rich in layer silicates allowed to choose materials which were studied in detail. However, authors failed to obtain the monomineralic sample or subsample.

Chlorite was ubiquitous in the studied samples. Any symptoms of the degradation of chlorite structure were detected. Positions, relative intensities and integrality of basal reflections of chlorites persist practically unchanged after saturation with potassium and heating at 500°C as well as after solvation with ethylene glycol. All chlorites were 1A₂ - I polytype modification according to notation of Weiss and others (in prep.) or IIb after notation of Brown and Bailey (1962). The chlorites were accompanied by an admixture of smectite being probably a product of the chlorite alteration.

The mineral of micaceous appearance in polarizing microscope is a vermiculite, since it contracts readily up to 10 Å after saturation with potassium and heating at 500°C, and swells up to 14 Å after glycerol treatment of Mg-sample. X-ray transmission patterns obtained by means of the oblique texture method show that raw- and Mg-vermiculites are 2M₂-VII-meso polytypes after Weiss and others (in prep.) or Ia modification (Bailey, 1980). The vermiculite saturated with potassium forms a phlogopite-like structure (1M₂-I after Weiss and Wiewióra, 1986), thus a trioctahedral mica may be considered as a very probable parent mineral of the vermiculite.

Other layer silicates: talc, mica (dioctahedral), interstratified mineral with chloritic layers were also found in the studied samples, most of them as a minor admixtures hardly recognisable on the X-ray tracings.

Taking into account the space relations of mineral assemblages, results of the X-ray investigations, and results of experimental works on the formation of talc, chlorite, vermiculite, amphibole etc. four episodes of mineral development divided by three tectonic events may be outlined:

- I - formation of mica and chlorite
- II - formation of talc I; mica and chlorite were unchanged

III - formation of amphibole; previously formed layer silicates persisted

IV - formation of vermiculite (+ mixed-layer mineral with chloritic layers) at the expense of mica; mild alteration of chlorite giving rise to smectite and talc II developments; the amphibole and talc I were inert during this episode.

Origin of described mineral assemblages is still controversial. They may be considered as a tectonized rodingite blackwall as well as a hornfels depending on the relation of granite and serpentinite which is not fully cleared, yet.



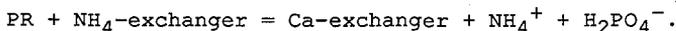
Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FERTILIZER MADE FROM CLAY

D. D. EBERL, T. M. LAI AND K.A. BARBARICK*

U.S. Geological Survey, MS 404, Federal Center, Denver, CO 80225, (U.S.A.). *Department of Agronomy, Colorado State University, Fort Collins, CO 80523, (U.S.A.).

Nutrients are released to plants from phosphate rock (PR) when ammonium-saturated ion exchangers (e.g. smectite or zeolite) are present. The generalized reaction is:



The ion exchanger is a sink for Ca ions, thereby decreasing Ca activity in the soil solution and permitting further dissolution of the phosphate rock. This system offers the possibility of using low-grade phosphate ore as fertilizer, particularly if an ion exchanger, such as smectite, is present in the ore and if the ion exchanger can be ammonium saturated. The system also makes N and Ca available to plants and can be regenerated by adding additional $\text{NH}_4\text{-exchanger}$ to soil-phosphate rock mixtures or by resaturating the ion exchanger with NH_4^+ . Only the $\text{NH}_4\text{-exchanger}$ needs to be added to soils that already contain phosphate compounds; by this method, phosphate that has been fixed as apatite in soils by the reaction of soluble phosphate fertilizer with the soil can be made available for uptake by plants. The rate of nutrient release can be adjusted by varying the ratio of exchanger to phosphate rock.

Seedling uptake experiments indicate that the ion-exchange fertilization system surpasses a soluble P system in P uptake by barley after several cuttings from the same pots.

Results from greenhouse pot trials using sudangrass and a Colorado agricultural soil indicate that dry yields, P-uptake, and the uptake of some trace nutrients are directly related to the exchanger/phosphate rock ratio (see Figure 1).

Fertilization by ion exchange offers an alternative technology to the application of readily soluble and concentrated plant nutrients and may circumvent some of the problems associated with soluble fertilizers.

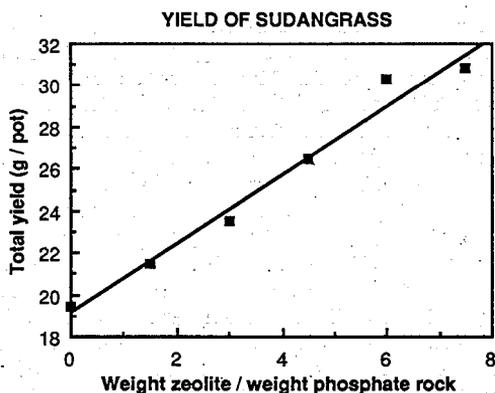


Figure 1: Yield of sudangrass (sum of four cuttings) correlates well with the weight ratio of exchanger (NH_4 -clinoptilolite) to phosphate rock (from North Carolina).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CHROMIUM ABUNDANCE AND DISTRIBUTION IN CERAMIC CLAYS FROM WESTERWALD (RFD).

B. FABBRI, N. MORANDI (1), M.C. NANNETTI (1)

Istituto di Ricerche Tecnologiche per la Ceramica, C.N.R., Faenza.

(1) Dipartimento di Scienze Mineralogiche, Università di Bologna, Italy.

In a previous paper it was demonstrated that the appearance of yellow blods on calcareous earthenware type articles is a defect connected with efflorescence of alkaline chromates during the drying of the glazed piece. Such compounds form during firing to obtain the biscuit body through reactions involving the chromium contained in traces in the kaolinitic clays which constitute the starting mix (1). These raw materials come from the large and well known deposits of ceramic clays in the Westerwald region, western Germany (2). These deposits supply the main part of the clayey raw materials used to produce white stoneware tiles in Italy. Notwithstanding their diffusion, not all the characteristics of these clays have been sufficiently investigated and divulged. For example, it is difficult to get informations about their chromium abundance and distribution, when such an information should allow the chromium poorest clays to be selected for the ceramic purposes pointed out at the beginning. The present paper represents a contribution in that sense, being planned to define the approximate variation limits of the chromium contents and to provide some indications on the distribution of this element in the different clay types.

At this purpose, ten commercial clay materials from the Westerwald deposits have been selected in such a way that they represent practically all the compositional variety of the same deposits. In particular, all they are materials used to obtain white ceramic bodies for pottery. For each sample, the chemical and mineralogical compositions have been investigated, including the concentration of chromium and some other interesting trace elements (Co, Cu, Mn, Ni and V). In addition, two samples have been treated to separate fractions less than 2 μm ; then these fractions have been analysed as the tout-venant samples. The chemical data have been obtained by both XRF and AAS procedures; while the mineralogical compositions have been quantitatively evaluated by the IRTEC method of rational analyses

based on the chemical composition and the minerals revealed by the X-ray diffractometry.

Other than kaolinite, the mineralogical composition is made up mainly of quartz and, with only one exception, illite. Furthermore, one sample contains abundant smectite too; while little amounts of feldspars have been revealed for the main part of the samples. The principal mineralogical composition allows the samples to be subdivided into four groups, which are distinguishable among them by comparing the ratios kaolinite/quartz and kaolinite/illite or considering the presence of smectite. The four groups are as follows: 1- both K/Q and K/I less than 3; 2 - K/Q less than 3 and K/I more than 5; 3 - both K/Q and K/I more than 5; 4 - presence of abundant smectite. The differences among these groups are evidenced in the ternary diagram kaolinite - quartz - illite shown in figure. The first group includes five samples; the second and the third group two samples each and the last group is represented by one sample.

The chromium content ranges between about 60 and 230 ppm and the concentration values seems to be similar for the samples belonging to a same group. In particular, the five samples of the first group show the highest chromium contents, with an average value of 190 ppm. The two samples of the second group contain about 150 ppm of Cr, while the chromium concentrations of the other three samples are the lowest ones, i.e. about 60 ppm. According to the behaviour of chromium during weathering and alteration of rocks, the clay fractions are richer in chromium than the coarser fractions.

From a practical point of view, the results obtained suggest that it is possible to reduce the probability of appearance of the yellow blods mentioned at the beginning. This can be obtained by using preferentially the Westerwald clay types with the lowest chromium concentration.

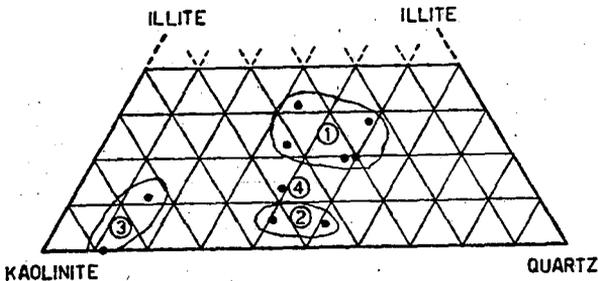


Figure 1

References :

1 - B. FABBRI, F. DONATI - Efflorescenze di cromati alcalini causa delle macchie gialle su stoviglie ceramica a pasta bianca. Relation presented at the 11th International Technical Colloquium on Ceramics Processing "Present Status and Evolutionary Trends in Traditional Ceramics Tecnology", Rimini, October 1-2, 1986.

2 - WBB and FUCHS-TON Technical Departments: The production and properties of Westerwald clays. Part I. cfi/Ber. DKG 63/8 (1985) 394-400. Part II: Mineralogy and geology. cfi/Ber. DKG 63/9-10 (1985) 455-458.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

TECHNOLOGICAL STUDY AND INVESTIGATION ON THE RAW MATERIALS
OF PREHISPANIC POTSHERDS FROM GRAN CANARIA (SPAIN)

B. FABRI, M.G. ARIAS*, F. PHILIPPART DE FOY*, R. MALDERA*

Istituto di Ricerche Tecnologiche per la Ceramica, C.N.R.,
Faenza (Italy).

*Istituto Statale d'Arte per la Ceramica "G. Ballardini",
Faenza (Italy).

This paper deals with the technological characterization of fictile fragments from an archaeological site near Guayedra (Gran Canaria, Spain). The ceramic material found in this ancient habitation unit is represented mainly by "terracotta" fragments without engobe; engobed potsherds are present too, but they have been neglected on purpose. In fact, the aim of the work was to investigate about the identity of the ceramic material with particular reference to its possible raw materials and, moreover, to give some indications on the cultural continuity in the same site.

Firstly about thirty sherds were accurately classified from a macroscopic point of view, then representative samples of each stratigraphic level of the excavation were selected. After examination of many samples by X-ray powder diffraction method too, finally eight fragments were chosen to represent all the ceramic material in the six stratigraphic levels. For these samples, chemical analyses, thermal analyses, determinations of the "melting temperature" and observations at the optical microscope + thin section were carried out.

The X-ray analysis revealed that the sherds are rich of scarcely crystalline material, other than alkali feldspars, plagioclase, pyroxene and quartz as main crystalline components. The alkali feldspars are of high temperature type, i.e. high sanidine. The chemical compositions of the different samples are quite similar each other, particularly showing some typical ratios among the element concentrations, CaO/MgO and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ for example. The alkali content is very high and the sum of sodium and potassium concentrations varies about from 5 to 7 percent. The observations at the polarising microscope evidenced coarse grains prevalently consisting of volcanic rock fragments with pyroxene and some plagioclase as phenocrysts in a groundmass made up of opaque minerals and microcrystalline plagioclase as main phases. Monomineralic coarse grains of both pyroxene and plagioclase were present in all samples, while potassium feldspar and quartz were occasionally observed. The melting temperatures of the sherds resulted little more than 1200°C , with the exception of the sample 4A, the temperature of which was about 1330°C . The substantial homogeneity of the technological characteristics of the sherds was confirmed by the thermal gravimetric analysis, which showed a weight loss up to about 600°C probably due to rehydration during the burial.

In the second part of the work several clayey or sandy raw materials from different areas of the island of Gran Canaria were collected and analysed from a chemical and mineralogical point of view. The clayey minerals are represented mainly by disordered kaolinite, while the detrital fraction is constituted of alkali feldspars in the high temperature form (high sanidine) and pyroxene; quartz is sometimes present in traces.

By comparing the chemical compositions of the raw materials and the potsherds, the type of mixture used to produce the ancient pottery has been reconstructed. The mineralogical composition and the melting temperature of the resulting mix well agree with that of the potsherds too. Finally, some production tests demonstrated the validity of the ceramic body hypothetically attributed to the pottery produced in the antiquity.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PREPARATION AND CHARACTERIZATION OF ZIRCONIUM-PILLARED MONTMORILLONITES.

E.M. FARFAN-TORRES, P. GRANGE, B. DELMON

Groupe de Physico-Chimie Minérale et Catalyse
Place Croix du Sud, 1
B-1348 Louvain-la-Neuve (BELGIUM)

Pillared-clays are smectite clay minerals in which cationic, three-dimensional species are exchanged between the mineral layers.

The shape and size of these exchange cations allows the internal surface of clays to be accessible to adsorption of different substances. In this way, pillared clays have the same behaviour as a molecular sieve, and become interesting for different applications such as catalysis.

There are different approaches for the preparation of pillared clays, but the knowledge and understanding of their formation is not clear up to now. The effects of the preparation variables such as aging time, temperature, concentration of both clay dispersion and oligomeric solution, on thermal stability, texture, properties and characterization of these materials are discussed here.

Wyoming montmorillonite or Weston-L of Eccagum Company was used in all studies. A $< 2\text{-}\mu\text{m}$ fraction was treated with Na Cl solution, then washed and dried. The clay contained no impurities detectable by XRD and a cation exchange capacity of 86 meq/100g of clay.

Several different series of hydroxy-Zr-Montmorillonite were prepared. The general preparation mode consists of adding a $\text{Zr OCl}_2 \cdot 8\text{H}_2\text{O}$ 0.1 M solution to an aqueous or organic montmorillonite suspension. After stirring in the 50-100°C temperature range for 2 hours, the exchange was essentially complete. The resulting system was washed and dried by liophilization.

All samples were heated at between 100-600°C to study their thermal stability. For each series different variables were studied. Concerning

clay dispersion, two variables were considered : (i) Aging time and (ii) solvent nature. As for the dispersion obtained after adding Zr solution to clay, we have analysed the effects of (iii) temperature and time of contact and (iv) final washing.

All samples were examined as powders by XRD. Langmuir and Bet plots of nitrogen adsorption were obtained, and surface areas determined from Langmuir isotherms.

Acidity of cross-linked products was determined by pyridine adsorption and IR spectroscopy.

We found that :

i) the aging of clay dispersion during a span of time varying between 25 and 60 days was favorable for the obtention of a homogeneous product with a high reproduction capacity of basal spacing and a higher thermal stability.

ii) use of an organic solvent like ethanol, ethyleneglycol and acetone allow for the obtention of a greater basal spacing.

iii) aging time for clay dispersion treated with Zr must be short (2-3 hs), to avoid further degradation of clay. In the same way, maturation temperatures must be between 40-70°C in order to favour polymerization of complexes species. At higher temperatures, a product with a different structure was obtained. This product is a delaminated type of clay according to XRD analysis. Delaminated clays are characterized by a macroporosity related to an edge-to-edge aggregation of layers, instead of the typical face-to-face organisation of pillared clays.

iv) Plots of nitrogen adsorption isotherms show that Zr-pillared-Montmorillonites exhibit a deviation from linearity in BET plot and follow Langmuir adsorption isotherms. Surface areas remained quite high, about 250 m²/g, after heating for several hours at various elevated temperatures up to 500°C.

Zr-delaminated clays show linearity for BET plots. Their surface areas are quite elevated and remained nearly unvaried after heat treatment, about 340 m²/g at 200°C and 300 m²/g at 500°C.

v) Concerning acidic properties, adsorption of pyridine shows the presence of two types of acidic sites, Bronstéd and Lewis according to observed bands at 1540cm⁻¹ and 1450cm⁻¹ respectively. Bronstéd sites are strongly enhanced for pillared clays, compared with analysis of Na-Montmorillonite.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAY MINERALS AND TRACE ELEMENTS IN THE MARINE SEDIMENTS OF THE
CENTRAL ADRIATIC

O. FERRETTI*, E. HELIOS**, I. NICCOLAI*, F. VENIALE***

* ENEA Centro Ricerche Energia Ambiente, S. Teresa (ITALY)

** University of Krakow (POLAND)

*** University of Pavia (ITALY)

ENEA has concluded an environmental research program on the Central Adriatic. A mineralogical and geochemical study of surficial sediment samples has been carried out to identify the mineralogical composition of the clay fraction and their possible relationship with trace elements.

Some undisturbed core samples and alluvional sediments of the region, were also examined.

Granulometric data was obtained using classical methods. Clay minerals were determined by x-ray diffraction analyses of the $< 2 \mu\text{m}$ fraction of the sediment. Geochemical analyses were done on the $< 63 \mu\text{m}$ and the $< 2 \mu\text{m}$ fractions. Samples were dissolved using a hot concentrated nitric acid digestion and a cold nitric acid digestion followed by successive treatments with hydrochloric, nitric and hydrofluoric acids to determine the total metal content. Metals were analysed in the acid solutions using atomic absorption spectroscopy.

Among the more important minerals, Mg calcite was found to be more abundant in offshore than nearshore sediments. Plagioclase were found in many samples and there was a tendency for K-feldspars to disappear in offshore samples. The $< 2 \mu\text{m}$ fraction was composed of smectite, chlorite, illite, kaolinite and mixed layer minerals. The alluvional sediments from the southern rivers had a high content

of smectite and kaolinite.

The smectite content was also high for shelf sediments in the southern area.

The mineralogical composition of core samples was found to be similar throughout the cores.

The trace element content of the sediment was higher for the total dissolution method compared to the hot nitric acid leach results and for the clay fraction ($<2 \mu\text{m}$) compared to the $<63 \mu\text{m}$ fraction. Mn, Cu, Zn, Ni and Co showed an increase in concentration for offshore sediments compared to those closer to shore. On the contrary, the Cd content was higher in samples found closer to shore. Cu and Pb content was lower in the southern and offshore areas when compared to more northerly and near shore samples.

Several correlations relative to the position of platform sediments were detected (Ni-Cr, Cr-Mn and Zn-Mn). The trace elements do not show significant correlations with the different clay fraction composition, however Zn, Cu and Mn showed a slight correlation with the clay fraction content.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGICAL CLASSIFICATION OF THE CLAYISH BODIES FOR THE ITALIAN TILE PRODUCTION

C. FIORI, B. FABBRI, F. DONATI, I. VENTURI

C.N.R., Istituto di Ricerche Tecnologiche per la Ceramica
Via Granarolo 64, 48018 Faenza (Italy)

The Italian ceramic tile production has undergone a rapid evolution through the last 10-15 years. The aims were an increasing productivity of the processes and a lowering of the production costs. Thus, the factories evolved towards the maximum level of automation and the least employment of labour. In particular, it has occurred a spread change from double-firing to single-firing of the glazed tiles. Furthermore, the firing cycles have become exceptionally short (in some cases close to half an hour) with the aid of the modern single-layer or multi-channel tunnel kilns.

In this context, also the products have undergone an evolution so that, while some traditional types (i.e.: majolica and earthenware) are tending to disappear, others have been introduced into the market and are obtaining a growing success, such as the "single-fired porous tiles". The necessity of adapting the composition of the bodies to the new rapid cycles and the trend of using less expensive raw materials have occurred.

The present-day list of the types of tile products is schematically reported in Table 1. The distinction among the commercial types of tiles is done on the basis of some practical or technical characteristics, as follows:

- colour of the fired support, with red-brown or similar colours in anthitesis to light colours such as white, grey, pink; etc.;
- porosity of the fired support, from porous or semi-vitrified to vitri-

fied with an open porosity quite null;

- the type of milling: i.e. wet- or dry-milling;
- the type of shaping: i.e. pressing of a powder with low humidity or extrusion of a plastic body.

Table 1

PRODUCT	milling
A) Tiles shaped by pressing:	
a) "coloured" types:	
1 - porous: "cottoforte" (double fired);	wet-
"porous single-firing";	dry-, wet-
2 - semi-vitrified: "single-fired semi-gres";	dry-, wet-
3 - vitrified: "single fired red-gres";	dry-, wet-
"non-glazed red-gres";	wet-
b) "light coloured" types:	
1 - porous: "earthenware" (double fired);	wet-
"porous single-firing";	wet-
2 - vitrified: "single fired white-gres";	wet-
"porcelain gres";	wet-
B) Tiles shaped by extrusion:	
1 - "klinker" (red and light colours)	wet-
2 - "cotto toscano"	wet-

The aim of this work is that of differentiating from a mineralogical point of view the clayish bodies employed at present in the Italian productions of ceramic tiles. A collection of representative samples of bodies for each type of product has been analyzed using the classical techniques and methods available in a research laboratory for ceramic technology. For each sample the fine fraction ($\leq 4 \mu\text{m}$) has been separated to carry out a more careful characterization of the portion subjected to the greatest transformations during firing. In fact, espe-

cially with the present rapid firing cycles, the reactions affect principally the clay minerals and the finest particles of the other components. The data relative to each body have been utilized as a useful reference for the discussion about the mineralogical differences among the various types of products. To this purpose, the mineralogical analyses have been carried out following a computerized method of rational analysis developed at IRTEC (1,2). Thus, the present study can be considered as a basis work for a mineralogical classification of bodies for ceramic tiles and as a reference for the researchers interested in the industrial application of clays.

PRINCIPAL REFERENCES

- 1 - A. KRAJEWSKI, B. FABBRI, C. FIORI, R. VALMORI,
"Analisi mineralogica di materie prime ceramiche con computer"
Ceramica Informazione, 20 (1985) 391
- 2 - B. FABBRI, C. FIORI, A. KRAJEWSKI, R. VALMORI, A. TENAGLIA
"Comparison between Traditional Mineralogical and Computerized
Rational Analysis of Ceramic Raw Materials"
Journal de Physique, Colloque C1, supplement au no.2, Tome 47,
fevrier 1986, page C1-57



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

INTERACTION OF DEXAMETHASONE AND MONTMORILLONITE

M. FORTEZA, E. GALAN AND J. CORNEJO*

Dpto. de Geología, Facultad de Química, Universidad de Sevilla (Spain).

*Instituto de Recursos Naturales y Agrobiología, C.S.I.C., Aptdo. 1052, Sevilla (Spain).

Clay-drug interactions have been widely studied during the last decade. However, the reaction mechanisms responsible of these interactions only have been elucidated in some cases (1,2), most of them when cationic drugs are involved. Neutral molecules are known to interact with clays by physical adsorption (3), and/or by hydrogen bonding (4). Digoxin is adsorbed onto montmorillonite by a reversible adsorption mechanism (5) and degrades by acid-catalyzed hydrolysis. The mechanism of adsorption and degradation of the neutral steroid hydrocortisone by palygorskite and sepiolite has been recently studied (6,7). Two types of ferric iron present in these clays may be responsible for the different degradation rates of hydrocortisone.

Dexamethasone was chosen as the model drug because it is one of the most powerful antiinflammatory steroid, which is orally or topically administered because of its minimal mineralocorticoid properties. This neutral drug degrades by oxidation and may be coadministered with clay-containing pharmaceuticals.

Montmorillonite was used as a model clay because it possesses the highest accessible surface area and exchange capacity of the clays commonly used in pharmacy.

EXPERIMENTAL

All chemicals were either official or reagent grade. An X-ray diffractogram of the clay sample indicated that it was composed of montmorillonite and traces of quartz. A high-pressure liquid chromatographic method useful for the analysis of hydrocortisone and its degradation products (6) was slightly modified for this study. Changes in

the A-ring of dexamethasone were monitored by UV spectrometry at 240 nm.

Kinetic studies were carried out at 25, 35 and 55°C. 100 mg of clay was mixed with 30 ml of an aqueous solution of dexamethasone (50 µg/ml) in 50 ml stoppered centrifuge tubes and aged in a shaker-incubator. At appropriate intervals, aliquots were centrifuged and supernate was filtered and analyzed by HPLC and UV spectrometry. The pH of each suspension was maintained within a range 8.7-9.0.

The sample preparation for the study of adsorption as a function of concentration was carried out according to the method described for the kinetic study, but 5-50 µg/ml dexamethasone concentration and 50 mg of clay were used.

RESULTS AND DISCUSSION

Dexamethasone exhibited a very slow degradation in aqueous solution at pH 6-9 and 25°C (Fig. 1b). In a montmorillonite suspension it was observed that dexamethasone content of the aqueous phase continuously decreased as determined by HPLC analysis (Fig. 1a, D). The degradation profile shown in Fig. 1a suggests that compounds A (acidic product) and N (neutral product) arise directly from dexamethasone. However, the degradation profile (Fig. 1a) was treated as consisting in three different reaction phases (Fig. 1b): a) the initial decrease of dexamethasone concentration from 50 to 9 µg/ml, suggested that the drug is adsorbed by montmorillonite. This effect was also observed by UV spectrometry and is similar but greater than that reported (6) for sepiolite-hydrocortisone interaction; b) a second reaction phase could be consistent with a rapid degradation rate of dexamethasone as shown by HPLC analysis together with dexamethasone adsorption by the clay; c) the third reaction phase suggests a slow degradation rate of dexamethasone as indicated by HPLC and UV analysis.

The d(001) spacing for montmorillonite in the absence of drug under dehydration conditions was 9.6 Å, indicating that no interlayer molecules (i.e., water or drug) were present in the control sample. Adsorption of drug molecules between the layers of montmorillonite increased the d(001) spacing to 14.9 Å. This result indicated that dexamethasone penetrated into the interlayer space of the clay and is in agreement with the first reaction phase of the degradation profile above described.

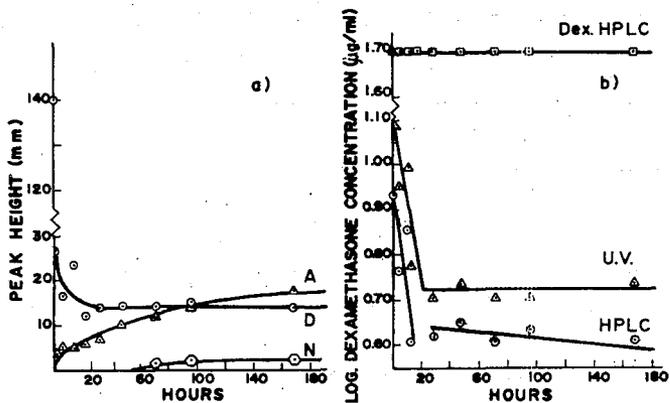


Fig. 1

The IR spectrum of dexamethasone-montmorillonite complex supports weak adsorption mechanism. The carbonyl-stretching vibration of the C-17 dexamethasone side-chain shifted from 1705 to 1690 cm^{-1} . In addition, the carbonyl-stretching vibration of the C-3 dexamethasone A-ring also shifts from 1660 to 1650 cm^{-1} , as a result of the interaction with montmorillonite. This shift to lower frequency indicates hydrogen bonding as the main adsorption mechanism, although van der Waals' forces also may contribute. Desorption studies confirmed that dexamethasone is weakly adsorbed by montmorillonite since it was easily desorbed by washing with water.

It may be concluded that the montmorillonite-dexamethasone reaction mechanism is consistent with a reversible adsorption process and simultaneous degradation reaction.

REFERENCES

- (1) White, J.L. and Hem, S.L. (1983), *Ind. Eng. Chem. Prod. Res. Dev.*, 22, 665.
- (2) Hem, S.L. and White, J.L. (1985), *Chemtec.*, 1, 44.
- (3) Bradley, W.F. (1945), *J. Am. Chem. Soc.*, 67, 975.
- (4) MacEwan, D.M.C. (1948), 44, 349.
- (5) Porubcan, L.S., Born, G.S., White, J.L. and Hem, S.L. (1979), *J. Pharm. Sci.* 68, 358.
- (6) Cornejo, J., Hermosín, M.C., White, J.L., Peck, G.E. and Hem, S.L. (1980), *J. Pharm. Sci.*, 69, 945.
- (7) Hermosín, M.C., Cornejo, J., White, J.L. and Hem, S.L. (1981), *J. Pharm. Sci.* 70, 189.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SEPIOLITE DEPOSIT IN CENTRAL ANATOLIA, TURKEY

Y. FUKUSHIMA AND K. SHIMOSAKA^{*}

Toyota Central Res. & Develop. Labs., Inc., Nagakute, Aichi, Japan.

*Nagoya office of Geological Survey of Japan, Nagoya, Aichi, Japan.

The sepiolite deposit in this work occurs near the village of Yenidogan, which is situated 120 km south-east of the city of Eskisehir, Anatolia, Turkey. This deposit was recognized and reported briefly by Turan (1975). Its extent is approximately 4 km² and the thickness the sepiolite layer is about 10 m. The sepiolite layer, which is composed of white and brown parts, are sandwiched between the dolomite layers. The white part contains about 65% of sepiolite and 35% of dolomite. The sepiolite content in brown part is fairly pure (more than 98%), being accompanied by quartz, palygorskite, sulfur, dolomite and organic matters.

EXPERIMENTAL

Samples collected from the deposit were studied by X-ray powder diffraction (XRD), chemical analyses, TG/DTA, transmission electron microscope (TEM), TG with evolved gas analysis by FT-IR, IR of organic matters extracted from the brown sepiolite and quantitative analyses of carbonates. The evolved gases from samples during TG measurements were introduced into a light-tube for FT-IR analysis for tracing the origins of the weight loss. The organic matters were not easily extracted by organic solvents or acid or basic aqueous solutions, because of strong interactions between the sepiolite surface and organic matters.

They were, however, easily extracted by dimethylsulfoxide or aqueous solution of NaOH after destruction of the sepiolite crystals by the treatment with aqueous solution of HCl. The extracted matters were analyzed by IR and compared with IR spectrum of usual humic acid. Carbonates in the samples were decomposed by 10 N aqueous solution of H₂SO₄, and the amount of evolved CO₂ was analyzed by using porous NaOH.

Table 1. Chemical compositions
of white and brown samples.

	white (wt%)	brown (wt%)
SiO ₂	41.4	62.5
MgO	26.1	25.0
Al ₂ O ₃	0.72	1.30
Fe ₂ O ₃	0.21	0.56
CaO	11.1	0.31
K ₂ O	0.10	0.25
Na ₂ O	0.03	0.06
TiO ₂	0.03	0.07
L. O. I.	25.2	12.0
Total	104.89	102.05
C	5.0	0.74
S	0.01	0.04
sepiolite	64.7	98.3
dolomite	35.0	1.0
organic	0.3	0.7

Table 2. Atom ratios of
cations in sepiolite.

	white	brown
Si	11.89	12.11
Mg	7.76	7.15
Al	0.24	0.30
Fe	0.05	0.08
Ca	0.00	0.00
K	0.04	0.06
Na	0.02	0.02
Ti	0.01	0.01

Atom ratios were normalized
by total charge (+64) of
cations in one formula unit
of sepiolite.

RESULTS AND DISCUSSIONS

The chemical compositions of brown and white samples are listed in Table 1. Contents of dolomite and organic matters in Table 1 were estimated by CaO and carbon contents. The dolomite contents shown in the table agree well with the results of quantitative analyses of carbonate. Atom ratios in sepiolite, shown in Table 2, were calculated by using the results of chemical analyses with correction of a contribution of dolomite. The ratio in sepiolite from white agrees well with the ideal ratio based on the Brauner and Preisinger model (1956). The ratio of Si in sepiolite from brown part, however, is greater than the ideal one, which is supposed to be due to the quartz or amorphous silica in the brown part.

The XRD results showed that the sepiolite from this deposit is poorly crystallized. Mean diameter and length of the sepiolite fiber were estimated to be about 10 nm and 0.5 μm respectively by TEM. Quartz and dolomite were also detected by XRD. Yellow and light green inclusions were found in the brown part. The former was pure sulfur and the latter was palygorskite.

The result of evolved gas analysis by TG/FT-IR is shown in Figure 1, which indicates that weight losses due to dehydration occurred in four steps accompanied by those due to decompositions of organic matters and dolomite. The extracted matters from brown samples were confirmed to be humic acid by IR. Differences in IR spectra from that of usual humic acid, however, also observed.

This deposit should be one of the most important sources of sepiolite in the world for industrial uses such as adsorbents, catalysis or rheological applications.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Y. Turan, president of Turan Madencilik Sanay Ticaret Ltd., and Mr. Toyomasu and T. Hirakawa, Toyoda Tsusho Kaishya Co. Ltd., for their cooperations and helpful suggestions. Discussions with Dr. O. Kamigaito and Mr. M. Sugiura were also helpful in this work.

REFERENCES

- Turan, Y. (1975) Proc. 1st Ind. Miner. Int. Congr., ed by Fleming, R.F.S., Met. Bull. Ltd., London: pp206-9
- Brauner, K. and Preisinger, A. (1956) *Teschermaks Min. Petr. Mitt.* **6**, 120-140.

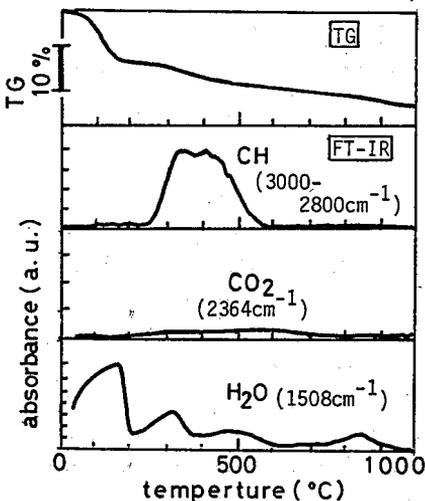


Figure 1. Results of TG/FT-IR



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ADSORPTION OF METHYLCARBAMATE BY MONTMORILLONITE

P. FUSI^{*}, M. FRANCI^{**} and G.G. RISTORI^{**}

^{*}Dipartimento Scienza del Suolo e Nutrizione della Pianta, Università di Firenze. ^{**}Centro Studio Colloidi Suolo-CNR-Firenze. Piazzale Cascine, 28, 50142 Firenze (Italy).

The carbamates (i.e. N-aryl, N-alkyl, ester derivatives of carbamic acid) are used in the agriculture management, because they have insecticide or herbicide properties. Moreover the pesticide adsorption by soil colloids is one of the major processes affecting their phytotoxicity.

Therefore the studies of the interaction between a simple carbamate molecule (i.e. $H_2N-CO-OCH_3$, methylcarbamate) and soil clay minerals can supply an useful model for understanding the adsorption mechanism which could be involved in the adsorption of more complex compounds of this family.

In this study the interactions of homoionic montmorillonite with methylcarbamate have been investigated. Montmorillonite, Upton Wyoming, was made homoionic to Na, Mg, Cu and Al by treating the $< 2 \mu m$ fraction with 1N solution of the corresponding chloride salt and then removing the excess salt by dialysis until the $AgNO_3$ test for Cl^- was negative. Thin, self supporting films (4 mg clay/cm^2) of the homoionic montmorillonite were prepared by allowing to air-dry few milliliters of a clay suspension on a polyethylene sheet and then carefully peeling away the clay film.

The mechanism of adsorption was investigated by infrared and X-ray diffraction analysis. The clay films were immersed in a CCl_4 saturated solution of purified methylcarbamate (m.p. = $52-53^\circ C$) for about 30 seconds. This time was enough to lead large amount of methylcarbamate to be

adsorbed by the montmorillonite. After a clay film was removed from the solution it was rinsed twice in solvent and air dried. The IR spectra were recorded in the 4000-1200 cm^{-1} region. The assignment of main bands of pure methylcarbamate in a CCl_4 solution was the following: 3550 and 3435 cm^{-1} (asym. and sym. $-\text{NH}_2$ stretching); 1750 cm^{-1} ($\text{C}=\text{O}$ stretching - amide I band); 1583 cm^{-1} (NH_2 bending - amide II band); 1460 cm^{-1} (CH_3 asym. deformation); 1345 cm^{-1} (CN stretching - amide III band).

The IR spectra of Na- and Mg-montmorillonite complexes showed a shift to lower frequencies (1710 and 1700 cm^{-1} respectively) of the $\text{C}=\text{O}$ stretching vibration. This was ascribed to a coordination of carbonyl group to the exchangeable cation. As a consequence of $\text{C}=\text{O}$ coordination, the double bond character of the CN group increases as confirmed by the shift of the CN stretching band to higher frequencies (from 1345 to 1370-1380 cm^{-1} respectively).

On Al-montmorillonite complex, the $\text{C}=\text{O}$ and the $\text{C}-\text{N}$ stretching band was at 1683 and 1385 cm^{-1} respectively, as a consequence of a stronger coordination with Al in comparison with Na and Mg cations. No evidence for $\text{C}=\text{O}$ protonation, as observed for acetamide, was revealed in the IR spectrum of this Al-clay complex. This different behaviour can be ascribed to the fact that in methylcarbamate the carbonyl bond is less polar than in amide as the π delocalization involves the ester oxygen atom as well as the OCN amide group.

Different characteristics are shown by the IR spectrum of Cu-montmorillonite complex: two new bands appear at 1480 and 1400 cm^{-1} (tentatively assigned to CH_3 deformation and CN stretching vibration respectively). On the other hand the $\text{C}=\text{O}$ stretching band at 1675 cm^{-1} , the CH_3 deformation at 1463 cm^{-1} and the CN stretching at 1385 cm^{-1} (shifted from the corresponding value of the free molecule) are yet well evidenced. These particular features can result from two different adsorption mechanisms of

methylcarbamate molecule, i.e. : by coordination of the carbonyl group only or by simultaneous coordination of both the carbonyl and the oxygen atom of the ester group.

In Na-, Mg-, Al- and Cu- clay complexes the asym. and sym. NH_2 stretching are shifted from 3550 to 3500 and from 3435 to 3400 cm^{-1} . This shift suggests an interaction between NH_2 group and the oxygen of the silicate layer.

The homoionic montmorillonite-methylcarbamate complexes were stable on heating at 80°C (12 hours) , and the adsorbed molecule decomposes to NH_3 , CO_2 and CH_3OH on equilibration of the complexes at 100% R.H. (12 hours).

X-ray diffraction analysis showed that methylcarbamate penetrates the interlayer space of homoionic montmorillonites.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS OF DEVONIAN AL-SHALES OF BADAJOZ, SW SPAIN.

E. GALAN, J.M. MESA, J.L. PEREZ RODRIGUEZ* and A. POLVORINOS.

Departamento de Geología. Universidad de Sevilla. (España).

*Centro de Recursos Naturales y Agrobiología. Sevilla. (España).

Al-clayey shales mainly composed of muscovite \pm pyrophyllite \pm kaolinite \pm quartz outcrop largely in the S and SW Iberian Massif, that is a segment of the Western European Hercynian Ranges. These colourless materials were used in Spain to whitewash homes for hundreds of years, especially in the Province of Badajoz, where they are popularly known as "Tierras blancas" (White earths). Also it has been used as carrier for insecticides and pesticides. Recent research has demonstrated the material's usefulness in the production of different porcelain types, Al-chamotte, refractories, etc., because it results in a great saving of energy. It is also useful as a substitute for kaolin, feldspar and clay (Espinosa de los Monteros et al., 1973, 1978).

From the geological, mineralogical and chemical study of twelve Al-shales deposits of the Province of Badajoz (Fig. 1), the following general characteristics can be outlined (Mesa, 1986).

1.- Al-shales are usually very altered and superficially they are white and very fine grained. They form part of detrital shaly series, without any stratigraphic unconformity with the other shales. Generally they are Middle-Upper Devonian, and have been affected by the regional Hercynian tectonism.

2.- Mineralogical and chemical compositions vary within a wide range. Muscovite (sericite) is the only mineral always present in these shales, also named "sericitic shales". Muscovite shows a 2M, polytype, a I_{004}/I_{002} ratio of 0.4 - 0.6, and a Kubler Index between 0.4 - 0.6 (≈ 29). Pyrophyllite can be the major component, but many times is absent. Kaolinite is usually not well ordered and of small particle size. Transformations of muscovite and pyrophyllite to kaolinite, and feldspar to kaolinite have been tested using SEM with

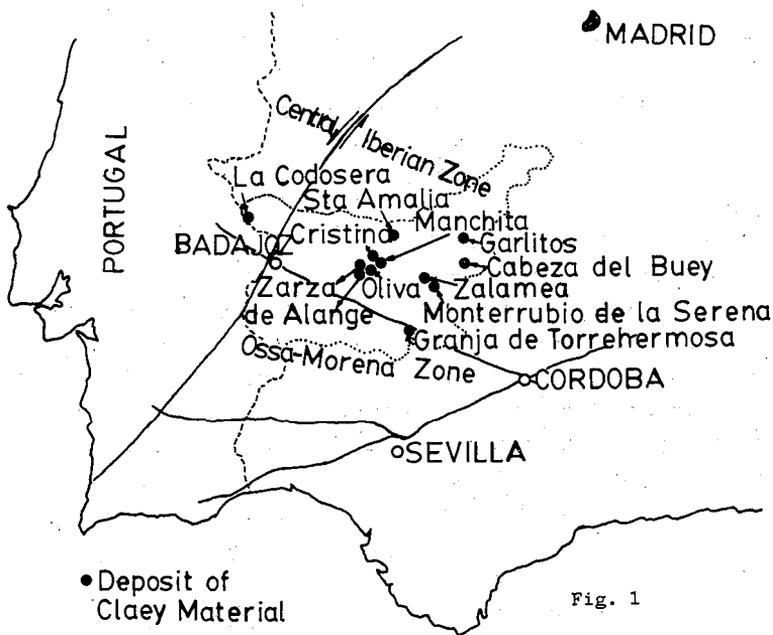


Fig. 1

an EDAX system. Minor components include feldspar, rectorite, rutile, goethite, alunite and pyrite.

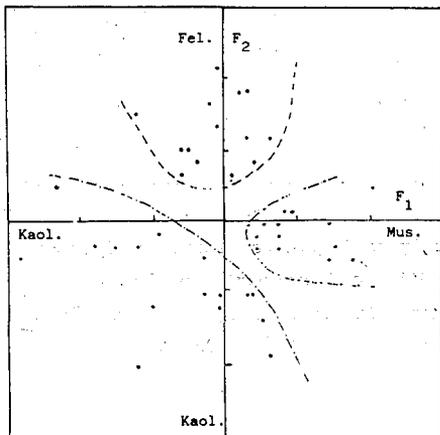


Fig. 2

3.- Particles of less than 20 μm represent in general more than 80 % of the sample, and fractions smaller than 2 μm less than 10 %. The Al_2O_3 percentage can be as high as 35 %, K_2O oscillates between 2 and 10 % and the percentages of CaO and MgO are very low.

A statistical study of the chemical and mineralogical data from both aluminic and country (regional) shales has been carried out using principle

components analysis of the 10 most representative variables (those with lowest variation coefficients). Four orthogonal factors accounted for 75 % of the variance, which can be expressed as follows:

F₁ (muscovite --- kaolinite, quartz);

F₂ (feldspar, Fe₂O₃ --- kaolinite);

F₃ (pyrophyllite, Al₂O₃ --- quartz, MgO);

F₄ (muscovite, K₂O --- kaolinite)

Factor score representations of F₁ vs F₂ (Fig. 2) and F₃ vs F₄ (Fig. 3) delineated different compositional domains that mainly characterized the population of pyrophyllitic shales. In these populations a new factor analysis led to identify four others factors with 90.6 % of cumulated variance. These factors repeat the above chemical and mineralogical relationships, but also suggest the transformation of pyrophyllite into kaolinite according to the relation:

F₄' (pyrophyllite, total silica --- quartz, kaolinite)

According to the geological survey carried out and considering the results of the statistical analysis, parent material for these shales is thought to be of volcanic-sedimentary origin, which was deposited during Devonian times in an euxinic marine environment. A very low grade metamorphism accomplished the formation of pyrophyllite from muscovite, according to P and T condi-

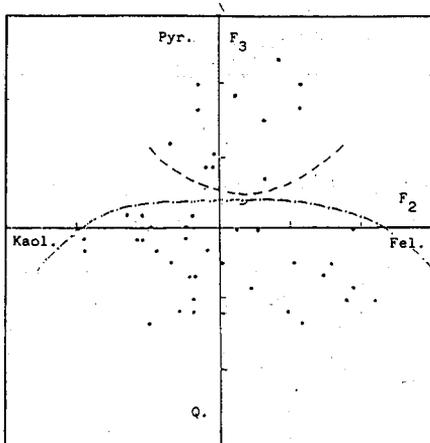


Fig. 3

tions and available silica. Apparently kaolinite was formed much later by the weathering of feldspar, muscovite and pyrophyllite (Factors F₁, F₂, F₄, and F₄'). At the same time, interstratified clay minerals (high crystallinity rectorite) from mica, and alunite and goethite from pyrite were also formed.

REFERENCES

ESPINOSA DE LOS MONTEROS, J., ALVAREZ, D. DURAN, P. y AZA, S. (1973). In Clay Mineralogy and Ceramic Processes and Products. AIPEA. Bologna. 243-249.

ESPINOSA DE LOS MONTEROS, J., ALVAREZ, D., MORALES, F. y DEL RIO, M. A. (1978). Bol. Soc. Esp. Ceram. Vidr. 17, 73-78.

MESA, J. M. (1986). Contribución al estudio mineralógico de las Pizarras Aluminicas del Paleozóico de la provincia de Badajoz. Tesis Doctoral. Universidad de Sevilla. 318 pp.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GLAUCONITE FROM THE GUADALQUIVIR BASIN, SOUTHERN SPAIN. CHARACTERIZATION AND ORIGIN.

E. GALAN, I. GONZALEZ AND E. MAYORAL

Department of Geology, Faculty of Chemistry, University of Seville, Spain.

INTRODUCTION

Since early this century glauconite occurrences in tertiary materials of the Guadalquivir Basin (Southern Spain) are known (Paul 1902, Hernandez Pacheco 1926). According to recent studies glauconite is stratigraphically concentrated in two levels, one lower (Miocene) at the boundary between a detrital-carbonate formation (Niebla calcarenites formation) and the "Blue Clays" (Martinez del Olmo 1984; Sierro 1984; Civis et al. 1985), and another higher (Pliocene) at the transition between the Blue Clays and the Huelva sands formation (Viguiet 1974, Sierro 1984, Mayoral 1986). Nevertheless at present there is no mineralogical and genetical study of these glauconitic levels. This paper accounts for these aspects and for the interest of the glauconite formation at a large scale in the paleogeographic evolution of the Guadalquivir basin.

MATERIALS

Glauconite was sampled near Aznalcollar (lower level) and Bonares (higher level) (Fig. 1). At a regional scale three units can be defined. The lowest is mainly composed of calcarenites which are very rich in organic remains. The uppermost part of this unit is a glauconite sand bed (2-4 m thick) (see Aznalcollar section). The middle unit is built up of blue clays and marls which thickness ranges between 60 and more than 1000 m. Macrofauna and bioturbation are scarce in this unit. The highest unit (Huelva sands formation), is composed of yellowish-brown silty-sands at the base, which become increasingly coarse upwards. This unit present an increase of glauconite from bottom to the centre part, where it is highly concentrated (higher glauconitic level, see Bonares section). Glauconite is always associated to very deeply bioturbated materials which are very rich in fauna (Venerides, Pectinides, marin vertebrate remains, etc).

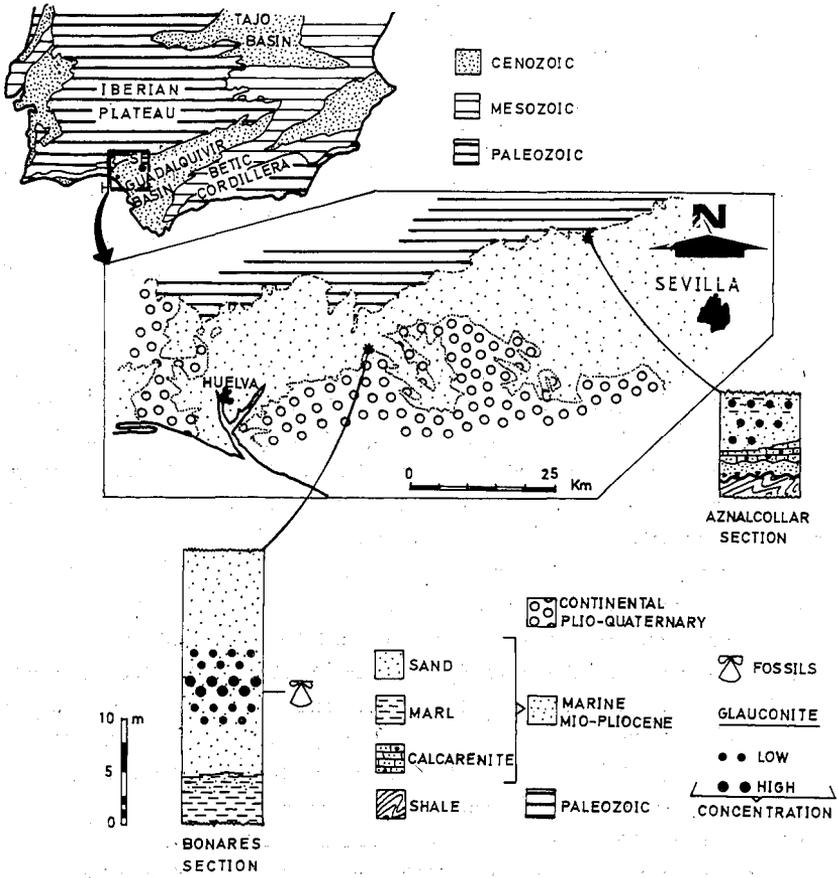


Fig.1.- Geological setting and location of the sections studied

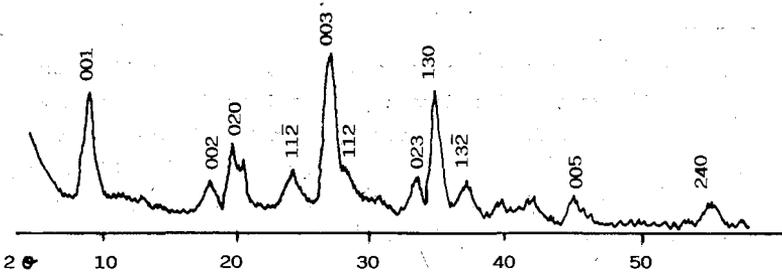


Fig.2.- X-ray diffraction pattern of 1Md glauconite

RESULTS

Glauconitic sandy materials described above are composed of quartz, calcite, dolomite, feldspars and phyllosilicates. The clay mineralogy for the less than 20 μm fraction is mainly composed of smectite and illite and minor amounts of chlorite and kaolinite.

For the glauconite identification, a fractionation and concentration of glauconitic materials were made as follows, first the sand was screened and each fraction was dried and weighed and examined under a stereo-microscope. For the 250-125 μm and 125-63 μm fractions, the richest in glauconite granules, were treated with a Frantz magnetic separator. A final concentration of green grains was carried out by hand - picking from the most paramagnetic fraction, and then they were cleaned by ultrasonics.

Selected grains were studied by X-ray diffraction, examined by scanning electron microscope, and analyzed by EDAX. Exposed impregnated thin sections allowed examination of internal structures of grains.

Two types of glauconite grains were possible to distinguish according to their colour: dark green grains and pale-green ones. Regarding their morphology green grains may be classified in lobate (botryoidal), irregular and ovoidal pellets. The two first are more abundant in Aznalcollar sands, while latter are in Bonares. Pellets from Aznalcollar are usually lesser than those from Bonares. X-ray diffraction patterns (Fig.2) show that glauconite is rather an intermediate structure between 1M and 1Md, with only 5-15% of expandable layers. Fe and K contents are higher in the darkest green pellets, which are very abundant in Bonares.

Oriented or random microcrystalline aggregates of glauconite of different particle size coat and/or substitute foraminiferal surfaces, quartz grains, iron oxides, etc.

DISCUSSION

Different glauconitization degrees of organic remains (foraminifera, ostracods, bryozoans, echinoderms, etc) have been observed in both glauconitic materials. In Aznalcollar many glauconite pellets are coated mineral grains, probably because this area is very rich of detrital supplies which came from the close source area (see Fig. 1). The glauconitization process is generally very evolved.

Environmental conditions for this sector of the Guadalquivir Basin during sedimentation of glauconite materials, as deduced from paleontological and sedimentological data, suppose that the glauconitic pellets should be formed in a open-sea sublittoral environment, at around 30-50 m deep. In this environment there was a very low sedimentation rate, which is reasonably supported by abundant bioturbation observed. Illite and smectites, the major clay minerals of these sandy materials, in a locally restricted environment, with not very oxygenated bottom waters (caused by organic matter degradation), could coat fecal pellets and/or mineral grains, and evolved to glauconite through a mixed-layering structure of-illite-smectite type. Shrinkage of this envelopment could deform pellet grain surface and contribute to its cracking, resulting in different glauconite morphologies.

Glauconite pellets from Bonares are bigger and more subrounded than those from Aznalcollar. These differences can be explained on the basis of that the size of original pellets was bigger in Bonares, as well because the evolution degree of the glauconitization process was also more evolved than in the Aznalcollar case.

All these data support that during the Tertiary sedimentation occurred in this basin there were two transgressive pulsations, which took place during Late Miocene, and Lower Pliocene, respectively.

REFERENCES

- CIVIS, J., SIERRA, F.J., GONZALEZ DELGADO, J.A., FLORES, J.A., ANDRES, J. PORTA, J. & VALLE, M.F. (1985) *Studia Geologica Salmaticensia*. Vol. Especial. (in press).
- HERNANDEZ PACHECO, E. (1926) XIV International Geological Congress. IGME 1-150.
- MARTINEZ DEL OLMO, W., GARCIA MALLO, J., LERET, G., SERRANO, A., & SUAREZ, ALBA, J. (1984) I Congreso Español de Geología, 1, 199-213.
- MAYORAL, E. (1986) Ph. D. Thesis. University of Seville, 599 pp.
- PAUL, A. (1902) *Bol. R. Soc. Esp. Hist. Nat.* 2, 94.
- SIERRA, F.J. (1984) Ph. D. Thesis. University of Salamanca, 391 pp
- VIGUIER, C. (1974) Ph. D. Thesis. University of Bordeaux, 450 pp.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**THE SEDIMENTATION ENVIRONMENT OF THE DIATOMITIC MARLY FACIES AT
SANLUCAR DE BARRAMEDA, GUADALQUIVIR BASIN, SW SPAIN.**

E. GALAN, I. GONZALEZ, E. MAYORAL, A. MIRAS AND M.A. VAZQUEZ.

Department of Geology, Faculty of Chemistry, University of Seville,
Spain.

INTRODUCTION

Occurrences of diatomaceous silica is widespread throughout the Oligocene-Miocene sedimentation of the Guadalquivir Basin (Fig. 1) (Chauve 1968, Calvo Sorando, 1981). No general survey of these diatomaceous materials has been carried out up-to-date, in order to clarify such questions as their environmental conditions of sedimentation, mineralogy, technical properties, etc. This paper accounts for some of these genetical aspects in Sanlucar de Barrameda, SW Spain, a selected area where the characteristic diatomitic facies of the Guadalquivir Basin is very well represented.

RESULTS

Materials studied in Sanlucar (Fig. 1) are white, grey, or yellowish foliaceous-like marls, which contain diatoms, radiolaria, foraminifera, silicoflagellates, sponge-spicules, etc. Some levels of 1.5 m thick, mainly contain diatoms, and they are regionally known as "moronitas" (Calderón & Paul 1886). These deposits are thought to be Late Tortonian (Pliego & Babiano, 1982).

Marls are mineralogically composed of quartz (<10%), calcite (20-55%), and phyllosilicates (10-50%), with minor opal, feldspars and dolomite. Diatomite materials contain up to 80% opal, calcite (<20%) and clay minerals (5-20%). Opal A and opal C-T have been detected by XRD, but both are not present at the same time.

Smectites (60-80%), illite (15-30%) and chlorite-kaolinite (10-15%) are the clay minerals in the <2 μ m fraction. Smectites are of the beidellite-montmorillonite type, with a Biscaye Index of 0.8.

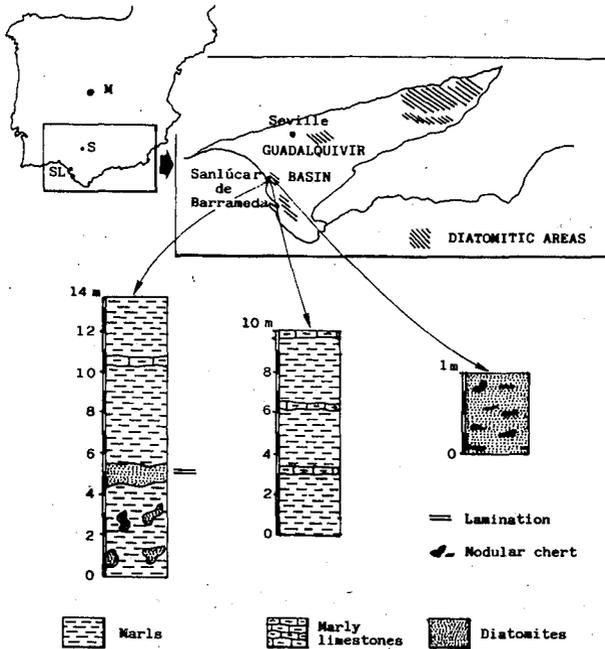


Fig. 1 Location of sections studied.

According to their particle-size distribution these sediments may be considered as silty clays or clayey silts. The colour of diatomitic materials is highly dependent on Fe-content. Brightness may varie between 52 and 75%.

The "moronic" facies described above, presents well-preserved pennal and centric diatoms, calcareous nanoplankton, radiolaria, sponge-spicules and foraminifera remains (Fig. 2). These associations led to considerer it as a radiolitic or spongiolitic diatomitic-facies rather than only diatomitic. Only some beds which are very rich in diatomaceous silica could be named diatomites.

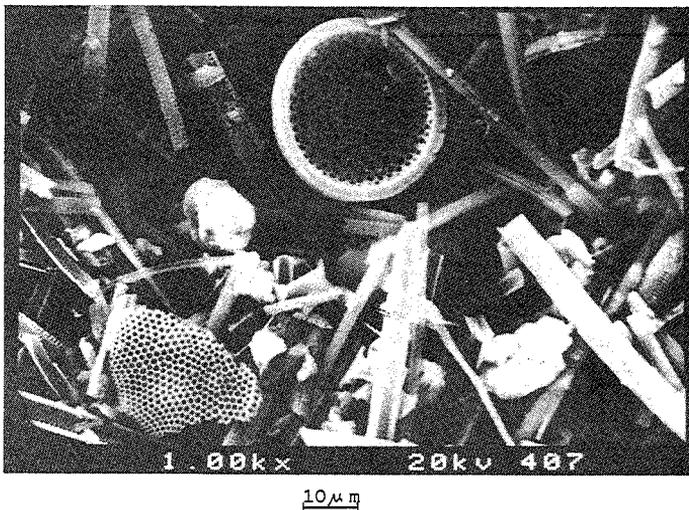


Fig. 2 Scanning electron micrograph of a typical association of organic siliceous remains of "moronita".

DISCUSSION

The described microfauna and microflora associations together with the absence of detrital minerals, other than typical clay minerals of open-marine environment, may support that sedimentation of the "moronitic" facies took place in a rather shallow marine basin (200-300 m) under stable warm or temperate conditions, and in calm and clear waters. Also the presence of removed remains suggests the possibility that shallow or deeper marine waters very rich in plankton were supplied to the basin during this sedimentary period from the Atlantic ocean.

The presence of opal-A and C-T, and of the high porosity material, and the absence of interstratified illite-smectite seem to indicate that sediments have only undergone an early diagenesis. The transformation of opal A into opal C-T was probably by dissolution of siliceous microfossils and later by silica precipitation as disordered cristobalite (opal C-T).

REFERENCES

- CALDERON, S. & PAUL, M. (1886). La moronita y los yacimientos diatomáceos de Morón. An. R. Soc. Esp. Hist. Nat. 15, 477-493.
- CALVO SORANDO, J.P. (1981). Los yacimientos de diatomitas en España. Bol. I.G.M.E., 92, 274-284.
- CHAUVE, P. (1968). Etude Geologique du Nord de la Province de Cadix. Memorias del I.G.M.E., 69.
- PLIEGO, D. & BABIANO, F. (1982). Las diatomitas en España. Tecniterrae, S-304, 47-52.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ASSESSMENT OF TALCS AND KAOLINS FOR TOPIC USE IN POWDERS

**E. GAMIZ MARTIN; G. DELGADO CALVO-FLORES; J. PARRAGA MARTINEZ y
R. DELGADO CALVO-FLORES**

Dpto. de Geología Aplicada. Facultad de Farmacia. Universidad de Granada.

INTRODUCTION

Talc and Kaolin are frequently used in pharmacy as therapeutic formulations, carriers or excipient in general; in the same way they are extensively used in cosmetics. In topical uses (external) these materials, which are from mineral sources, find their applications mainly in the form of powders, and are the basis of the preparations (1,5,7). The general requirements demanded by the Pharmacopoeias (2,3,8) to these materials, are not specific for the topic use in powders, and they are unaware of important characters (e. hardness, form of the particle, colour, etc.). Therefore, in this paper a method of valoration, which considers all characteristics, is proposed.

METHODOLOGY

To explain briefly, the method consists of the establishment and the numerical assessment of factors (important features), the making up of an equation and the calculation of a numerical index. The elaborated method is applied to six kaolins and two Spanish talcs (Table II) which have been studied by Gámiz Martín (4) in their mineralogical aspects and as raw material in pharmacy and cosmetics.

Factors

The factor purity collects the content of talc and kaolin (abundance) and the presence of undesirable minerals (toxics, cancerigenics, etc.). The value is assessed by X.R.D. semiquantitative mineralogical analysis.

The hardness factor reflects the medium hardness of a sample in the Mohs scale. It controls the possibilities of scratching the skin, or

physical abrasivity. The hardness of 2 has been assigned to kaolin (1 or 2 to 2'5 in the bibliography).

Colour affects visual acceptance and it is an indirect index of purity. The colour must be white and this is estimated with the Munsell charts.

The chemistry factor includes all the physical and the physicochemical characters which are demanded by the Pharmacopoeias (Calcium, heavy metals, chlorides, power of adsorption, etc.).

The granulometric factor considers the characteristics and the limitations which depend on the particle size, (qualities of surface, physical abrasivity, etc.). It is valued by the granulometrical analysis with the Robinson pipette and by the measurements of the silt and clay particle sizes with the scan electron micrography. As the Pharmacopoeias says, a powder of light kaolin must have more than 70% of clay and less than 0'5% of a bigger fraction of 15 microns, these requirements have been extended to heavy kaolin and to talc.

The morphologic factor represents the limitations related to the shape and the roundness of esteemed particles with S.E.M. In order to evaluate it, it has been assigned a numerical value which oscillates from 0 (elongated-angular) to 1 (plated-rounded).

Equation and numerical index

The equation is composed of letters and coefficients which express the assessment of each factor (Table I). The values can be easily modified (granulometric and shape) are represented by small letters. In the case of insuitability, the coefficient for any factor is 0. The numerical index goes from 0 to 100 and it is calculated by multiplying the coefficients of the equation.

RESULTS AND DISCUSSION (Table II)

The equation for the topical use powders is variable from some samples to others. All of them have the term t_0 , however it is not very important because the texture is modifiable and can be established employing previous treatments for the materials employed in pharmacy (grinding, peptonize, etc.) (6).

The samples with H., present high contents of quartz. The ones which are Ch. don't fulfil the adsorptive properties and the contents of chlorides and calcium. The dominating forms are in all the cases flat-subrounded followed by elongated-subrounded. The result of the numerical index is 0 in all the cases. The information given by the equation has a comparative value. As a result, we are dealing with an indirect method. It is not based on real data of the effect of each factor in the topical application of a powder, which doesn't exist in the bibliography. However, the equations themselves possess big and discriminate value between the samples.

To conclude, the proposed method could be very useful for the assessment of raw material, from mineral sources, for their employment in the pharmaceutical industry, or moreover the departure point of subsequent investigations in the fields of Pharmacy and Medicine with the objective of the appreciation in real terms of all the characteristics which have been analyzed.

BIBLIOGRAPHY

- 1.- BONADEO, I. (1963). Tratado de Cosmética Moderna. Ed. Científica Médica. Barcelona, 538 pp.
- 2.- BRITISH PHARMACOPOEIA (1980). Publ. Recom. Med. Comm. Med. Act. 1968. Vol I. 516 pp.
- 3.- FARMACOPEA OFICIAL ESPAÑOLA (1954). 9ª Ed. Vol I. Real Acad. Med. 764 p.
- 4.- GAMIZ MARTIN, E. (1987). Tesis Doctoral. Univ. Granada. En preparación.
- 5.- MARTINDALE (1982). The extra Pharmacopoeia. Pharm. Press. London. 2027 pp.
- 6.- OSOL, A.; PRATT, R. (1973). The U.S. Dispensatory. 27 th Ed. Lippincott Co. Phil. 1139 pp.
- 7.- QUIROGA, M.L.; GUILLOT, C.F. (1981). Cosmética dermatológica práctica. 4ª Ed. El Ateneo. Buenos Aires 386 pp.
- 8.- U.S. PHARMACOPOEIA (1980). Authority of the U.S. Pharm. Conv. Inc. Washington. 824 pp.

Table I.- Valorization of the factors.

Purity factor	Abundance Coef.	% Kaolin or Talc		Chemical factor	Chemical Coef.	Pharmacopoeia restraints	
	10 - 8	100 - 80			1	None	
0	< 80			0	One or several		
Purity factor	Impurities Coef.	Non desirable minerals(%)		Granulometric factor	Granulometric Coef.	Clay (%)	Silt (%)
	1	≤ 5			10 - 7	100 - 70	< 0,5
	0	> 5			0	-	≥ 0,5
Hardness factor	Hardness Coef.	1/Mean hardness			0	< 70	-
	1 - 0,33	≥ 0,33			Granulometric modifiers	Mean size (μ)	
	0	< 0,33				Clay	Silt
Colour factor	Colour Coef.	Value	Chroma	1	0-1	2-11	
	0	≥ 8	≤ 1	0,95	> 1-2	> 11-20	
Colour factor	1	< 8	> 1	Morphological factor	Morphological Coef.	Shape and roundness index	
					1 - 0,5	1 - 0,5	
					0	< 0,5	

Table II.- Location of samples. Equations and index for the topic use in powders.

SAMPLE	LOCATION	EQUATION	NUMERICAL INDEX
K-1 (light)	Arguisuelas (Cuenca)	$P_{8,3-1}, H_{0,36}, C_1, Ch_1, t_{0(1-1)}, s_{0,6}$	0
K-3 (heavy)	Cervo (Lugo)	$P_{0-1}, H_0, C_0, Ch_1, t_{0(1-1)}, s_{0,6}$	0
K-4 (light)	La Guardia (Pontevedra)	$P_{0-1}, H_0, C_1, Ch_1, t_{0(1-1)}, s_{0,7}$	0
K-5 (heavy)	Oviedo (Asturias)	$P_{0-1}, H_{0,37}, C_1, Ch_0, t_{0(0,95-1)}, s_{0,6}$	0
K-6-A (light)	Burela (Lugo)	$P_{8,7-1}, H_{0,40}, C_1, Ch_0, t_{0(1-1)}, s_{0,7}$	0
K-6-B (light)	Burela (Lugo)	$P_{8,0-1}, H_{0,37}, C_1, Ch_1, t_{0(1-1)}, s_{0,7}$	0
T-2 (grinded)	León	$P_{9,7-1}, H_{0,90}, C_1, Ch_0, t_{0(0,95-1)}, s_{0,6}$	0
T-4 (grinded)	León	$P_{9,5-1}, H_{0,88}, C_1, Ch_0, t_{0(0,95-1)}, s_{0,6}$	0



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ORE-DEPOSITS STUDY AND PROSPECTING OF KAOLIN DEPOSITS IN WESTERN-CENTRAL SARDINIA. MINERAL-PETROGRAPHIC AND ORE DEPOSIT CHARACTERISTIC OF KAOLIN AND ITS RELATIONS WITH TERTIARY ACID VOLCANISM.

C. GARRBARINO⁺, G. PADALINO⁺, M. PALOMBA⁺⁺, I. URAS⁺

+ Istituto di Giacimenti Minerari, Facoltà di Ingegneria, Università di Cagliari (Italia).

++ Centro Studi Geominerari e Mineralurgici del C.N.R., Facoltà di Ingegneria, Università di Cagliari (Italia).

In the western-central area of Sardinia (Tresnuraghes) are to be found some outcrops of kaolin in volcanic rocks, mainly of rhyolitic type of Oligo-miocenic age.

The mineral-petrographic study of the volcanites made it possible to divide them into two facies, the first characterized by a marked pseudo-fluid texture with the matrix more or less kaolinized, the second by spherulitic structure ("piromeridi") of cristobalitic-kaolinitic composition.

The most evident presence of kaolin seems to be localized principally in the inferior rhyolites, with pseudo-fluid texture, and this presence increases gradually from fresh volcanic rock to completely kaolinised one.

In order to carry out a comprehensive study of the various source-rock-kaolin transformation, a systematic sampling by a square grid of an area of 5 Km² (250 m per side) was carried out. A further more detailed sampling was carried out on the quarry-faces using a rectangular grid measuring 3 m per side horizontally and 2 m vertically. The total of 32 samples taken from the two quarries (Punta Salamura e Su Fongarazzu) made it possible to obtain the grade variations and a rough economic evaluation of the deposits.

All the samples were subjected in particular to a series of diffractometric, differential thermal and X-quantitative spectrometric analyses. Some samples were studied by electron microprobe in order to better define the alteration processes ^{that} influence on the crystals, on the matrix as well as on the structures.

On the basis of all studies carried through it was possible to:

- classify the volcanic rocks according to their chemical composition, by De La Roche's diagram (1980), into rhyolites and dacites, the former notably greater in number than the latter;
- determine the variation of grades in Al_2O_3 and in normative kaolinite in the kaolin samples;
- suggest a possible genetic model for the kaolin mineralization in this area;
- pinpoint the correlation between the volcanic facies, the structural characteristic of the examined area and mineralization, which can be used as a guide in the prospecting of ore deposits in terms of size and quality.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE RHYOLITES OF TRESNURAGHES (NORTH-WEST SARDINIA) AND THEIR KAOLIN MINERALIZATION: MICROPROBE STUDY OF ALTERATION PROCESSES AT MICROSCOPIC SCALE.

C. Garbarino⁺, M. Palomba⁺⁺

+ Istituto di Giacimenti Minerari, Facoltà di Ingegneria, Università di Cagliari (Italia).

++ Centro Studi Geominerari e Mineralurgici del C.N.R., Facoltà di Ingegneria, Università di Cagliari (Italia).

In the immediate south-western area of Tresnuraghes (North-western Sardinia) a rhyolitic volcanic formation of oligo-miocenic tertiary age outcrops, which is affected by kaolinization phenomena. On the basis of micro- and macroscopic characteristics it was divided into two facies:

- the first is composed of mostly pink rocks, with lighter, whitish striations, characterized by a pseudofluid texture;

- the second shows the typical "piromeridi", spherulitic structures, the origin of which is attributed to the volcanite devitrification phenomena.

The aim of the present work is to study, by means of an electron microprobe, the chemical composition of the rocks and in particular to study how and to what extent the alteration processes operate on minerals, on the structures and on the matrix. The square grid systematic sampling, using 250 m sides, made on the above mentioned area, provided a series of volcanite samples, 22 of which to be analysed at the microprobe were chosen. These observations were made on over 700 points of analysis which allowed us to define the chemical composition, the type and the development modes of alteration in the phenocrysts, in the matrix and in the structures that characterize these rocks. The results, from the data processing of the microprobe analysis obtained,

show that:

- the matrix shows colour variations from white to rosy-white to red; a compositional and probably structural variation corresponds with them. The white zones seem to have suffered from a devitrification and a consequent recrystallization. Furthermore in these parts of the rock, the first "germs" of the alteration into kaolinite appear. Instead, the red matrix has a constant and homogeneous chemical composition, it is vitreous and it does not appear to be affected by any alteration phenomena.

- The structures, in this case spherulitic ("piromeridi"), resulting from radial accretion (of cristobalitic-kaolinitic composition) which originates around a crystalline germinal core, vary from microscopic size to 5-6 mm in diameter. Compared to the matrix, these structures show a greater tendency to alteration, which begins with the weathering of the alkaline and alkaline-earth elements. It was also noticed that the alteration starts in the core of the structures and has a centrifugal trend.

- The phenocrysts of these rocks are almost exclusively plagioclases; immediate chemical analyses allowed us to determine their composition and homogeneity, in each individual sample and in the samples as a whole. From the observation of all the analyses we conclude that also the plagioclases alteration into kaolinite always occurs in a centrifugal trend.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**SOME SPANISH TERRA ROSSA:
GEOCHEMISTRY AND MINERALOGY OF THE CLAY FRACTION**
M.T. GARCIA-GONZALEZ and P. RECIO

Instituto de Edafología y Biología Vegetal, CSIC, Serrano 115 dup.,
28006- Madrid, Spain.

The object of this study is the mineralogical composition of the clay fraction of two profiles of Spanish terra rossa and its relation with the distribution of the concentrations of different trace elements.

The profiles lie in the central area of the Iberian peninsula, in the spurs of the sierra of la Calderina, which is part of an old rock formation of the mountains of Toledo which were formed during the hercynian orogenesis that took place from the carboniferous to the permian periods and affects the western half of the peninsula, producing tectonic alignments from NW to SE.

The profiles are approximately 160 cm thick and come directly to rest on the underlying limestone rock. Profile I consists of a development A1, B1, Bt21, Bt22, R. The development of profile II is A1, B+A, Bt21, Bt22, R. They have been classified as Mollic Palexeralf (profile I) and as intergrade Ultic Palexeralf-Ultic Rhodoxeralf (profile II). The pH of both is close to neutral, while the cation exchange capacity is relatively low with calcium being the basic exchange cation.

The mineralogical study of the clay fraction, after its separation was performed using X-ray diffraction, thermal methods and infrared spectroscopy. Quantitative determinations of the major, minor and trace elements (Cr, Co, Ni, Cu, Zn, Rb, Sr, Zr, Ba and Pb) was carried out using X-ray fluorescence spectrometry.

The study of the rocky substrat includes the mineralogical investigation of the limestone rocks at the base of both profiles.

Calcite is a major component, ~75% in profile I, ~70% in profile II. There is also a small amount of dolomite, ~10% profile I, ~12% profile II. Mica minerals, quartz and, in profile I, vermiculite have been detected in the insoluble limestone residues. The mineralogical aspect is completed with traces of feldspars, kaolinite and hematite.

The data from the mineralogical analysis and the concentrations of the different oxides determined in the clay fraction of the profiles show a decreasing mica content from the horizons A1 (around 60%) to those of Bt22 (55% in profile I and 45% in profile II) while there is a slight increase of kaolin minerals in the proportion of about 25-30% (horizon A1) and 30-40% (horizon Bt22) in profiles I and II respectively.

The absence of vermiculite in the clay fraction of profile I, is at variance with its existence in the limestone substratum. It appears therefore that this mineral has not been inherited by the horizons of the profiles, which is why the soil formation was accompanied by only a small alteration of the mica and kaolinite in the rock.

Among the iron crystalline compounds goethite stands out because of its importance, its proportion in profile I being less than 5% in horizon A1 and less than 15% in Bt22. In profile II there is less than 10% of it in the two deep horizons. In the latter profile has been pointed out the presence of small amounts of hematite in horizons Bt21 and Bt22.

It is to remark the high proportion of MnO in both profiles, however, these figures are supported by field operations in which black manganese spots were observed in some of the horizons of the soils.

No dependence at all has been observed between the concentrations of Fe_2O_3 and that of the different trace elements, although there are plenty of studies supporting that the crystalline or amorphous iron compounds are capable of housing elements (Schwertmann and Taylor, 1977; Koons et al., 1980). This apparent anomaly can be explained as resulting from the competition between Fe and Mn for the retention of trace elements. In accordance with Suarez and Langmuir (1976), Loneragan et al. (1981), the retention capacity of MnO is much greater than that of iron oxide. In the present study strong positive

correlations have been observed between the content of MnO and of Co, Pb, Zn and Ba which complete the experimental observations mentioned above.

The strong negative correlations that appear between Al and the majority of the trace elements determined, clearly show that the kaolin minerals do not play any part whatsoever in the retention of these elements, observations that were already made by Rambaud (1969), Hughes (1981) and Mosser (1982).

REFERENCES

- Hughes J. C.: Mineralogy. In : Characterization of soils in relation to their classification and management for crop production: Examples from some areas of the humid tropics. p. 3050 D. J. Greenland (ed.). Claredon Press, Oxford (1981).
- Koons R.D., Helmke P.A. and Jackson M. L.: Association of trace elements with iron oxides during rock weathering. Soil Sci. Soc. Am. J., 44, 155-159 (1980).
- Loneragan J. F., Robson A. D. and Graham R. D.: Copper in soils and plants. Academic Press, Australia (1981).
- Mosser C.: Elements traces des argiles: des Marqueurs. Clay Min., 18, 139-151(1982).
- Rambaud D.: Etude sur la repartition des elements trace dans quelques sols ferrallitiques. ORSTOM. These Sciences, Paris (1969).
- Schwertmann U. and Taylor R. M.: Iron Oxides. In: Minerals in soils environments. p. 145-180. J. B. Dixon and S. B. Weed (eds.). Soil Sci. Soc. Am., Madison, Wisconsin (1977).
- Suarez D. L. and Langmuir D.: Heavy metals relationships in a Pennsylvania soil. Geochim. Cosmochim. Acta 40, 589-598 (1976).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

COMPARABLE STUDY OF CERAMIC PROPERTIES OF SEVERAL INDUSTRIAL SPANISH KAOLINS.

G. GARCIA-RAMOS, M.T. RUIZ-ABRIO, P.J. SANCHEZ-SOTO, F. GONZALEZ-GARCIA, and M. RAIGON-PICHARDO.

Departamento de Química Inorgánica, Facultad de Química. Universidad de Sevilla.

The ceramic properties of four industrial kaolins with different mineralogical characteristic, selected from among some of the most important Spanish deposits, are studied (1)(2)(3).

They are:

K-2, (Burela) and K-15, (Vimianzo), from industrial factories.

K-14, (Poveda), from industrial factory (cyclonal installation).

K-10, (Alcañiz), material known as "refractory clay" by the industry that produces it.

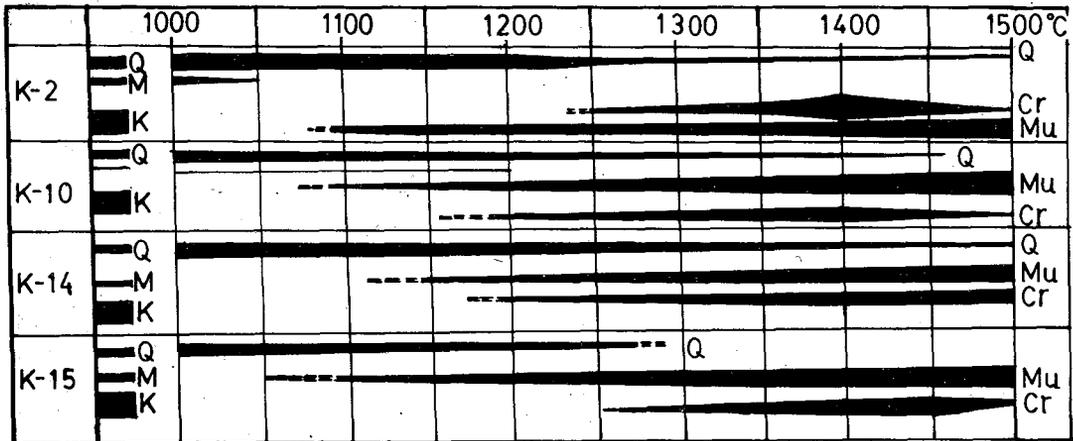
The materials have been characterized through the methods of X-Ray diffraction study, mechanical analysis (sedimentation), chemical analysis (A.A. and XRF), electronic microscopy (TEM) and by infrared analysis.

The ceramic test were: dilatometry (green and fired pieces), plasticity, linear firing shrinkage, water absorption capacity, bulk and porosity of bodies industrially pressed (4).

The formation and evolution of phases with the temperature has been studied by XRD in bodies fired for 2 hours to a maximum of 1500°C. Main interest was centered on mullite and cristobalite formation. Finally, the results are compared with others obtained by the authors, as well as some collected from the bibliography (4)(5)(6).

It is concluded that there is a great similarity between K-14 and K-15 kaolins, because of the great quantity of well crystallized kaolinite in both. Also, they are different from the more halloysitic K-2 and K-10 samples.

The forms of dilatometric curves obtained with the "green" materials show a characteristic kaolinitic appearance. Sample 10 in its original state is different from the others, but its $\phi < 63 \mu\text{m}$ fraction



agrees completely with the results of the rest.

The XRD data have been corroborated by DTA-TG. The K-10 kaolin is the most different on the average because of its properties. There are also some impurities such as iron and titanium oxides, or alkaline oxides of micaceous origin, and some content of feldspars from granitic rock origin.

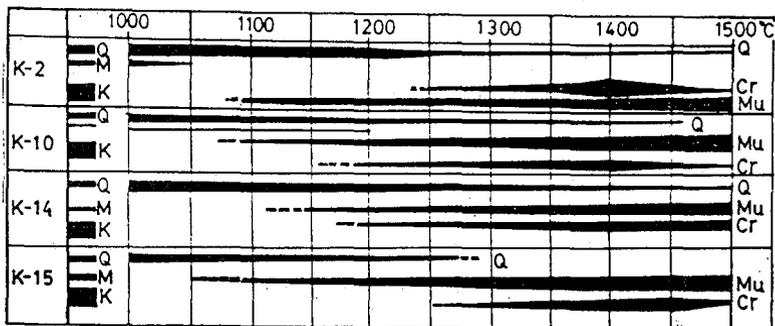
The K-10 sample, also, contains thick granulated pyrite, which is dispersed or disappears in the $<63\mu\text{m}$ fraction ($70\%<2\mu\text{m}$). This is the highest in plasticity, which justifies its use in casting slips preparation.

Sintering temperature diagrams show the good ceramic behaviour of the K-2, K-14 and K-15 kaolins (7).

A progressive decrease of the WAC is pointed out, with a continuous increase of the linear shrinkage. The diagrams show very high sintering temperature ($\sim 1.500^\circ\text{C}$).

With regard to the evolution of cristalline phases (fig. 1), the mullite formation in the K-15 sample is initiated at about 1.050°C . In the rest, the mullite formation occurs at higher temperature. The cristobalite shows a more changeable formation temperature (in the K-14 kaolin that reaction continues at 1.500°C)(8). That is why, this material has less thermal shock resistance.

Simultaneously, the quartz is dissolved in the glassy matrix with the temperature elevation. In the K-15 sample, the quartz is full reacted at 1.300°C , wich is related to a greater density of the sample.



Q=Quartz; M= Mica; K=Kaolinite; Mu=Mullite; Cr=Cristobalite.

Fig. 1.- Diagrams of the formation and evolution of mineral phases in the K-2, K-10, K-14 and K-15 samples, to 1.500°C .

REFERENCES

- 1.- GALAN E., ESPINOSA DE LOS MONTEROS J.
"El caolín en España" Ed. Soc. Esp. Ceram. y Vidr. Madrid (1.974).
- 2.- MENDUIÑA FERNANDEZ J.
1^{er} Cong. Iber. de Ceram. Vidr. y Refr. Torremolinos (Málaga) 623-645. Ed. S.E.C.V. Madrid (1.982).
- 3.- WATSON I.
Industrials minerals 1.984. 27-38 (1.984).
- 4.- GARCIA RAMOS G., GONZALEZ GARCIA F. SANCHEZ SOTO P.J. y RUIZ ABRIO, M.T.
Bol. Soc. Esp. Ceram. Vidr. 24, 2, 67-79 (1.985).
- 5.- GONZALEZ PEÑA J.M. y Cols.
Bol. Soc. Esp. Ceram. Vidr. 24, 6, 405-410 (1.985). Bol. Soc. Esp. Ceram. Vidr. 23, 5, 315-325 (1.984).
- 6.- CELOTTI G. et al.
J. Mat. Sci. 18, 1005-1014 (1.983). J. Mat. Sci. 19, 838-844 (1.983).
- 7.- NORRIS A.W., TAYLOR D., THORPE J.
Trans. J. Brit. Ceram. Soc. 78, 5, 102-108 (1.979).
- 8.- JOHNSON S.M. et al.
J. Am. Ceram. Soc. 65, 1, 31-35 (1.982).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

VARIATIONS OF CLAY MINERALOGY IN AN EVAPORITIC BASIN. THE
SOUTHERN PART OF THE TAJO BASIN (TOLEDO).

E.GARCIA ROMERO^{*}, M.DOVAL MONTOYA^{**} and J.M.BRELL PARLADE^{***}

* Sección de Químicas. Colegio Universitario de Toledo

** Dpto. de Cristalografía y Mineralogía. Fac. C.C. Geológicas.
Universidad Complutense de Madrid.

*** Dpto. de Estratigrafía. Fac. C.C. Geológicas. Universi-
dad Complutense de Madrid.

The Tajo Basin can be considered as a model of Miocene evaporitic basin. Its filling is made up of detrital materials at the borders and evaporites in the central part. Between them; there is an argillaceous unit which is difficult to be interpreted.

Several papers have been published in the last few years concerning the mineralogy of these materials in the northern part of the basin. As the southern part of the basin is less studied, this paper tries to provide new data about it.

The studied area is located between Añover de Tajo, Pantoja, Camarenilla and Bargas towns, approximately 20 kms north of Toledo.

Igneous and metamorphic rocks of Sierra de Gredos and Montes de Toledo form the basin edges. From these formations toward the center, detrital arkosic materials appears before finding the argillaceous unit, which forms a fringe from East to West and is 35 kms long and 20 kms wide.

250 samples have been studied belonging to 13 outcrops and 2 drilled hole, 300 and 375 m depth respectively.

Mineralogical study has been carried out by X-ray diffraction, chemical analysis and electron microscopy.

From the obtained results the following units can be established from the lowest to the highest parts of the sequence :

- Sagra Clays unit.

It is the lower unit found in the studied area. It changes progressively eastward into the evaporitic central sediments. Its mineralogical composition is : Illite 60-65%, dioctahedral smectite 5-25%, kaolinite 15%, chlorite always less than 15%.

Paligorskite can be found in minor amounts in a great number of samples, regardless of its location. The total amount of phyllosilicates goes higher than 70%, the rest being quartz and feldspar. The main mineralogical variations in this unit can be observed in E-W sense.

- Greenish clays unit.

It lies over the unit before and it is made up of green clays with some intercalations of sandy levels. In its upper part, carbonate are present, with a siliceous level at the top.

The thickness reaches 60 m and the mineralogy is the following: trioctahedral smectite 40-90%, Illite 5-45%. In a few samples, low amounts of kaolinite appear.

A very significant feature of this unit is the presence of some nodular pinkish clay levels very rich in sepiolite.

Westward both units become more detrital although the facies changes to the arkoses are difficult to observe.

- Arkoses unit.

It is the detrital border facies of the Southern Sistema Central and Montes de Toledo.

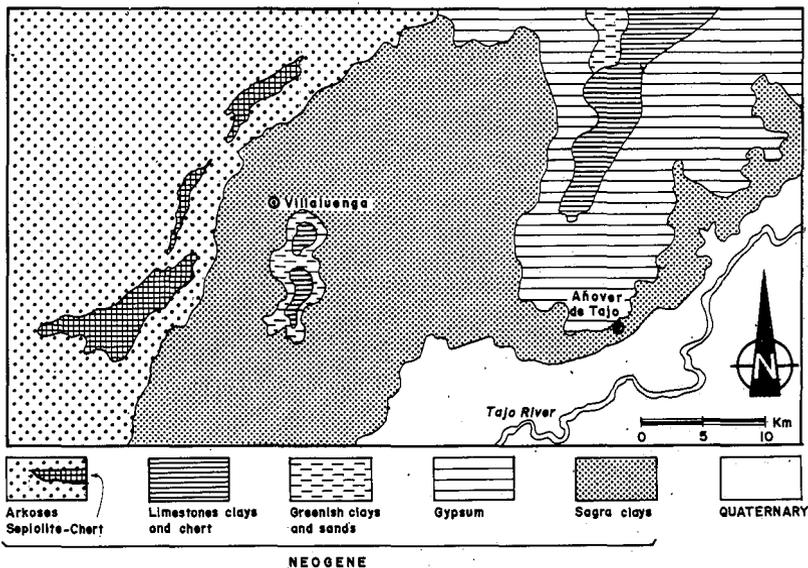
These facies are made up of argillaceous, silty and sandy sequences. Its mineralogical composition is : for the silty levels 50-75% of dioctahedral smectite and 20-40% of illite, for the clayey levels 30-55% of smectite and 35-55% of illite.

In the lower part of this unit, and near the unit before, levels mainly composed of sepiolite and/or smectite with chert and carbonates are found. In several places these levels are being mined.

In all the studied facies mineralogical variations can be observed, always in an East-West sense.

In the Sagra Clays Unit, these variations are mainly due to the sudden increase in the amounts of illite, decrease in smectite and appearance of palygorskite and clorite.

For the upper units, the main variations are related to the increase of smectite and in general to the high Mg contents of the interior studied materials.





Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERAL PHASES AND PROCESSES WITHIN THE GREEN PELOIDS FROM
THE RECENT DEPOSITS CLOSE TO THE CONGO MOUTH

P. GIRESSE,^{*} A. WIEWIÓRA, B. ŁĄCKA

^{*} Laboratoire de Recherches de Sédimentologie Marine, Université de Perpignan, Avenue de Villeneuve, 66025 Perpignan, France

Institute of Geological Sciences, Polish Academy of Sciences, A. Żwirki i Wigury 93, 02-089 Warszawa, Poland

The occurrence of the green peloids in the recent sediments of the West-African intertropical continental shelf is related to the availability of the active iron. A considerable amount of iron is supplied from the continent to ocean due to the rapid removal from the deeply weathered rocks during the heavy rainfalls. Last such a period has been dated here 10 000 - 6 000 years ago.

It has been observed that the enrichment of the sediments in Fe and C_{org} vary with the distance from the estuary from 20 - 30% Fe_2O_3 and 3 - 4% C_{org} /up to about 75 km away/ to 10 - 20% Fe_2O_3 and 2 - 3% C_{org} /up to 150 km away/. In order to follow a dependence of the mineral composition within the green peloids on Fe and C_{org} content, the samples were collected in various distances from the estuary and they were separated into several density fractions. The fractions from two samples were analysed chemically by the electron microprobe, studied by X-rays, IR and Mössbauer spectroscopy and the results are discussed.

In the both studied samples the heaviest density fractions consist of almost pure goethitic ovoidal peloids with shiny and smooth surfaces. Other fractions were differentiated chemically and mineralogically. In the green peloids from the proximity to the river mouth the content of goethite, Fe_2O_3 and Fe^{2+}/Fe^{3+} ratio decrease with the decre-

asing density. The morphology of the peloids varies from the deeply fissured brown ovoids with dull surfaces to the dark grey ovoids without any fissure. The transformation of kaolinite to berthierine was recorded by means of transmission X-ray diffractometry of non-oriented specimens as the gradual shift of d_{060} from 1,546 to 1,537 Å with the diminishing density of the peloids. The subordinate mineral in all of the density fractions was quartz.

The 2,70 - 2,53 g/cm³ density fractions of the green peloids from the deposits 100 km off the Congo mouth comprise almost pure glauconite with the small admixture of quartz. The glauconite occurring in the form of botryoidal grains is characterized by the very thin, up to 200 Å individual flakes. Such dimension of flakes strongly affected the "apparent" d_{001} position which frequently used to be interpreted as mixed-layering. The chemical composition determined by means of X-ray analyser proved the AL content increased in the outer parts of the glauconite peloids.

The formation of glauconite and berthierine within peloids /mainly the fecal pellets composed of kaolinite and goethite/ on the intertropical shelves is due to the two different processes. Berthierine is formed in the result of the transformation of kaolinite to berthierine in the reducing microenvironments containing the active iron. The glauconite is neofomed from the dissolved components of fecal pellets, as proposed by Odin and Matter.

We suggest that the low salinity and the low pH of marine waters close to the river mouth may be the factors favouring the transformation of highly degraded kaolinite to berthierine without the kaolinite dissolution.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

X-RAY DIFFRACTION AND INFRARED ABSORPTION CRYSTALLINITY INDICES IN KAOLINITES. THEIR SIGNIFICANCE, CAPACITIES AND LIMITATIONS.

C.S.F. GOMES

Centro de Cerâmica e do Vidro do INIC, Universidade de Aveiro (Portugal).

INTRODUCTION

The use, in clay minerals, of XRD and IRAS crystallinity numerical indices provided by experimental data is quite widespread. Nevertheless, comprehensive study dealing with their significance, capacities and limitations has not been carried out so far.

CRYSTALLINITY INDICES-GENERAL REQUIREMENTS

The CI general requirements should be the following: high degree of significance, good reproducibility, general application, absence of interfering factors, appreciable range of variability and low sensitivity to specimen preparation procedure and to analytical equipment performance conditions.

X-RAY DIFFRACTION CRYSTALLINITY INDICES IN KAOLINITES

Data found in the literature, relative to XRD crystallinity indices in kaolinites, were analysed and compiled in tables. Other indices developed by the author have been considered as well. The indices studied were the following: i) $I(1\bar{1}0)/I(020)$ -Murray and Lyons (1956); ii) $\Delta(001)$ - Brindley and Kurtossy (1961); iii) $I_c = \frac{A+B}{At}$ - Hinckley (1963); iv) $Q_F = \frac{F_{II}}{F_I + F_{II}}$ - Range et al. (1969); v) $\Delta(02,11)$ - Gomes (1979); vi) $(131) \leftrightarrow (13\bar{1})$ - Gomes (1979); vii) $S_k(001)$ - Gomes (1979); viii) $HYD = \frac{I_k}{I_k + (I_k + h)/8}$ - Tchoubar et al. (1982). The author proposed indices to serve some particular considerations.

$\Delta(02,11)$ - width of $(02,11)$ diffraction band at half maximum intensity. A $(02,11)$ band non modulated and with asymmetric profile appear in highly disordered kaolinites and represents the extent of layer stacking disorder parallel to the layer plane. This index is applicable only to highly disordered kaolinites and among them enables crystallinity differen-

tiation-values ranging from $0.20^\circ (2\theta)$ up to $0.45^\circ (2\theta)$.

It is applicable only to texture-free specimens. Cristobalite and goethite impurities can interfere in the index determinations.

$(\bar{1}\bar{3}1) \leftrightarrow (131)$ - resolution of the diffraction lines due to structural planes $(\bar{1}\bar{3}1)$ and (131) . Both reflections are well resolved in well-crystallized kaolinites; in poorly crystallized kaolinites they tend to coalesce. Being structural planes of the same general type (hkl) , their intensity, profile and resolution will denote the structure general organization. It appears that the resolution between $(\bar{1}\bar{3}1)$ and (131) lines is an indication of the unit cell symmetry. Therefore the magnitude of the resolution-values ranging from $0.45^\circ (2\theta)$ up to $0.95^\circ (2\theta)$ - can be considered as a triclinicity index. It is applicable only to texture-free specimens. Interferences are due to mica or illite impurities.

SK(001) - asymmetry of the (001) peak profile at half maximum intensity. For index determination well oriented mounts scanned at a speed of $1/4^\circ (2\theta) \text{ min}^{-1}$ are recommended. (001) peak asymmetry is related particularly with irregularities in the layer stacking arrangement perpendicularly to the layer plane, due to random interstratification of kaolinite layers with layer sequences typical of other clay minerals.

IRAS CRYSTALLINITY INDICES IN KAOLINITES

The most relevant characteristics of kaolinite IRAS crystallinity indices found in the literature are commented and compiled in a table for comparison purposes. Some of those indices are of common use: i) $IA\ 3696\ \text{cm}^{-1}/IA\ 3624\ \text{cm}^{-1}$ - Lyon and Tuddenham (1960); ii) $IA\ 3696\ \text{cm}^{-1}/IA\ 3625\ \text{cm}^{-1}$ (in oriented specimen inclined at 45°) vs $IA\ 3695\ \text{cm}^{-1}/IA\ 3625\ \text{cm}^{-1}$ (in randomly oriented specimen) - Parker (1969); iii) $IA\ 3700\ \text{cm}^{-1}/IA\ 910\ \text{cm}^{-1}$ - Neal (1974).

Another index $IA\ 795\ \text{cm}^{-1}/IA\ 755\ \text{cm}^{-1}$ developed by the author is considered as well and deserves some particular comments.

The absorption bands at $795\ \text{cm}^{-1}$ and $755\ \text{cm}^{-1}$ have been attributed to Al-O-Si modes by Stubican and Roy (1961) and to symmetric stretching modes of Si-O-Si bonds by Pampuch and Blaszczyk (1964).

Experimental data carried out in kaolinites and dickites with various degrees of crystallinity show that the ratio $IA\ 795\ \text{cm}^{-1}/IA\ 755\ \text{cm}^{-1}$ reflects the variability in crystal symmetry due to distortion, more or

less pronounced, of the silicon-oxygen anion. On the basis of the index values determined, some highly disordered kaolinites can be considered as intermediate members situated between well-crystallized (triclinic) kaolinites and dickites (monoclinic).

CONCLUSIONS

i) any assessment of crystallinity in kaolinites should take into account the interference of certain impurities upon certain crystallinity indices;

ii) crystal size and texture can effect crystallinity measurements; any comparative studies should be carried out in specimens with equivalent purity, crystal size and crystal orientation;

iii) the real significance of most crystallinity indices is still not well established; however, some indices developed by the author such as: $\Delta(02,11)$, $(\bar{1}\bar{3}1) \leftrightarrow (131)$, SK (001) and IA 795 cm^{-1} /IA 755 cm^{-1} were found to be very convenient either for the differentiation of kaolinites or for characterization of the structural organization of kaolinites in more specific terms.

REFERENCES

- BRINDLEY, G.W. and KURTOSSY, S.S. (1961) - Amer. Mineral. 46, 1205.
GOMES, C.S.F. (1979) - Ph. D. Thesis, Univ. of Leeds.
GOMES, C.S.F. (1979) - Proc. Brit. Ceram. Soc. 28, 107.
HINCKLEY, D.N. (1963) - Clays and Clay Min. 11, 225.
LYON, R.J.P. and TUDDENHAM, W.M. (1960) - Nature, 185, 835.
MURRAY, H.H. and LYONS, S.C. (1956) - Clays and Clay Min. 31.
NEAL, M. (1974) - Ph. D. Thesis, Univ. of Leeds.
PAMPUCH, R. and BLASZACK, K. (1964) - Polska Acak. Nauk Prace Kom. Nauk. Tech. Cerm. 3,5.
PARKER, T. W. (1969) - Clay Min., 8, 135.
RANGE, K. J. and WEISS, A. (1969) - Ber. Deut. Keram, Ges. 46, 231.
STUBICAN, V. and ROY, R. (1961) - Amer. Mineral. 46, 32.
TCHOUBAR, C. et al. (1982) - Bull Mineral. 105, 477.

TABLE I - XRD CRYSTALLINITY INDICES

Crystallinity Index/Parameter	I(110)/(040) Murray and Lyons (1956)	A(001) Kinsley and Hartog (1963)	$V_c = \frac{d_{111}^2}{d_{111}^2 + d_{110}^2}$ Hunkeler (1963)	$Q_c = \frac{I_{111}}{I_{110}}$ Range et al. (1969)	A (02-11) Coats (1973)	(111) vs (110) Coats (1979)	SK(001) Coats (1979)	$IPD = \frac{I_{111}}{I_{110}} \sqrt{\frac{d_{111}}{d_{110}}}$ Tschubar et al. (1980)	
Significance	Provides good information about the Oa related with the layer stacking arrangement. Increasing disorder due to the layer stacking is indicated as the result of layer contraction. The Oa will be clearly shown up.	Whether defect between the structural layers can lead to a washing of the interlayer space, consequently an increase of the (001) reflections.	Clear separation between the Oa and a small additional structural zone as indicated by the (001) and (040) reflections in the index.	Measures the relative intensity of the 111 and 110 reflections, both in direction and amplitude will be shown up.	Measures the relative intensity of the 111 and 110 reflections, both in direction and amplitude will be shown up. It can provide crystallinity differentiation between different lamellar thickness.	Measures the general orientation of the structure. Gives an indication of the symmetry arrangement. The magnitude of the coefficient is considered as a crystallinity index.	Measures the general orientation of the structure. Gives an indication of the symmetry arrangement. The magnitude of the coefficient is considered as a crystallinity index.	Measures the general orientation of the structure. Gives an indication of the symmetry arrangement. The magnitude of the coefficient is considered as a crystallinity index.	Provides good information about defects that appear in the layer stacking arrangement. The Oa will be clearly shown up. The Oa will be clearly shown up. The Oa will be clearly shown up.
Reproducibility	Reasonable	Good in agreement with equivalent grain size and texture.	Reasonable	Good	Good	Good	Good reproducibility in specimens with equivalent texture.	Good in specimens where intercalation attains its maximum ability.	
Limitations	Applicable only to kaolinite with medium to good crystallinity. Not applicable to poorly crystallized.	Almost non-existing limitations.	Applicable to completely amorphous to well crystallized. Not applicable to poorly crystallized. Not applicable to poorly crystallized.	Not applicable to highly disordered kaolinites.	Applicable to kaolinites with various types and degrees of disorder.	Applicable to kaolinites with various types and degrees of disorder.	As for index A (001).	Intercalation is complete or almost complete in specimens where intercalation becomes more difficult and increasing defectiveness.	
Disturbance	Sensitive to the presence of other minerals, particularly illite and mica which may give rise to (001) reflection.	Little disturbance by impurities, only known disturbing impurity.	Influenced by impurities such as illite, gibbsite, goethite, hematite, etc. Influenced by lamellar thickness and orientation.	Impurities such as illite, gibbsite, goethite and graphite can interfere.	Crystallite and graphite impurities may disturb.	Crystallite and graphite impurities may disturb.	As for index A(001).	Impurities such as illite and chlorite can interfere.	
Range of Variability	Appreciable. > 1 - well crystallized. 0.7 - medium crystallized. < 0.7 - poorly crystallized.	Appreciable.	Large range variability. From 0.1 to values just over 1.0. Well crystallized. 0.9-1.2-well crystallized. 0.5-0.9 - medium crystallized. < 0.5 - poorly crystallized.	Appreciable.	Limited but appreciable. Values ranging from 0.30 (poor) to 0.45 (good).	Appreciable. Values ranging from 0.35 (poor) up to 0.55 (good). Values increasing with increasing crystallinity. < 0.5 - poorly crystallized.	Values close to 1 for low defective kaolinites. Values increasing with increasing defectiveness lower kaolinites.	Appreciable. Values increasing with increasing defectiveness.	
Correlation with other indices	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	Correlation with other indices is not clear.	
Application	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	Applicable to specimens with equivalent grain size and texture.	

TABLE II - IRAS CRYSTALLINITY INDICES

Cristallinity Indices General Requirements	IA 3696cm ⁻¹ /IA 3624cm ⁻¹ Lyon and Tuddenham (1960)	IA 3695cm ⁻¹ /IA 3625cm ⁻¹ (orient. specimen inclin. at 45°) vs. IA 3695cm ⁻¹ /IA 3625cm ⁻¹ (randomly oriented specimens). Parker (1969)	IA 3700cm ⁻¹ /IA 910cm ⁻¹ Neal (1974)	IA 795cm ⁻¹ /IA 755cm ⁻¹ Gomes (1979)
Significance	Provides good information about the kaolinite structure organization and in some cases facilitates the differentiation of the kaolin mineral species.	Provides a classification of kaolinites according to their general O-D but cannot provide information on the quality or type of disorder. Both ratios decrease with increasing kaolinite disorder. Satisfactory correlation between Parker's IRAS crystallinity index and Hinkley's XRD crystallinity index has been found.	Measures the disorder in the structure produced mainly by atomic isomorphous substitution.	Provides information about the symmetry of the unit-cell. The index reflects the variability in crystal symmetry due to distortions of the silicon-oxygen anion. Distinguishes the pseudo-monoclinic kaolinites of the triclinic ones
Reproducibility	Good in low-impurity and non-textured kaolinite bearing specimens.	Good in low-impurity kaolinite bearing specimens.	Good whenever the impurity quantities able to cause disturbing absorption coincidences are not influential.	Good in low-impurity and non-textured kaolinite bearing specimens.
Limitations	Applicable to kaolinites with any type and degree of crystal defectiveness.	Applicable to kaolinites of all types and degrees of crystallinity.	Applicable to kaolinites of all genetic types and degrees of crystallinity.	Applicable to kaolinites of all genetic types and degrees of crystallinity.
Disturbances	Impurities of 2:1 clay minerals (micas, illites and smectites) diminish the index values. Other kaolin mineral species such as dickite and halloysite can interfere with index assessments. Dickite and halloysite diminish the index values.	Very sensitive to impurities such as: 2:1 clay minerals and dickite. These impurities produce an enhancement of the absorption band at 3625cm ⁻¹ unbalanced in both oriented and non-oriented specimens.	Dickite associated to kaolinite affects the intensity of the 3700 cm ⁻¹ absorption band of kaolinites. 2:1 clay minerals associated to kaolinite affect the intensity of the 910 cm ⁻¹ absorption band.	Quartz is an impurity which can interfere with the triclinicity index measurements.
Range of Variability	Appreciable. 1.2-1.5 - kaolinites 0.8-0.9-halloysites 0.6-0.8-dickites	Wide range of variability.	Wide range of variability, 0.5-1.2, with values increasing towards the low defective kaolinites.	Appreciable. < 0.9 - well crystallized. 0.9 - 1.1 - medium crystallized. > 1.1 - poorly crystallized.
Sensitivity to specimen preparation procedure and analytical equipment performance conditions	The intensity of the 3696cm ⁻¹ absorption band is orientation dependent. The intensity of the 3624 cm ⁻¹ absorption band is little affected by the texture of the specimens.	Texture effects are not important if the preparation of oriented and non-oriented specimens is carried out properly.	Applicable only to non-oriented mounts.	Applicable only to non-oriented mounts.

MINERALOGICAL CHARACTERISTIC AND CERAMIC PROPERTIES OF A GROUP OF CLAYS FROM ANDALUCIA AND EXTREMADURA (SPAIN), OF INDUSTRIAL INTEREST

F. GONZALEZ-GARCIA, M^a. T. RUIZ-ABRIO, P.J. SANCHEZ-SOTO, M. RAIGON-PICHARDO AND G. GARCIA-RAMOS.

Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla (España).

The most relevant results of research carried out by the group of "Clays, Silicates and Ceramic products" of the Departamento de Química Inorgánica, about some materials from various Spanish deposits of different geological characteristics from Andalucía and Extremadura are presented (1)(2).

The mechanical analysis was carried out on the $< 63 \mu\text{m}$ fraction as well as the chemical analysis (A.A. and gravimetric), X-Ray diffraction study, D.T.A, T.G. and dilatometric analysis, plasticity, linear firing shrinkage of pressed bodies and water absorption capacity of test pieces, bulk and porosity, from the refractarity point of view (3).

According to the granulometric aspect of the samples, the following groups were established:

(I) Raw materials with $\sim 10\%$ of particles, $\phi < 63 \mu\text{m}$. (3 and 11).

(II) Raw materials with $\sim 25\%$ of particles (4 and 14).

(III) Raw materials with $\sim 80\%$ or more (7, 8, 9, 12, and 13).

The last samples present a greater content in $\phi < 2 \mu\text{m}$ fraction (Fig. 1).

The Al_2O_3 content of these raw materials is high, and higher in $\phi < 2 \mu\text{m}$ fraction, although the silica content decreases.

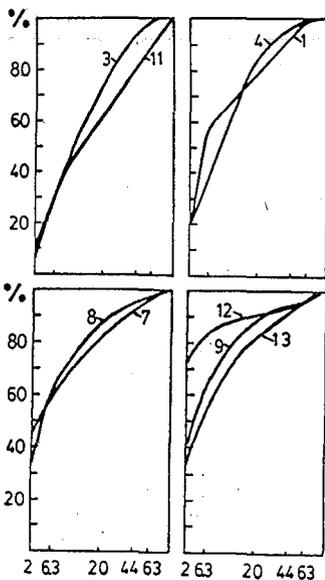


Fig. 1. Granulometric curves of samples studied.

The origin samples contain a larger quantity of fluxes than the argillaceous fractions. The less kaolinized ones and the more feldspathic or micaceous - materials are higher in fluxes content.

It is concluded that the samples are kaolinitic and illitic-kaolinitic nature, with variable amounts of quartz. Also, there are other illitic and feldspathic materials. These results are ratified by ATD, TG and dilatometric analysis (4).

The kaolinitic and illitic-kaolinitic materials have a great plasticity and above all, the K-12 sample, which contains the greatest clay content (1).

According to their ceramic properties, the samples can be classified as the following groups:

TABLE I

Classification of materials according to its mineralogy and ceramic properties.

MINERALOGY	KAOLINITIC AND KAOL.-ILLITIC	FELDSPATHIC	ILLITIC-KAOLINITIC
SAMPLES	1. Traslasierra (Huelva) 9. Garlitos (Badajoz) 11. Villanueva del Río y Minas (Sevilla)	3. Cazalla de la Sierra (Sevilla) 4. Cazalla de la Sierra (Sevilla)	5. Guadalcanal (Sevilla) 6. Guadalcanal (Sevilla) 7. Zalamea (Badajoz) 8. Monterrubio (Badajoz) 12. Conquista (Córdoba) 13. S. Eufemia (Córdoba)
T_v	HIGH $\gg 1.200\text{ }^\circ\text{C}$	LOW $\sim 1.200\text{ }^\circ\text{C}$	MIDDLE $\sim 1.250\text{ }^\circ\text{C}$
APPLICATIONS	Refractories Chamottes	Feldspar ear- thenware Stoneware Vitreous cera- mic ware	Chamottes Stoneware Light aggregates Half refractories

T_v = Initial temperature of vitrification.

The evolution of crystalline phases when the temperature is increased has been studied through X-Ray analysis. The influence of the physical-chemical properties of different materials in mineral formation and in the decomposition process through temperature elevation are studied.

The X-Ray diagrams allows us establish that the crystalline phase mullite ($3 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, fundamentally) is first formed at about 1.050°C in the illitic-kaolinitic samples and afterwards, the kaolinitic-illitic ones (1st. group).

The more feldspathic samples become mullitic at higher temperatures with a sudden melting of feldspars at 1.200°C , at the same time as the vitrification of ceramic-fired bodies.

All samples show a progressive dissolution of the quartz, which is the vitreous phase, in liquid state at the studied temperatures.

We can see that the mullite is the only crystalline phase which is present in almost all of the samples.

Finally, the principal applications of these materials are suggested and debated.

REFERENCES

- 1.- GARCIA RAMOS G.; MESA J.M.; RUIZ ABRIO M.T.; SANCHEZ SOTO P.J.
XXVI Reunión Anual S.E.C.V. 34 Córdoba 8-12 de Junio (1.986).
- 2.- GARCIA RAMOS G. y Cols.
XXI Reunión Bienal de la Real Soc. Esp. de Quim. 427 Santiago de Compostela 22-26 Septiembre (1.986).
- 3.- SANCHEZ SOTO P.J.
Tesis de Licenciatura. Universidad de Sevilla (1.985).
- 4.- GARCIA RAMOS G.; GONZALEZ GARCIA F.; SANCHEZ SOTO P.J. y RUIZ ABRIO M.T.
Bol. Soc. Esp. Ceram. Vidr. 24, 2, 67-79 (1.985).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ILLITIC CALCAREOUS AN RELATED CLAYS AS RAW MATERIALS IN THE INDUSTRY OF THE ORNAMENTAL TILES IN SEVILLA.

F. GONZALEZ-GARCIA, G. GARCIA RAMOS AND V^a ROMERO ACOSTA.

Department of Inorganic Chemistry, University of Seville (Spain).

The manufacturing of ornamental tiles is one of the oldest and most typical ceramic industries of Seville. It began in the middle of the 13th century and the beginning of the 14th, and its technique has been constantly evolving throughout time. After some periods of decline it has recovered in recent years and acquired a great importance in the present days.

A piece of tile consists of two parts: the base, obtained by baking a mixture of clay and other materials, and the top surface, of ceramic enamel, in one or several colours. A paste suitable for ornamental tile must provide the baked base with a good capacity for the absorption of water, a great resistance to bending, etc. Hence it must be made of suitable raw materials.

The Sevillian industry of tiles has traditionally used clay materials from tertiary period (Miocene) deposits, near to Seville, on the right bank of the Guadalquivir river, mixed with silty sediments from the alluvial beds near to the river.

The revival of this industry has boosted interest in the search for suitable new raw materials and in the study of chemical reactions and mineral phases formed during the firing process.

In this paper we present the results of a study carried out with several illitic calcareous clays, with illitic-kaolinitic clays and with a tremolitic material from the same general area, so as with mixtures of materials of the above two groups with the aim of ascertaining their use as raw materials for manufacturing of tiles.

The study samples can be classified as follows:

- a) Mainly illitic clays containing very finely divided calcium carbonate (samples 21, 23, 24, 25).

- b) Kaolinitic-illitic clays without CaCO_3 (Samples 22, 26, 31, 34).
 c) Tremolitic material from Calera de León (Badajoz) (Samples 29, 30).

The used experimental methods were: chemical analysis, DTA and XRD. Samples grounded to $\phi < 0.12$ mm and different mixtures of them were studied by XRD at room temperature and after baking for two hours at 950 1020 and 1100°C. Some technological tests such as shrinking by drying and by baking, porosity expressed as the water absorption capacity, dilatometric diagrams, resistance to bending etc. were also carried out.

TABLE I
 MINERALOGICAL COMPOSITION OF CLAYS

Illitic samples								
$\phi < 0.12$ mm (containing CaCO_3)				$\phi < 1.12$ μm (after elimination CaCO_3)				
21	23	24	25	21	23	24	25	
Illite %	35	32	37	43	58	66	80	80
Kaolinite %	10	6	5	5	16	12	10	8
Smectite %	8	5	5	5	14	9	5	8
Quartz %	15	15	24	19	5	-	-	-
CaCO_3 %	25	30	19	22	-	-	-	-
Felspars (P) %	5	9	9	6	5	-	-	-
Fe_2O_3 %	5	5	5	5	6	13	8	9
Kaolinitic-Illitic samples containing no CaCO_3								
	22	26	31	34	22	26	31	34
Kaolinite %	5	47	47	5	7	57	50	5
Illite %	57	20	28	65	82	24	29	88
Smectite %	-	8	-	-	-	10	-	-
Quartz %	27	12	9	14	5	-	7	-
Felspars %	7	6	6	9	-	-	-	-
Fe_2O_3 %	4	7	10	7	9	9	14	6

Table I contains the approximate mineralogical composition of the two materials from each samples of clay according to XRD and chemical data.

Firing at 950°C the illitic-calcareous clays 21, 23, 24, 25 causes the disappearance of the calcite, kaolinite and smectite diffractions. Only a few very weak diffractions of illite remain since this clay mineral decomposes just at this temperature. Some diffractions due to CaO are also observed together with those corresponding to calcium orthosilicate larnite (Ca_2SiO_4), as well as calcium diorthosilicate kilchoanite ($\text{Ca}_2\text{Si}_3\text{O}_7$), wollastonite ($\beta\text{-CaSiO}_3$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$). The most remarkable point however, is the appearance of intensive diffractions corresponding to feldspar, plagioclases, possibly close to anorthite, which are notably intensified at 1020 and 1100°C. Upon increasing the temperature, the diffractions of wollastonite are also intensified while those of quartz decrease in intensity. No diffractions due to mullite have been observed.

On the contrary firing the no calcareous kaolinitic-illitic samples at the same temperatures, allows detection of mullite, spinel and hematite, while the intensity of the diffractions of quartz and feldspar decreases.

Binary mixtures of sample 21 (70%) with samples 22, 26, 31 or 34 (30%) fired at the above mentioned temperatures contain (as shown by XRD) small amounts of larnite, wollastonite, some gehlenite, crystalite and hematite together with large quantities of plagioclases. These last minerals become the major component of the product obtained by firing a mixture of sample 21 with 22 or 26, the latter two having the largest proportion of kaolinite.

Baking sample 39 (pure tremolite) at 950°, 1020°C causes transformation into diopside, enstatite and quartz. The more complex sample 30' (containing kaolinite, some tremolite, illite, smectite, serpentine and quartz) produces at those temperatures hematite, forsterite, crystalite, spinel and few enstatite.

The transformations mentioned in this paper can be justified by thermodynamic considerations.

The technological tests show that the mentioned binary mixtures of clays have excellent properties to be employed for manufacturing of the bases for ornamental tiles.

(This research work has been financed by CAICYT, research project number 2033/83).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

A low temperature Mossbauer spectroscopic study of iron-rich chlorites

B.A. Goodman^a, D.C. Bain^a and P.D.E. Dickson^b

^a Macaulay Land Use Research Institute, Aberdeen, AB9 2QJ, U.K.

^b Department of Physics, Liverpool University L69 3BX, U.K.

One of the major problems in describing the structure of iron-containing chlorites is establishing the distribution of iron between the 2:1 and hydroxide layers. In principle this would appear to be a problem that could be resolved by the use of Mossbauer spectroscopy, since the spectral parameters vary sensitively with the electronic and coordination environments of the iron. However, results obtained at 77K and ambient temperatures show only a small range of parameters for both the Fe(II) and Fe(III) components and do not provide a reliable assessment of the number of different types of environment occupied and certainly shed no light on the distribution over the two types of layer.

In the present paper results are reported of a low temperature investigation of three iron-rich chlorites. This experiment was performed with the objective of observing magnetic ordering in the structure and then using the greater sensitivity of the magnetic hyperfine parameters to the iron environment to distinguish different coordination sites in a manner analogous to that used by Borg and Borg (1974) with iron-rich amphiboles. Each of the three samples showed magnetic ordering when cooled to low temperatures, the results being qualitatively similar in each case. These are illustrated in Fig. 1 for two of the samples at 1.3K. In both spectra, there is a significant fraction of the Fe(II) that remains unordered, with a quadrupole splitting of ca. 2.9 mm/s. Analysis of the magnetically-ordered component is difficult because of the comparable magnitudes of the magnetic hyperfine and electric quadrupole terms and approximate peak positions are indicated on the figure. This analysis suggests that the hyperfine field is ca. 16T in each case, although it is not possible from these spectra to determine whether there is more than one hyperfine component present. This value of 16T for the hyperfine field is similar to that reported for Fe(II) in other aluminosilicate minerals (Coey, 1987).

Raising the temperatures of the samples to 4.2K produced little change in the spectral envelope thus showing that there is no significant difference in the magnetically-ordered fractions at these two temperatures. The most likely explanations of these results is that the minerals contain regions of high and not-so-high iron contents. Although all of the minerals contained some Fe(III), which could be clearly seen in the Mossbauer spectra at 77K and room temperature, its contributions to the spectra at low temperatures were not clearly identified. There appears to be some weak absorptions around -8.0 and +9.0 mm/s but these are not unambiguously identified. However, it does appear that the Fe(III) components are magnetically-split since there is no evidence for a paramagnetic doublet component with isomer shift ca. 0.5 mm/s. The Fe(III), therefore, would appear to be in the high iron content regions of the samples. If these regions were to correspond to the two types of

layer in the structure then the high iron region could be equated to the 2:1 layer, since Fe(III) would not be expected to be favoured in the hydroxide layer. However, in our opinion such conclusions are unjustified since we are unable to establish whether or not the Fe(III) is distributed throughout the structure or just occurs in surface oxidized regions. Indeed, these measurements are unable to distinguish between structural Fe(III) and the possibility of a small amount of a separate poorly crystalline oxide phase. Therefore, although these measurements establish that the iron is not evenly distributed throughout the chlorite specimens, they do not provide estimations of the relative population of the different layers.

References

Borg, R.J. and Borg, I.Y. (1974). *J. Phys (Paris) Colloq. C6*, **35**, 553-556.

Coe, J.M.D. (1987). Chapter 14 in "Iron in Soils and Clay Minerals" (Ed. J.W. Stucki, B.A. Goodman and U. Schwertmann), D. Reidel, Dordrecht.

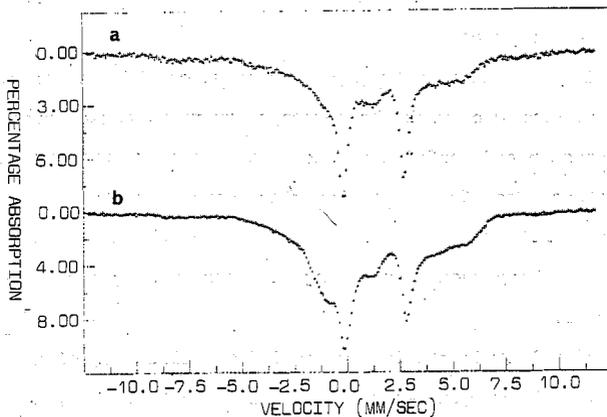


Fig. 1 Mössbauer spectra of iron-rich chlorites at 1.3K (a) thuringite and (b) daphnite



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SPATIAL CORRELATIONS OF GEOTECHNICAL PROPERTIES OF "BACINO DI SANT'ARCANGELO" BLUE CLAYS (SOUTHERN ITALY).

F.M. GUADAGNO, G. VALENTINI*

Department of Geophysics and Volcanology, University of Naples (Italy)
*Department of Earth Science, University of Rome (Italy).

This article deals with the results obtained from a study of the geotechnical properties of "Bacino di Sant'Arcangelo" clay sediments. The area covers over 100 km² and it is characterized by the presence of a regressive cycle, formed by blue clays, yellow sands and conglomerates.

In the Plio-Pleistocene period this area was a vast bay formed in a tectonic depression of the Apennine chain and connected to the sea through the Gannano area (Fig. 1).

The lithological and structural characteristics and the morphological evolution, connected with the tectonic activity, cause intense process of erosion and landslides. These particularly interest the clayey lithotype. Therefore, the blue clays have been studied to individuate clayey units with homogeneous geotechnical characteristics. Over 250 samples have been taken along the four stratigraphic sections shown in Fig. 1.

The statistical study has led to the individualization of units for each section, with homogeneous geotechnical characteristics, differentiated by significant statistical variations of the parameters under consideration. It has also been established the statistical correlation between the various geotechnical units of the stratigraphic successions examined (Fig. 2).

The variations of geotechnical properties, stratigraphic as well as spatial, have thus been reconstructed. Such variations have then been compared with the characteristics of Sant'Arcangelo Bacino palaeomorpho-

logy and of the various terrigenous drifts to which the area has been subjected.

In the end the index properties have been correlated to the mechanical ones and in particular to the parameters of compressibility and shear strength of reconstituted materials (Fig. 3).

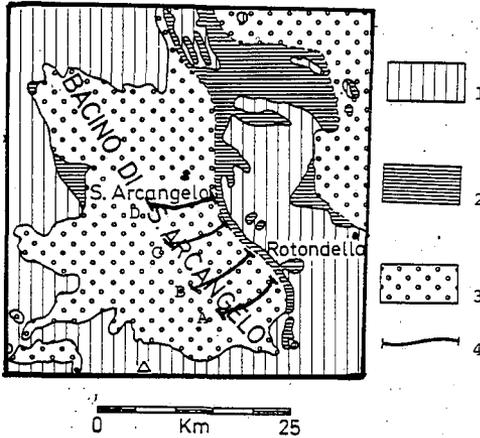


Fig. 1 - Simplified geological Planimetry. 1) Pre-pliocenic Formations; 2) Infrapliocene Sediments; 3) Plio-Pleistocenic Sediments; 4) Studied Litostratigraphic sections.

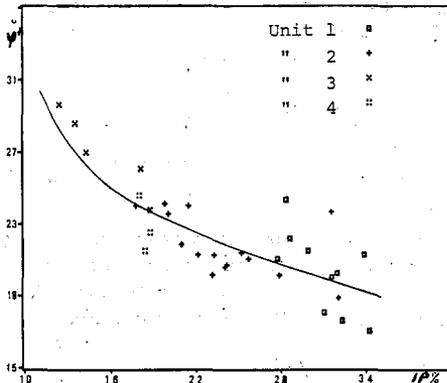


Fig. 3 - Correlations between peak friction angle for remoulded materials and Plastic index.

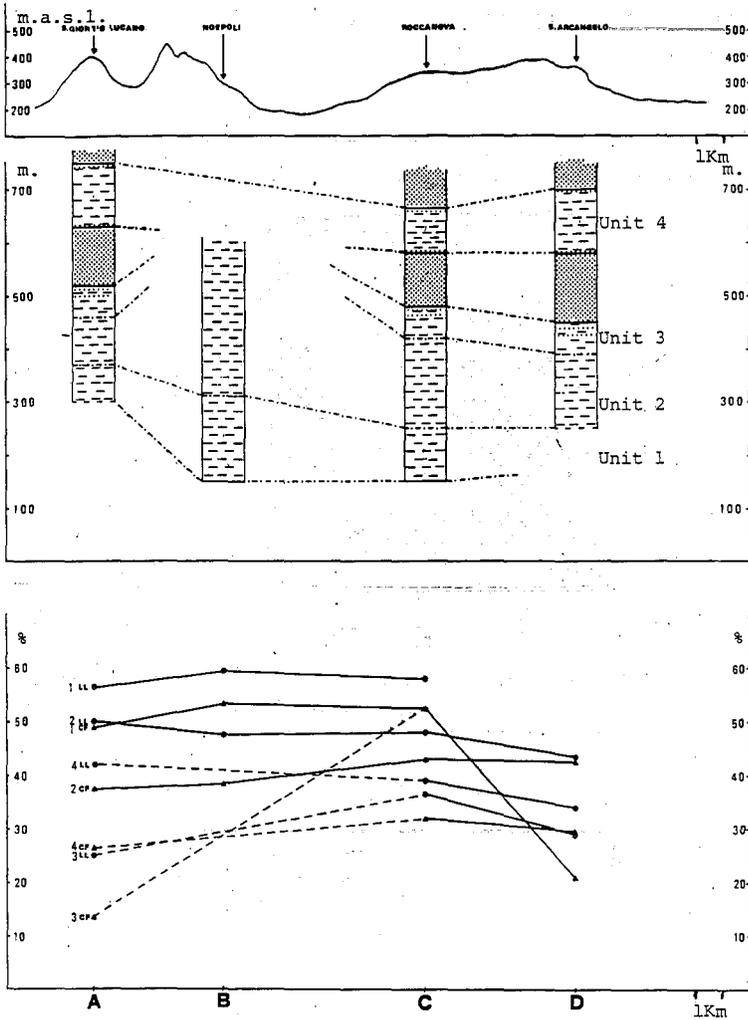


Fig. 2 - Space reconstruction of homogeneous clayey layers (a): variations and correlations of mean values of geotechnical parameters of clays belonging to four clayey units (LL = Liquid Limit, CF = clay fraction).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

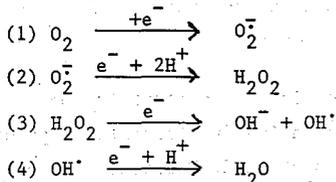
SURFACE ACTIVITY OF MINERALS IN REDUCING OXYGEN TO HYDROXYL RADICALS
Consequences to toxicology, pedology and pollution phenomena

J. GUIGNARD, R. ZALMA, D. COSTA and H. PEZERAT

Université P. et M. Curie, Laboratoire de Réactivité de Surface et
Structure, CNRS, U.A. 1106, 4 Place Jussieu - 75252 PARIS Cédex 05,
France

Oxygen reduction arising from the surface activity of some minerals
in aqueous medium produces oxyradicals, which can play an important
role in various phenomena (pollution, toxicity, evolution of mineral
or organic matter of soils).

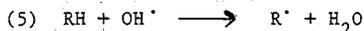
The following cascade reactions can occur :



All these reactions imply intervention of minerals possessing
electron donor surface sites.

The evidence for the existence of OH^\cdot has been obtained from the
formation of a radical adduct with a spin trapping agent like DMPO
(5,5-Dimethyl-1-Pyrroline-N-Oxide). The radical adduct which has a
much longer life time than the radical OH^\cdot itself, can be identi-
fied and also quantitatively measured by ESR Spectroscopy (Varian
CSE 109). The number of spins was standardized with a DPPH solution
in benzene. To avoid reaction (4) and in order to make sure that
the $(\text{DMPO-OH})^\cdot$ was not an artefact of direct DMPO oxidation, an or-
ganic agent RH (such as $\text{CH}_3\text{CH}_2\text{OH}$ or HCO_2^-) having a high rate con-
stant for the reaction with OH^\cdot was added to the medium.

The following reaction could then occur :



The radical R^{\cdot} gives on adduct $(\text{DMPO-R})^{\cdot}$, which is identified by spectroscopy.

The results show that in a buffer medium (potassium hydrogenophosphate 1M), the minerals which are more reducing are those containing essentially Fe^{2+} : for example :

- some silicates such as ferrous biotite, chlorite or berthierine
- some carbonates such as siderite or others containing Fe^{2+}
- some hydroxides such as brucite with Fe^{2+} in substitution.

Materials containing Fe^{3+} or Al^{3+} such as goethite, montmorillonite or kaolinite are either inactive or poorly active.

The accessibility of the Fe^{2+} sites is an important factor of reactivity. Activation of sites by grinding or lixiviation, passivation by aqueous medium or coating was studied. Particularly, on the surface of pyrite dusts, after a long time in air, a coating of Fe^{2+} sulfate exists which is very active in the formation of OH^{\cdot} radicals.

Results will be presented with the intensity of $(\text{DMPO-CO}_2)^{\cdot}$ signal in arbitrary scale from 0 to 2000. The standardization gives a signal intensity of 1000 for the presence of approximately $8 \cdot 10^{15}$ R^{\cdot} in the reactor with 45 mg of solid.

The emerging paradox is that the stronger reducing minerals will be the more active in the oxidation process via the reduction of O_2 into OH^{\cdot} which is a very oxidative radical.

These processes can play an important role in various fields : such as,

- in the evolution of soil materials (mineral or organic),

- in the eutrophization of lakes,
- in the phenomena of oxidative pollution
- in some toxic effects on human beings from the inhalation of electron donor minerals (inflammation, tissues ageing, fibrosis, cancer).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

INTERCALATION AND CATALYTIC REARRANGEMENT OF PINACOL IN HOMOIONIC
MONTMORILLONITES

E. GUTIERREZ and E. RUIZ-HITZKY

Instituto de Ciencia de Materiales, C.S.I.C., c/ Serrano, 115 bis.
28006-MADRID (Spain).

INTRODUCTION

Adsorption of ethylene glycol and glycerol in clay minerals has been extensively used for X-ray identification and surface area determination (1,2). The mechanism of intercalation of ethylene glycol in smectites has been clearly established, consisting in a replacement of the water belonged to the natural hydration shell of the exchangeable cations by the glycol molecules (3).

The role of certain homoionic smectites as catalysts for dehydration reactions of several diols has been recently reported (4), and it has been found that the controlling factor for these processes is the acidity of the hydrated interlayer cations.

It is well known that α -glycols are able to rearrange to carbonyl compounds in homogeneous conditions (5), being these reactions acid-catalyzed (i.e. in presence of H_2SO_4).

This work concerns with the intercalation of pinacol (2,3-dimethylbutane-2,3-diol, I) in homoionic montmorillonites and its subsequent quantitative rearrangement to pinacolone (3,3-dimethylbutan-2-one, II) taking place in the conditions of soft chemistry.

INTERLAYER ADSORPTION

Intercalation of I in different homoionic (Na^+ , Ca^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} , La^{3+} , ...) montmorillonites produces an increase of the basal spacing of about 5.5 Å. This value agrees with the thickness of a pinacol molecule and, taking into account the adsorbed amounts (~1 mmole/g) we can deduce that a monolayer of I is reached. The

infrared spectra show a strong decrease in the intensity of the absorption bands assigned to the water molecules in the starting silicates simultaneously to the detection of the bands corresponding to the intercalated pinacol. The stretching OH vibrations which appear at relatively low frequencies ($\sim 3350 \text{ cm}^{-1}$) can be interpreted as: i) intermolecular interactions between the intercalated I molecules, or ii) associations with the residual water molecules.

PINACOL REARRANGEMENT

The thermal treatment of the M^{n+} -montmorillonite/pinacol system produces the conversion of I to II. The reactions have been followed by IR and GC /MS techniques in order to determine the nature of the reactions products and the yields of the process. The most significant feature after treatment of the montmorillonite/pinacol complexes is the presence in the IR spectra of an intense band at 1680 cm^{-1} , assigned to $\nu(\text{C=O})$ vibrations of the resulting carbonyl compound II.

The yield of the intracrystalline reaction is clearly dependent on the acidity of the interlayer cations (Table 1).

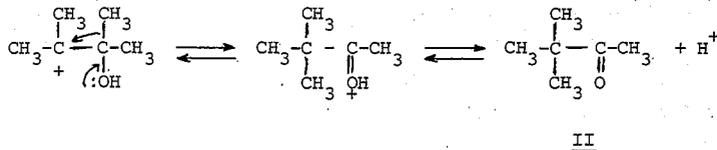
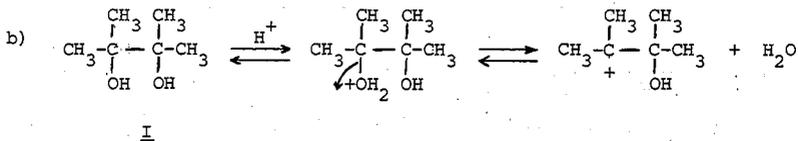
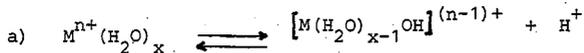
TABLE I

Intracrystalline rearrangement of pinacol to pinacolone in M^{n+} -montmorillonites at 100°C , 1 h.

	M^{n+}	Yield (%)
ACIDITY ↓	Na ⁺	16
	Cu ²⁺	81
	Al ³⁺	100

The mechanism for these reactions is well known in homogeneous conditions (5,6). We can suppose that a similar mechanism occurs in the interlayer space of clays, the source of protons being the water molecules coordinated to the exchangeable cations (Scheme 1).

SCHEME 1



REFERENCES

- (1) BRINDLEY, G.W. (1966) *Clay Minerals* 6, 237
- (2) DIAMOND, S. and KINTER, E.B. (1958) *Clays, Clay Miner.* 5, 334
- (3) DOWDY, R.H. and MORTLAND, M.M. (1968) *Soil Sci.* 105 (1), 36
- (4) KOTKAR, D. and GHOSH, P.K. (1986) *J. Chem. Soc., Chem. Commun.*, 650
- (5) COLLINS, C.J. (1960) *Quart. Rev.* 14, 357
- (6) BETHELL, D. and GOLD, V. (1967) *Carbonium ions*, Academic, London and New York, 206.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGICAL AND MECHANICAL CHANGES OF CLAY BARRIERS
BY CHEMICAL WASTE

R. Hasenpatt

Institute of Foundation Engineering and Soil Mechanics,
Laboratory for Clay Mineralogy, Federal Institute of
Technology, CH - 8093 Zürich, Switzerland

Clays are more and more used as geological or technological barriers to insulate toxic waste or to avoid their percolation into the groundwater and thus entrance into the food chain.

Aim of this study was to analyse mineralogical and soil mechanical properties of a bentonite, an illite and a kaolinite before and after contact with various chemicals. Representing substances of potentially hazardous chemical waste as heavy metal complexes (cobaltethylenediamine) and active carbon-hydrogen compounds (diammoniumdodecane) were used to react with the clays in batch experiments. The clays were tested for their aggregation behaviour, swelling property, shear strength and plasticity.

The intercalation of the cobalt-complex and the cationic detergent into the montmorillonite causes an irreversible closure of the interlayer space. After this reaction the bentonite has lost its swelling potential.

The chemicals, which are adsorbed on the outer surface of the different montmorillonite crystals, cause an aggregation. This aggregation is explained by the joint attraction of several crystals to the positive charged ions.

The adsorption of the chemicals and the attraction forces lead to an increase in shear strength for the clays, highly for montmorillonite and illite, weaker for kaolinite. Table 1 shows as an example the maximum and minimum shear strength measured in a ring shear apparatus.

	natural		cobalt-comp.		diammonium	
	ϕ_{\max}	ϕ_{\min}	ϕ_{\max}	ϕ_{\min}	ϕ_{\max}	ϕ_{\min}
bentonite	17.6°	5.8°	36.5°	22.1°	41.0°	17.1°
illite	13.8°	11.0°	35.2°	35.0°	34.7°	34.2°
kaolinite	20.1°	16.1°	25.9°	22.2°	25.9°	22.0°

Tab. 1: Shear strength before and after reaction with the cobalt-complex and diammoniumdodecane ($\sigma=300 \text{ kN/m}^2$)

Furthermore, the diffusion velocity of the chemicals and an organic solvent (ketone) into the clays were studied in diffusion experiments under various conditions. A comparison between the instationary diffusion of the chemical solutions in bentonite, illite and kaolinite with the diffusion of water, shows that for the instationary case the diffusion of water controls the diffusion velocity.

The results which shall be presented show that the same clays may completely lose their mineralogical barrier capability, i.e. their positive adsorption and sealing properties through reacting chemicals.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THERMAL DEHYDRATION OF ALLOPHANE IN RELATION TO ITS MORPHOLOGY

Teruo Henmi

Department of Agricultural Chemistry, Faculty of Agriculture,
Ehime University, Matsuyama 790, Japan

Allophane is a naturally occurring inorganic colloid composed of hydrous aluminosilicate. The material frequently exists as a main component of clay in soils derived from volcanic ash and podzolized soils, governing physical and chemical properties of such soils. Even though the aluminosilicate is amorphous or poorly-ordered in X-ray crystallography, recent high resolution electron microscopy has revealed that the silicate possesses a definite morphology characterized by very small hollow spherules with diameter of 35-50 Å. There are many holes on the wall of the spherules. From the morphology, it is expected that allophane has at least two kinds of micropores which can accommodate water molecules in them, intra-spherule pore and inter-spherule pore.

The purpose of the present study is to investigate the waters adsorbed on allophane in relation to its spherical morphology, by means of thermal analysis.

Allophane samples were prepared as follows. Weathered pumices which originated from different volcanoes in Japan were collected, and fine clay fractions ($<0.2 \mu\text{m}$) were separated from the central part of pumice grains to avoid possible admixture of primary minerals like volcanic glass and other impurities. The fine clay fractions were examined mineralogically by some conventional analyses (X-ray diffraction method, infrared spectroscopy and chemical analysis etc.), and confirmed to be allophane. Furthermore, electron microscopic observation showed that the clay fractions were aggregates composed almost only of the hollow spherules, indicating that the present samples were pure allophane. For obtaining information on a mode of presence of

water molecules in allophane, a thermogravimetric analysis was carried out with a microcomputer-controlled heating device in the manner that the samples (10 mg) were heated to increase their temperature by 5°C and allowed to retain them at the temperature for 30 min and then recorded their weight, and repeatedly did by the same way, from 20°C (room temperature) to 200°C. And then, the weights of samples were plotted against the retention temperatures. Crystalline clay minerals such as montmorillonite and halloysite were also analyzed to take reference data on adsorbed water.

The plots showed that as retention temperature rose the weight decreased linearly with breaks in two at the temperatures of 85 and 140°C for the allophane samples. This indicates that there generally are three types of water molecules present in allophane: those molecules can be thermally removed up to 85°C, 85°C to 140°C, and over 140°C, tentatively designated type I, type II and type III, respectively, and shows that the water of type III is most strongly adsorbed on the material, and that of type I most weakly. The type III may partly be contributed by the structural OH. Meanwhile, the weights of crystalline clay minerals decreased until the temperature of around 100°C, and almost no weight loss was recognized over 100°C. This showed that the water molecules adsorbed on those crystalline clays were almost completely removed by heating up to 100°C, and hence weakly held compared with the water on allophane. The prevailing method for determining H₂O (-), adsorbed water of clays, which is usually based on a loss of weight between materials dried at room temperature and at 105-110°C, was found suitable for crystalline clay but inadequate for allophane.

The measured value of the water content of type II was approximately 10 % (based on 140°C oven-dry weights) for all the allophane samples. The value was compatible with calculated value of the content of water in the space of intra-spherules. For the calculation, specific gravity of 2.72-2.78 g/cm³, wall thickness of 7-10 Å and outer diameter of 35-50 Å were used for the allophane spherule. The observed compatibility is suggestive of the type II corresponding with the water molecules present in the intra-spherule pores. Consequently, it is inferred that the types I and II are ascribable to the water molecules respectively occupying inter-spherule pore and intra-spherule pore, and the type III to the molecules bonding to aluminium atoms in the

circumference of hole of the wall. Some H_2O (+) (structural OH) may be involved in the type III, as described above.

The obtained results on the relationship between the state of water molecules of allophane and its morphology give an important information for better understanding of soil water upon effective utilization of soils in various fields. Method, which employs the oven-drying temperature of $140^\circ C$, can be proposed to measure the content of H_2O (-) for amorphous or poorly-ordered clay materials.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE DISPERSION OF CHARGE IN TETRAHEDRAL SHEETS OF PHYLLO-
SILICATES.

C.P. HERRERO, J. SANZ AND J.M. SERRATOSA.

Instituto de Ciencias de Materiales, CSIC., c/ Serrano 115
dpdo, Madrid-28006, Spain.

^{29}Si NMR spectra of phyllosilicates 2:1 consist of several components which correspond to the different possible environments of Si in the tetrahedral sheets, i.e. Si surrounded by 3Si, 2Si1Al, 1Si2Al and 3Al⁽¹⁾. Si,Al distribution can be expressed in terms of the relative distribution of Al cations in the tetrahedral sheets⁽¹⁻³⁾. The analysis of this distribution has been made by means of certain parameters deduced from the ^{29}Si NMR spectra and also by comparison between experimental and model generated line intensities. This study has confirmed the avoidance of Al in contiguous tetrahedra (Loewenstein's rule) and has shown the existence of other restrictions which favour a higher homogeneity and dispersion of tetrahedral aluminium over the sheets^(4,5).

For all the analyzed layer silicates, with an Al fractional content between 0.12 and 0.5, the model that best fits the experimental NMR results is one in which the number of Al per hexagonal ring is maintained as close as possible to the average value corresponding to each composition⁽⁴⁾. This model favours a homogeneous dispersion of charge deficits on the tetrahedral sheets of these aluminosilicates. However, the maximum dispersion of tetrahedral charge deficits is clearly not present in these minerals (figure 1), demonstrating that Dempsey's rule claimed for zeolites is not operating in phyllosilicates.

It is clear from our work that the conditions found to be operative in this cation distribution do not require it to follow a regular pattern. This conclusion agrees with those obtained by diffraction methods according to which only in a few cases there are clear evidences for long-range order.⁽⁶⁾

In figure 2 we show the influence of the relative dispositions "meta" and "para" of Al on the proportions of the different Si environments for the tetrahedral composition Si_3Al . After an examination of this figure, it is clear that a disordered mixture of both types of dispositions is necessary to explain the ^{29}Si NMR spectra of samples with that composition. Only for samples with fractional Al content greater than ~ 0.3 , probabilities for meta are higher than those for para dispositions. For the composition of margarite (equal fractions of Al and Si) all Al are in meta disposition in rings with 3Al .

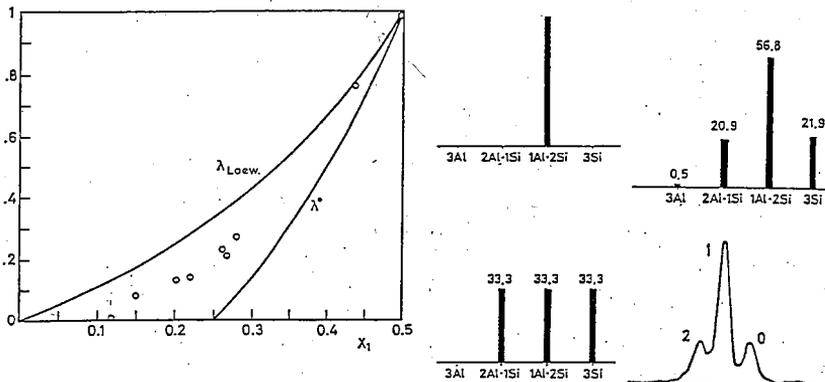


Figure 1: Probability of meta dispositions versus Al fractional content for Loewenstein's (λ) and Dempsey's (λ^*) models. Open circle represent experimental values.

Figure 2: Experimental and model generated intensities for patterns in which Al is disposed in a) para, b) meta and c) random distribution of Al in hexagonal rings with 2 Al.

REFERENCES

- 1 Sanz, J. and Serratosa, J.M., J. Amer. Chem. Soc., 106, 4790 (1984).
- 2 Lipsicas, M., Raythatha B.H., Pinnavaia, T.J., Jhonson, I.D. Giese, R.F. Jr., Costanzo, P.M., Robert, J.L., Nature, 309 604, (1984).
- 3 Barron, P.F., Slade, P., Frost, R.L., J. Phys. Chem., 89, 3880 (1985).
- 4 Herrero, C.P., Sanz, J. and Serratosa, J.M., Solid State Comm., 53, 151 (1985).
- 5 Herrero, C.P., Sanz, J. and Serratosa, J.M., J. Phys. C: Solid State Phys., 18, 13 (1985).
- 6 Bailey, S.W., Clays and Clays Miner., 32, 81 (1984).
- 7 Herrero, C.P., Sanz, J. and Serratosa, J.M., J. Phys. C: Solid State Phys., 19, 4169 (1986)



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

INFRARED FTS - ELLIPSOMETRY OF CLAY MINERALS

T. HÖDING¹, A. RÖSELER², M. STÖRR¹

¹Department of Geological Sciences, University of Greifswald (G.D.R.), Jahnstr. 17a, Greifswald, 2200, G.D.R.

²Academy of Sciences of the G.D.R., Central Institute of Optics and Spectroscopy, Rudower Chaussee 6, Berlin, 1199, G.D.R.

To study the reaction of clay minerals in the IR region, IR spectra of several structural types of clay minerals were measured in the region 1200-400 cm^{-1} , using three different methods: absorption measurements in transmission (KBr-method), infrared Fourier transform spectroscopy - ellipsometry (FTS-ellipsometry) and measurements of thermal emission. For the two latter methods the samples were prepared as textures. Among the minerals investigated were kaolinite (Bath/South Carolina), montmorillonite (Wyoming, clay spur), nontronite (Garfield/Washington) and pyrophyllite (Robbins/North Carolina).

The data obtained by the FTS-ellipsometry method are spectra of the dielectric function ($\hat{\epsilon}$), refraction indices (n) and absorption number (k) in the above-mentioned region. These quantities cannot be determined in geological samples using conventional techniques.

The imaginary part of the dielectric function (ϵ_2) shows the genuine frequencies of resonance between sample and radiation. These data are more accurate than data from absorption measurements in conventional spectrometers. The spectra of refraction indices, which have not been obtainable until now, often show additional details. The spectra of the refraction indices show peaks which are situated some wave numbers lower than those of the ϵ_2 -spec-

tra, i.e. at first the refraction index increases followed by an increase in the real frequency of resonance.

Thus peaks of the n-spectra of kaolinite Bath at 463, 528, 1003 and 1028 cm^{-1} are followed by peaks at 469, 540, 1009 and 1034 cm^{-1} in the spectra of ϵ_2 (absorption peaks of these structures: 473, 540, 1008 and 1032 cm^{-1} according to VAN DER MAREL & BEUTELSPACHER, 1976).

The Si-O-Fe-vibration of nontronite, a very characteristic structure, appears at 486 cm^{-1} in the n-spectra, compared to 490 cm^{-1} in the ϵ_2 -spectra (VAN DER MAREL & BEUTELSPACHER, 1976: 492 cm^{-1}).

Still higher wave numbers are found in the spectra of the absorption number. The quantity ϵ_2 can be considered as relevant to the interpretation of all spectra. Refraction index and absorption number are contained in this quantity because of the equation $\epsilon_2 = 2 n k$.

Measurements of thermal emissivity are easy to carry out in the Fourier transform spectrometer. The samples are heated with a thermostate up to about 345 K. The results are spectra of thermal emission. They permit a precise differentiation between the various clay minerals. This laboratory method offers the possibility to collect data which may be helpful in evaluating results of remote sensing.

The bands in the spectra of all these quantities are in good correlation to each other and an assignment of vibrations is possible in accordance with the bibliography and in an empirical way.

References:

VAN DER MAREL, H. W. and BEUTELSPACHER, H.: Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures.- Amsterdam-Oxford-New York; 1976, 396 pp.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MIXED-LAYER MINERALS FROM TALAGIU

V. IANOVICI, G. NEACSU* and VASILICA NEACSU*

National Council for Environmental Protection, 5 Bd Ilie Pintilie
71902 Bucharest, Romania

* Geological and Geophysical prospecting Enterprise, 1 Caransebes
Str., 78344 Bucharest 32 Romania

The hornblende- and pyroxene-bearing andesites occurring in the Neogene caldeira at Talagiu area (W Romania) have been argillized by hydrometasomatic diffusion on a large area (3/5 Km).

253 samples collected from this zone have been analysed by X-ray diffraction, the main clay minerals are smectites, kaolin minerals, chlorites, pyrophyllite, micas, interstratified clay minerals and allophane. Mixed-layer minerals of various types are frequently found (45 percent of the analysed samples contain interstratified clay minerals). Regularly interstratified clay minerals are of Al-chlorite-smectite (tosudite), smectite-illite (rectorite) or chlorite-illite type; partially ordered minerals of IIS or PPS Kalgberg-type occur more rarely.

Randomly mixed-layer minerals are of smectite-illite type, more rarely of chlorite-illite, chlorite-pyrophyllite, illite-pyrophyllite, smectite-pyrophyllite or chlorite-smectite type, and their Reichweite is usually 1. Randomly interstratified clay minerals of smectite-chlorite-illite type are very rarely found.

This paper describes in details the interstratified clay minerals used as indicators in the prospection and exploration of the ore deposits in the Talagiu area (gold telluride veins and complex sulphides, irregular porphyry-copper bodies).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

DISTRIBUTION OF CLAY MINERALS IN A SANDSTONE RESERVOIR,
SLEIPNER FIELD, NORTH SEA

I.K. Iden¹, H. Qvale¹, R.E. Ferrell², K. Reksten³ and A. Hurst⁴

1 Institute for Energy Technology, Box 40, N-2007 Kjeller, Norway

2 Basin Research Institute, Louisiana State University, Baton Rouge,
Louisiana 70803-4101, USA

3 Institute of Physics, University of Oslo, Box 1048, N-3016 Blindern,
Oslo 3, Norway

4 Statoil, Forus, Box 300, N-4001 Stavanger, Norway

This presentation which reports results of a study, supported by Statoil, on the clay mineralogy of sandstones from the Heimdal Field, Norwegian North Sea. Core samples from the depths interval 2407-2419 m were examined.

The samples are quartz arenites with a porosity of 20-30%. The sheet silicates, which are scarce and fine-grained, occur as three major morphological varieties: 1) detrital grains; 2) grain coatings; 3) clusters in pore spaces. The latter may be further subdivided: 3a) fine laminated aggregates; 3b) fine dense aggregates with more clearly defined grain boundaries.

Analyses by SEM, TEM and microprobe in most cases revealed composite grains, i.e. more than one mineral phase is present. The analyses have therefore been recalculated into the structural formula for both "mica", i.e. illite and smectite (22 O) and chlorite (28 O). The majority of samples are compatible with both structural types, indicating mixtures of chloritic and illitic/smectitic material.

Detrital (type 1) grains were identified microscopically as chlorite, white mica, biotite and glauconitic pellets. Detrital clay-casts of smectitic composition are found at the other localities in the same formation. In $MR^3-2R^3-3R^2$ diagrams, the detrital grains plot either as illites or chlorites. Grains showing incipient delamination, consist of both illitic and chloritic mineral phases. The grain coatings (type 2) are mixed layer illites and smectites, with no chlorite. The majority of the clusters (type 3) exhibit compositions intermediate between illite and chlorite, and the data span the entire compositional range between the two (Fig. 1). A typical picture is one in which clear, chloritic clay flakes are surrounded by irregular flaky masses of illitic material. Variation diagrams of oxides vs. silica support the interpretation that detrital sheet silicates have reacted with pore solutions, and were transformed to smaller grains of illitic/smectitic compositions, as seen in the type (3b) aggregates. The compositions vary continuously depending on the degree of reaction completeness. In this process muscovite has consumed Si, and released K + Al. The chlorites have consumed both Si and K, released Fe + Mg, with constant Al.

The TEM analysis was concentrated on the type 3a aggregates. They are sheaf-formed, the clay grains ranging down to a few tens of Å in width. Lattice periodicities of 7 Å, 14 Å and 10 Å indicate berthierines, chlorites and illites or collapsed smectites (Figs. 2 and 3). Compositions are dominated by Al-rich chlorites, with no significant difference between 7 Å and 14 Å types. This is shown in Fig. 4, an AFM-diagram of all analyzed grains within the pore space aggregates. Mixed-layering of chlorite-berthierine is observed, as

well as illite (10 Å) layers within chlorite, and within chlorite/berthierine, although the chlorites predominate.

These aggregates are interpreted as having formed by precipitation from solution, with an external supply of Al. The metastable 7 Å/14 Å chlorite interlayering is due to rapid crystallization at relatively low T.

The grain coatings were formed at an earlier stage either by precipitation from solution, or from migrating fine particles.

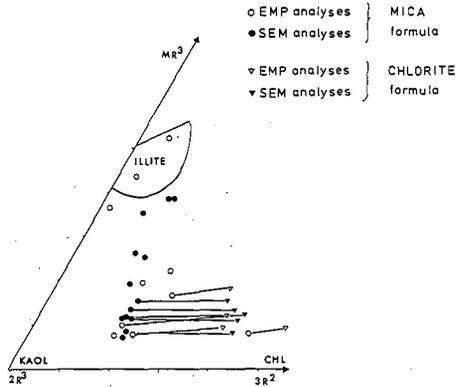


Fig. 1

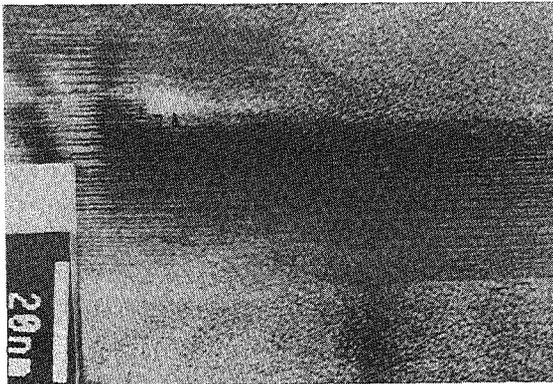


Fig. 2

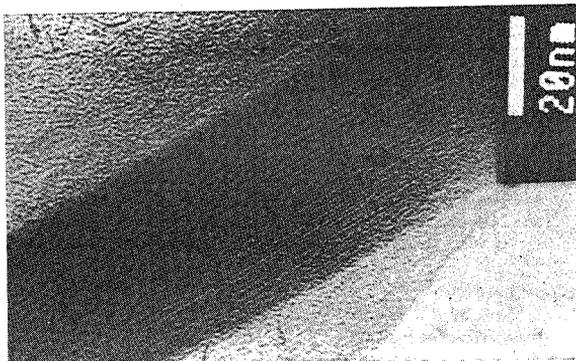


Fig. 3

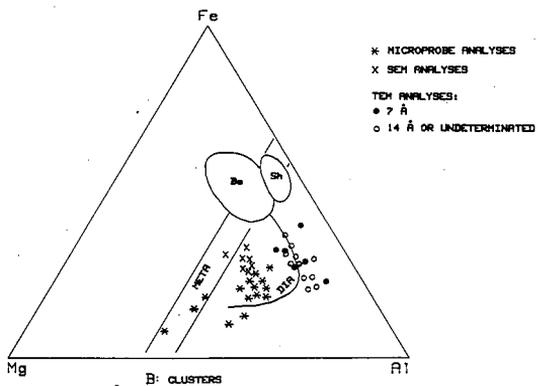


Fig. 4



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PORE SIZE DISTRIBUTION AND ADSORPTION SELECTIVITY OF SEPIOLITE

S. INAGAKI AND Y. FUKUSHIMA, H. Doi and O. Kamigaito

Toyota Central Res. & Develop. Labs., Inc., Nagakute, Aichi, Japan.

Sepiolite is fibrous clay mineral with fine tunnels running parallel with the fiber. Chemical reactions, such as synthesis of organic molecules, polymerization and thermal or chemical decompositions, in the tunnels should be one of the most excellent applications of sepiolite. Although the tunnel structure has been confirmed by X-ray powder diffraction (Brauner and Preisinger, 1956) or electron microscopes (Tchouber et al, 1973), adsorption properties of the tunnel have not been clarified yet. Adsorption properties of sepiolite have been also studied by Barrer et al (1954), Serna and Van Scoyoc (1979) and etc. However, the distinction between the adsorption in the tunnel and that on the outer surface was still ambiguous.

The relative surface area of outer surface and in the tunnels were measured by BET method combined with adsorption of water molecules in the tunnels in this work. Adsorption selectivities in the sepiolite tunnels were also studied.

EXPERIMENTAL

A sepiolite sample used in this study was a natural sepiolite from central Anatolia, Turkey, whose properties shall be reported separately. (Fukushima and Shimosaka, 1987). About 0.2g of granular (0.5-2.0 mm in diameter) samples were vacuum dried for 2 hours at 110°C. Water molecules were adsorbed by the sepiolite sample under several vapour pressures, followed by measurements of BET-surface area by means of N₂ gas adsorption. Pore size distribution of dried sepiolite was also calculated by Inkley (Cranston and Inkley, 1957) method and the N₂ adsorption isotherm curve.

The BET-surface areas of the sepiolite, vacuum dried at 25°C and 150°C, for water, ammonia, nitrogen, ethanol, pyridine, benzene, tri-methylbenzene and t-butylbenzene were also measured by using a micro-balance with quartz spring.

RESULTS AND DISCUSSIONS

The result of the pore size distribution by means of Inkley method shows the existence of pores whose mean diameter is about 50 Å. The data in the region of small pore size, however, contains much errors.

Figure 1 shows the BET-surface area of the sepiolite adsorbing water molecules under various vapour pressures. Water molecules were condensed and filled the pores, which decreased the surface area of the sample. The mean diameter of the pores filled with water depends on the vapour pressure and can be calculated by Kelvin equation (Zigmondy, 1911). The diameter of the pores, which is so called Kelvin-condensation diameter, is also shown in Figure 1. The result shows that the total surface area of the sample is about 290 m²/g, which is a sum of 120 m²/g of the surface in the tunnel and 170 m²/g of outer surface. The ratio of the surface areas in the tunnel and that

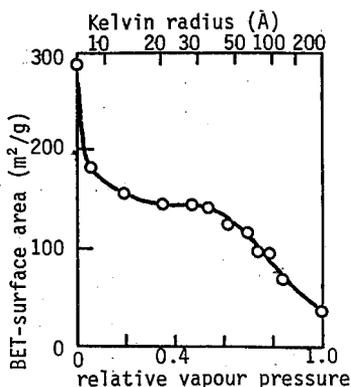


Figure 1. Surface areas of the sepiolite adsorbing water under various vapour pressures.

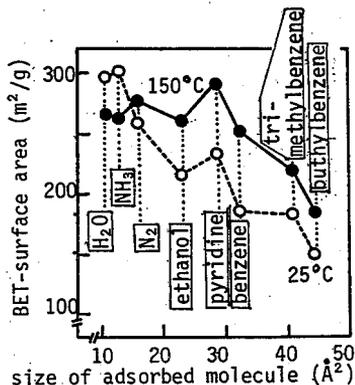


Figure 2. Surface areas of the sepiolite vacuum dried at 25°C and 150°C for various molecules.

of outer surface suggests that the mean thickness of the sepiolite fiber used in this work is about 95 Å, which agrees well with the TEM observation.

In Figure 2, surface areas for the various molecules are shown. The results suggest that although water and ammonia adsorbed both in the tunnels and on the outer surface of the sepiolite vacuum dried at 150°C, others adsorbed only on the outer surfaces. On the other hands, molecules except for trimethylbenzene and t-butylbenzene seems to be able to penetrate into the tunnel of that vacuum dried at 25°C.

REFERENCES

- Barrer R.M., Mackenzie N and Macleod D.M. (1954), J. Phys. Chem. Ithaca, 58, 362-370.
- Brauner, K. and Preisinger, A. (1956) Teeschemaks Min. Petr. Mitt. 6, 120-140.
- Cranston R.W. and Inkley F.A. (1957) Adv. in Catalysis 9, 143.
- Fukushima Y. and Shimosaka K. (1987) Abstract of this conference.
- Serna J.C. and Van Scoyoc G.E. (1979) Proc. Int. Clay Conf. 1978, Oxford, pp197-206. Elsevier Sci. Publ. Co., Amsterdam.
- Zigmondy R. (1911) Z. anorg. Chem. 71, 356.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAY-MINERAL DISTRIBUTION IN MARINE AND NON-MARINE EOCENE DEPOSITS OF THE SE EBRO BASIN (SPAIN)

M. INGLÉS AND P. ANADÓN*

Depart. Geoquímica, Petrología, Prosp. Geol. Univ. Barcelona (Spain).

*Institut J. Almera, CSIC, c/ Martí i Franqués s/n. 08028-Barcelona. (Spain).

The Eocene sequence along the central part of the SE margin of the Ebro Basin (Igalada area) consists of alternating marine and non-marine deposits up to 2000 m thick. This sequence records two major transgressive-regressive cycles that occurred through the Eocene in the Ebro Basin: Ilerdian-Cuisian Cycle (early Eocene) and Lutetian-Priabonian (middle to late Eocene). During the Ilerdian transgressive maxima a shallow carbonate platform existed in the studied area leading to the deposits of the Orpi Fm. (30 to 100 m thick) mainly consisting of limestones and dolostones. The late Ilerdian-Cuisian regression culminated in the development of lacustrine and lagoonal environments where mudstones and carbonates were deposited. (Pontils Group, lowermost levels). Non marine conditions persisted though the Cuisian-early Bartonian (early-middle Eocene) and resulted in the deposition of the Pontils Group (up to 900 m thick). Only near the beginning of the Bartonian areally restricted lagoonal deposits up to 100 m thick, announced the subsequent Bartonian transgression.

During the late Bartonian-early Priabonian (late Eocene) the studied area was affected by the Bartonian transgression, responsible for deposition of the Santa Maria Group. This unit, up to 1000 m thick, is composed of fine-grained terrigenous rocks and subordinate carbonates. Close to the basin margin, these marine desopits interfinger with deltaic and fan-delta facies (Montserrat Conglomerate). The marine sequence ends with the Odena Gypsum, accumulated in restricted areas near the basin margin during the late Eocene (Priabonian regression).

X ray diffraction, TEM and SEM with EDAX facilities and chemical analyses of samples from mudstones and marls along the Eocene sequence

(Pontils and Santa Maria Groups) indicate that clays from marine and diverse non-marine and transitional environments can be distinguished from one another on the basis of the clay-mineral content:

- Pontils Gr, lowermost levels. Transitional deposits are characterized by illite and chlorite. In addition, minor kaolinite is present in lagoonal subaerial deposits. In lacustrine mudstones, the most common assemblage is illite and smectite, sometimes with palygorskite. Upwards in the sequence, red mudstones with interbedded sandstones were deposited in well-drained floodplains and mud flats. Several hydro-morphic paleosols are present. Illite with minor amounts of chlorite and kaolinite constitute the most frequent assemblage observed in this red bed succession. However, variegated mudstones related to local poorly-drained areas are characterized by palygorskite prevailing over illite.

- Pontils Gr, intermediate levels. Through the middle Eocene, mud-flat environments prevailed in the studied area leading to thick red sandy mudstone sequences with sparse interbedded channel sandstones several m thick. The red mudstones are rich in palygorskite with minor amounts of illite.

- The upper levels of the Pontils Gr were deposited in a complex assemblage of non-marine and transitional, subenvironments. Illite and palygorskite are the most common clay-minerals in the sediments from flood plains and mud flats. Minor amounts of chlorite, smectite and kaolinite have been observed in several samples. Mudstones and marls interbedded in thick fresh-water paludal limestones show an assemblage dominated by illite and smectite, although sometimes are rich in kaolinite and chlorite. Shallow lacustrine mudstones and marls, in some cases associated with dolostones and nodular gypsum beds (sabkha facies), are characterized by large amounts of palygorskite and smectites, with minor illite. The same assemblage plus chlorite is found in lagoonal mudstone-dolostone sequences, whereas chlorite and illite with minor smectite constitute the most frequent assemblage in clastic lagoonal sequences.

- The most frequent clay-minerals assemblage in the marine mudstones from the Santa Maria Gr, is formed by illite, chlorite and smectite. Kaolinite is also present in several samples. A similar clay-mineral distribution is found in laterally equivalent non-marine deposits.

In the studied sequence the original detrital assemblage probably were formed by a high concentration of illite, associated with smectite and chlorite, and minor amounts of kaolinite. A similar clay-mineral assemblage has been observed in marine and siliciclastic lagoonal mudstones.

Illite is the only mineral present in all the studied samples. In general, the illite concentration is high and shows a good crystallinity in the red mudstones from the lower Pontils Gr, in the sabkha sediments and in that deposits formed under stable subaqueous conditions.

Smectite is well preserved in the sediments from sabkhas and subaqueous environments. It is absent in the sediments that were subjected to subaerial exposure and water-table oscillations (flood-plain and mud-flat deposits).

Palygorskite, with minor amounts of degraded illite and sometimes chlorite, is the dominant mineral in flood-plain and mud-flat sediments. Palygorskite is absent in true lacustrine sediments and, on the other hand, dominates in sabkha and carbonate-lagoonal sediments.

According to these clay-mineral distribution trends the lacustrine, lagoonal and marine sediments preserve the detrital clay-minerals. In that environments which underwent repeated flooding and dissection phases chlorite and smectite were eventually eliminated and palygorskite formation was favoured. In the mud-flat and flood-plain sediments there is a conspicuous abundance of calcite and dolomite. Dolomite rhombohedra partially dissolved have been observed in SEM. On the dolomite-crystal faces, submicron fibers of palygorskite have been recognized. TEM observations confirms that palygorskite frequently forms laminar aggregates of fibers with a parallel arrangement. In samples with smectite and palygorskite, smectite laminae display a fibrous aspect in their borders. These evidences suggest that in mud-flats and flood-plains palygorskite mainly were formed by transformation of smectite in a Mg-rich environment.

In the sabkha facies, the abundance of smectite and palygorskite, frequently associated with dolomite and chert suggest palygorskite neof ormation in a Si and Mg rich environment.



THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS

Seville, Spain, 1987. Sociedad Española de Arcillas

USE OF SMECTITE-ZEOLITE ALTERATION PRODUCT OF RHYOLITIC
IGNIMBRITE FROM PUERTAS VIEJAS /NICARAGUA/ IN THE
MANUFACTURE OF TILES

J. JIRÁNEK

Department of Raw Materials, Geological Survey /ÚÚG/,
Malostranské nám. 19, 118 21 Praha 1 /Czechoslovakia/

Nicaragua is short in kaolins having noncommercial deposits restricted to granite massifs and Recent volcanics. Therefore, the local tile manufacture should use also other materials of light colours after firing, even if untypical. The 70 % of the country area is covered by Tertiary volcanics altering to bentonitic materials with zeolite admixture in all primary occurrences. The raw material from Puertas Viejas /Km. 69.5 Panamerican Highway-North/ is of the best quality of the six biggest deposits studied.

The fresh parent rock - rhyolite ignimbrite from the base of the Upper Miocene /the Lower Coyol Group/ - is composed of phenocrysts of quartz, oligoclase-andesine, \pm K-feldspar, basaltic hornblende, an ore mineral, devitrified pumice fragments and ash particles inserted in the vitrite matrix. By probably hydrothermal alteration processes in the border of a vast ancient caldera, a white relatively solid clayey rock /volume weight of $1.49-1.71 \text{ g cm}^{-3}$ / arose. It is formed in 90 % by a mixture of clay minerals, zeolites, and fine silica minerals /altered mesostasis, pumice fragments and ash particles/; the phenocrysts - with the exception of K-feldspar and hornblende - remain preserved. Within the mesostasis, some 5 % of newly formed zeolite columns appear. The semiquantitative X-ray analysis established 41 % of cristobalite + tridymite + quartz, 36 % of smectite, 18 % of K-feldspar, 5 % of zeolites /clino-

ptilolite prevailing/ and traces of goethite. According to the results of the EDAX-analysis, smectite was specified as a Fe-rich kind /nontronite/.

During the alteration process, the SiO_2 content increased from 69.80 to 78.39 % /the new-formation of the free silica forms/ while that of Al_2O_3 relatively decreased from 19.16 to 14.17 %. The contents of rest of the oxides did not differ substantially. The content of the smectite mineral increased within the weathered surface portions of the deposit. Rather high contents of Fe_2O_3 in all the samples /1.64-3.75 %/ exclude the use of the altered rock for white tiles.

The grain-size of the crude /carefully disintegrated/ raw material is rather coarse: 11.7-77.4 % are formed by particles over 2 mm and only 8.2-33.6 % are formed by particles below 0.063 mm. Because the local tile industry is based only on a simple dry treatment /crushing and milling/, all the tests were performed on the ground raw material as a whole, without separation of any fraction.

The raw samples are white-grey to - rarely - light beige, medium to highly plastic /water of plasticity: 23.0 - 38.3 %/. The shrinkage after drying reaches 2.28 to 8.22 %, the crushing strength under bending is 13.6-19.7 kg cm^{-2} . The whiteness - because of the non-separated mixture of the free silica forms - is too low /51.7 % of the absolute scale/, even in the case of white colours.

As a supposed raw material for ceramics the altered ignimbrite possesses low refractoriness values: by firing to 999 and 1045°C the absorptivity remains excellent while at 1125°C some - and at 1280°C all the samples are sintered and fusion and deformation begin. The free silica mixture functions as a natural grog. The bodies fired to 1125°C possess - due to the mixture - acceptable values of total shrinkage /7.43-14.02 %/ and a very high crushing strength under bending /68.1-166.1 kg cm^{-2} /, while the absorptivity sometimes is too low /2.1-25.4 %/. The colour of the fired bodies is light grey to pink, in some cases up to reddish-brown. No dependence on the Fe_2O_3 and FeO

contents nor smectite content nor raw colour was revealed; the contribution of the variable amount of the altered originally lithic fragments /pumice etc./ is supposed. The variations of the technological properties are influenced by the smectite-free silica proportion: while smectite increases the plasticity, shrinkage /both in drying and firing/, and the absorptivity of the fired bodies, the rise in the quartz content increases the strength.

The described characteristics can be combined and/or corrected when mixing with kaolins: a raw kaolin admixture results in mainly higher refractoriness, white colour after firing, and good absorptivity of the fired products, while the altered ignimbrite helps to save imported raw materials and secures high strength of the products. Numerous industrial tests of the mixtures with local kaolins /Volcano Momotombo, Volcano Mombacho/ and with addition of wollastonite or talc, were performed. The recommended composition comprises 45 % of the altered ignimbrite, 45 % of kaolin and 10 % of wollastonite; the amount of the altered ignimbrite can be lowered up to 25 % in case of the reddish-brown colours after firing. Occasional bending of the tiles is being solved by two firings /the first at 1150°C and the second - enameled - at 980°C/. The industrial production has started in 1984. Further, the use of the raw material as a filler in soap production was tested.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS AND GEOCHEMISTRY OF THE ARKOSE-TYPE KAOLINS IN
THE PLZEŇ BASIN, CZECHOSLOVAKIA

J. JIRÁNEK, J. JIRÁNKOVÁ^x

Department of Raw Materials, Geological Survey /ÚÚG/,
Malostranské nám. 19, 118 21 Praha 1

^xGeoindustria, n.p., Přístavní 24, 170 04 Praha 7 /ČSSR/

Continental sediments of the Upper Carboniferous of the Bohemian Massif are represented by an intermontane molasse of the Variscan Orogeny which culminated in the Namurian-Westphalian boundary by the Sudetic phase as a consequence of the collision of the North- and South-European paleoblocks. The molasse sediments cover parts of the W, N and NE Bohemia and they stratigraphically range between the Westphalian B - Stephanian C. The sedimentary filling is mostly composed of arkoses to arkosic sandstones of various grain-sizes, with interbeds of carbon, claystones and sandy claystones, frequently with a volcanoclastic admixture produced by mostly rhyolitic ignimbrite volcanism in the north periphery of the zone /the Teplice rhyolite body and Saxony/ during the Westphalian A - Autunian.

A weak partial kaolinization took place locally in great part of the Upper Carboniferous profile during the sedimentation; plagioclases are the first minerals that underwent the alteration process. The rocks contain a completely kaolinized biotite together with a fresh one, of different provenances. Workable kaolin deposits have developed in the westernmost Plzeň /Pilsen/ Basin /Kužvart et al. 1975/. As it follows from the study of heavy minerals, the clastic material is derived from granite massifs, from mesozonal-katazonal crystalline complexes, and from non-metamorphosed to epizonally metamorphosed Proterozoic rocks /clay shales, silicites, volcanics/. The Proterozoic material prevails in the varicoloured claystones forming

intercalations even within the kaolin sequences of mostly granitic origin. There is a transgression of the sediments of the Plzeň Basin over two granite bodies of Cadomian age: the Merklín Massif /S/ and the Tis-granite of the Louny Massif /N/. The latter served as a source of the most of the K-feldspars of the Plzeň- and Central Bohemia Basins, as follows from the study of triclinicity, Ab-contents and trace elements of K-feldspars.

The workable kaolin deposits have developed in all the four formations of the Plzeň Basin: the Kladno F. /Westphalian B-D/, the Týnec F. /Stephanian A/, The Slaný F. /Stephanian B/ and the Líně Formation /Stephanian C/. The greatest deposits are located in the Týnec Formation /Horní Bříza, Kaznějov/. Climatically conditioned kaolinization processes took place in the area of the Bohemian Massif during two periods: in the Upper Carboniferous and in the /Upper Cretaceous-/ Miocene; the two phases acted also throughout the Plzeň Basin. Several genetic types of kaolin deposits are involved. The deposits of the oldest Kladno Formation originated by kaolinization of the outcrops of arkoses both in the Carboniferous and during the younger period of kaolinization. The kaolins of such deposits are passing down through the so called "feldspar kaolins" into non-kaolinized arkoses. However, most of the deposits have arisen in the Carboniferous: during the transport of material, during its sedimentation, and probably also shortly after deposition. Some of them /both located inside and outside the Basin/ were probably removed and redeposited in the form of dense kaolin suspensions that carried even extremely coarse clastic material, and probably fragments of fresh feldspars. We suppose that this genetical type of kaolin has taken place in the case of the greatest Kaznějov deposit as testified by enormous thicknesses of kaolins - up to 120 m, by alternation of kaolins and fresh arkoses in the basement of the deposit, by red claystone intercalations inside the white kaolins, by findings of fresh or subsequently kaolinized angular

feldspars in the kaolins, and by geochemical evidence /Jiránek 1976, 1977/. The younger /Cretaceous-/ Miocene phase of kaolinization was manifested there in the form of bleaching /deferrizing/ of the coloured portions along fault systems /the Horní Bříza deposit, Jiránek 1976/.

Petrographically, the mined kaolins include silty-sandy to clayey-sandy conglomerates, conglomeratic silty sandstones and clayey-silty sandstones. Kaolinite is principally present in the form of cement /up to 30%/. The geochemistry was studied in a 61 m thick vertical profile through the Kaznějov deposit /Jiránek 1982/. As a typical arkose-type kaolin, the Kaznějov kaolin is characterized by relatively higher contents of various trace elements /Sr, Ni, V, Pb, Mn, Zn, Ba/. No variations of the trace elements with the depth were established; a striking enrichment in all the trace elements analyzed /Be, C_{inorg}, C_{org}, Ca, Cr, F, Fe, Mg, Mn, Ni, Pb, Sr, Ti, V, Zn/ was determined in the intercalations of reddish clayey-silty sandstone with high content of fraction below 20 μm /simultaneously accompanied by elevated contents of fine quartz/. The distribution of trace elements in the Kaznějov kaolins is in conflict with the principles that should control the weathering processes occurring in kaolin profiles: The content of all the traces increases with the decreasing content of kaolinite, and rises also with the increasing contents of CaO and alkalis /Na₂O above all/. High contents of Mn /while that of Cr remain relatively low/ indicate an oxidizing environment during the genesis of kaolin.

R e f e r e n c e s

- Jiránek, J., 1976: Geological evidence of the genesis of the Horní Bříza and Kaznějov kaolin deposits: Proc. 7th Conf. Clay Mineralogy and Petrology, 243-250. Praha.
- , 1977: Geology, petrology and genesis of the kaolin sediments of the Horní Bříza and Kaznějov deposits in the Plzeň Basin: Folia Mus. Rer. natur. Bohemiae occident., Geologica, 8, 1-34. Plzeň.

Jiránek, J., 1982: The Kaznějov deposit: grain size, geochemistry and whitening of kaolins in its vertical section /In Czech/: Sbor. geol. Věd, Lož. Geol., Mineral., 24, 141-160. Praha.

Kužvart, M. - Neužil, J. - Pešek, J. - Šindelář, J., 1975: Origin and age of the kaolin deposits in the Plzeň Basin /In Czech/: Sbor. geol. Věd, Lož. geol., Mineral., 17, 125-194. Praha.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THERMAL EXPANSION OF SOME VERMICULITES

A. JUSTO*, C. MAQUEDA AND J. L. PEREZ RODRIGUEZ.*

* Instituto de Ciencia de los Materiales.

Instituto de Recursos Naturales y Agrobiología. Apartado
1052. Sevilla. Spain.

The principal characteristic in which most of industrial uses of the vermiculite are based is its property of exfoliation when the mineral is suddenly heated up to a high temperature. This property of exfoliation is explained as due to the explosive release of water molecules from between the silicate layers, and causes the flakes to expand in a direction normal to the basal cleavage. The highest expansibility is achieved with regular mica/vermiculite interstratifications, because during thermal shock, the water molecules -- from the vermiculite hit the mica layers, producing a large gap between them (Couderc and Douillet, 1973).

The objective of this work is to show that although the sudden release of interlayer water should be the most important factor in the thermal exfoliation of vermiculite, other factors must influence that process, which in some particular minerals may be very important.

Six samples have been selected for the study (Justo, 1984). Four of them come from two abandoned vermiculite quarries located near Ojén, Málaga (samples P-1 and C-1), and Santa Olalla, Huelva (samples SO-1 and RJ-1). They have been identified by X-ray powder diffractometry, differential thermal analysis, thermogravimetry and chemical analysis as pure -- vermiculites, with moderate to low iron content and almost absence of mica ($K_2O < 0.03\%$). Sample Bu-1 comes from an old iron mine in Burguillos del Cerro, Badajoz, and is composed by vermiculite and regular mica/vermiculite interstratifica

tion. Sample named Ru-1 is a commercial vermiculite from an unknown locality in USSR. It is composed by vermiculite and mica.

The expansibility was measured by the change in the apparent density after thermal shock to 600°C and 900°C, and also after heating up to the same temperatures at a heating rate of 7°C/min.

From the experimental data, it can be concluded that -- those samples containing mica, either as a separate phase or interstratified with vermiculite (samples Bu-1 and Ru-1), present the higher values for the expansibility.

Pure vermiculites give also products with low apparent densities; however, there exist appreciable differences --- among them. Thus, vermiculites from Málaga show higher expansibility than vermiculites from Huelva. Even vermiculites from the same deposit show differences in their expansion values, as for example SO-1 and RJ-1. The differences in -- expansibility cannot be exclusively attributed to the sudden release of the interlamellar water. When vermiculites expanded by thermal shock at 600°C and cooled to room temperature in a dessicator, are again heated to 950°C, also by thermal shock, they suffer another small expansion. This new expansion must be related to water from the hydroxyl groups. It has been found that samples with higher octahedral iron content, show higher values for expansibility at any temperature. This can be related with the influence of the octahedral Fe^{2+} and Fe^{3+} during dehydroxylation (Rausell-Colom and Serratos, 1985; Vedder and Wilkins, 1969).

Sample Bu-1, due to its mineralogical and chemical composition, presents high value for the expansibility. It -- presents a peculiar behaviour as compared with the rest of the samples. Unlike sample Ru-1 and pure vermiculites, most of its expansion takes place at about 600°C, either by thermal shock or with a low heating rate (7°C/min). This sudden expansion is related with the dehydroxylation of the altered mica in the interstratification.

REFERENCES.

- JUSTO,A., 1984. Estudio fisicoquímico y mineralógico de vermiculitas de Andalucía y Badajoz. Thesis. Universidad de Sevilla. 408 pp.
- COUDERC,P. and DOUILLET,PH., 1973. Les vermiculites industrielles: exfoliation, caractéristiques minéralogiques et chimiques. Bull. Soc. Fr. Ceram., 99, 51-59.
- RAUSELL-COLOM,J.A. and SERRATOSA,J.M., 1985. Dehydroxylation of micas and vermiculites. The effect of octahedral - composition and interlayer saturating cation. Miner. petrog. Acta, 29-A, 399-408.
- VEDDER,W. and WILKINS,R.W.T., 1969. Dehydroxylation and -- rehydroxylation, oxidation and reduction of micas. Am. Miner., 54, 482-509.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GEOGRAPHIC DISTRIBUTION AND PARAGENESIS OF CORRENSITE IN ONTARIO,
CANADA

C.R. DE KIMPE AND N. MILES

Agriculture Canada Land Resource Research Centre, Central Experimental
Farm, Ottawa, Ontario, Canada K1A 0C6

Corrensite, a regularly interstratified chlorite/smectite mineral, was found near Sharbot lake, 40 km southwest of Perth, Ontario. The site is located within the Grenville geological province. The latter extends over 2000 km from Ontario, north of the Great Lakes and the Saint Lawrence river, to Labrador and it is approximately 450 km wide. The geology of the Grenville province is very complex. In our study area, rocks of Helikian age (1600 - 850 MY) are represented by the Grenville and Hastings Groups. Both contain sequences of marble, quartzite and paragneiss. Basic and intermediate metavolcanic rocks are found in the lower part of the Grenville and metavolcanic rocks are also intercalated within the metasedimentary rocks. At a later stage, hydrothermal and/or pneumatolytic fluids penetrated these rocks. The primary magmatic gases, which are acid, reacted effectively with the basic rocks such as limestone, that acted as a filter. Various minerals were thus neofomed, among which was phlogopite. Phlogopite was indeed observed as tiny (≈ 2 mm) crystals randomly scattered throughout limestone and marble outcrops, and also as large (≈ 5 cm) crystals in fractures and veins.

Loose material samples were collected in the veins of over 40 limestone and marble outcrops in an area approximately 125 km long and 50 km wide, from Kingston to Ottawa. The samples were air-dried, sieved to pass a 2 mm-sieve, and separated according to particle size. Mineralogical analyses were performed by x-ray diffraction and microscopic observations. In most samples, corrensite was closely

associated with phlogopite, the former mineral being the major constituent of the clay and silt fractions, while the latter was more abundant in the coarser fractions. Microscopic observation of phlogopite books indicated that the interstratified mineral had developed at the expense of the mica through hydrothermal alteration. Whenever corrensite was present, it was indeed found associated with large - or micro-size fractures. On the contrary, individual mica crystals in the rock mass were unaltered.

In this study, corrensite and phlogopite were identified as the most common phyllosilicates present in the marble, but they were sometimes associated with smectite and chlorite, and traces of talc. Non-phyllosilicate minerals commonly observed were carbonates, graphite, feldspar and hematite. In particular, the presence of well-crystallized graphite was indicative of high temperature and/or pressure reaction. However, the prevailing hydrothermal alteration conditions were not adequate to produce kaolinite at the expense of feldspar and mica. Smectite and chlorite, when present, were generally restricted to those outcrops where "ground preparation", i.e. the number of fractures and veins per m^2 , was not large. Ground preparation was indeed considered to be associated with the initial dolomitization of the limestone. When smectite and chlorite were present, the corrensite content was low. In several outcrops northeast of the study area, smectite was the only phyllosilicate besides phlogopite and its possible significance, besides graphite, as an indication of hydrothermal activity is presently investigated.

Near the limit of the present study area, a different corrensite, more likely a chlorite/vermiculite mineral, has been also identified. With respect to the other corrensite samples, it was found at a larger distance from the reported plutons, thus at a place where contact metamorphism was possibly less intense. On the other hand, vermiculite is a common weathering product of phlogopite under temperate climates. The possible formation of this particular corrensite through either weathering or hydrothermal alteration will be considered and some additional samples will be collected and analyzed to better support a general discussion on the corrensite formation in eastern Canada.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**GEOCHEMISTRY OF ROCKS FROM RED BEDS IN OSTRAVA -
KARVINÁ COAL BASIN.**

Z. Klika

Department of Geology and Mineralogy, University of Mining
and Metallurgy, Tř. Vítězného února, 708 33 Ostrava 4,
Czechoslovakia.

INTRODUCTION

Red and variegated beds occur in all members of Ostrava - Karviná Coal Basin in the adjacent territories to the prominent tectonic structures. The rocks of melaphyres and zeolites of harmotome composition have been sporadically found in effusions along the tectonic structures. The transition between grey and red facies is gradual with the preservation of all the structural and textural features of normal grey sediments. The granulometry, flora and fauna in most cases are also the same. The coal in coal seams of red beds changes strongly its petrologic and technologic properties and dies out completely at very short distance from grey-red beds boundary. The disappearance of coal seams is very often connected with brecciated roof rocks. In last years the postsedimentary origin of red beds due to the oxidation of subaerial weathering is considered (Králík 1980, Králík 1982).

GEOCHEMISTRY AND MINERALOGY OF RED BEDS

In red bed bodies two types of altered sediments have been differentiated on the intensity of the postdepositional oxidation basis.

1) Terrigenous sediments of the claystone - siltstone-sandstone - conglomerate group with low degree of epigenic oxidation. They differ from normal grey sediments in their

red and green colours which are in red beds most frequent. Red colour has been formed after the deposition by the hematite which is probably formed by the alteration in situ of iron - bearing minerals (Turner 1979). Green colour is caused by fine dispersed chlorite and Fe-illite. Clay minerals present in these rocks are nearly the same association as in normally developed grey sediments (kaolinite, illite, chlorite).

2) Terrigenous sediments with the high degree of epigenetic alteration due to the high temperature effect of oxidized coal seams. They are fine to coarse - grained, mostly of porcelanite - like character exhibiting a conchoidal fracture. The comparison of these rocks with those mentioned above shows substantial changes in composition of minerals. The highly altered rocks contain either montmorillonite, halloysite matrix with cristobalite and mullite, or they contain zeolitic matrix (harmotome, phillipsite, analcite).

To carry out a geochemical study, a collection of 76 samples was chosen to which the results of 34 analyses carried out beforehand were added. The collection under study contained original (grey unaltered), low-temperature altered (red, green, white, black) and highly altered terrigenous sediments. As the statistical methods have shown, the decisive criterion for dividing the collection was the granulometry, while the intensity of oxidizing alteration or the colour of terrigenous sediments was of secondary importance only.

CONCLUSION

Geochemical study of the red beds in the Ostrava-Karviná Coal District has not given any evidence that it would be the hydrothermal solutions that caused the oxidizing alteration in the extensive regions of the coal-bearing sediments of the Upper Silesian Coal Basin. Most phenomena may be - on the contrary - explained by weathering processes, the final

products of which were modified by a complicated matter redistribution which could be connected with penetrating saline waters of Miocene from superficial deposits of the Upper Carboniferous sediments.

REFERENCES

- Králík J. (1980): Epigenic Oxidation in Red Beds from Czechoslovak Part of the Upper Silesian Coal Basin - Sbor. věd. prací Vys. šk. báň. XXVI, 107 - 123.
- Králík J. (1982): Mineralogy of Red Beds in Ostrava-Karviná Coal Basin - Čas. Slez. Muz. Opava (A), 149 - 171.
- Turner P. (1979): Diagenetic origin of Cambrian marine red beds: Caerfai bay shales, Dyfed, Wales. - Sed. Geology, 24, 269 - 281.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

REDUCTION OF STRUCTURAL IRON IN SMECTITES BY MICROORGANISMS

PETER KOMADEL*, JOSEPH W. STUCKI, AND HENRY T. WILKINSON

Department of Agronomy, University of Illinois, Urbana, IL 61801 (USA)

*Institute of Inorganic Chemistry, CCR, Slovak Academy of Science, 84236 Bratislava (Czechoslovakia)

Iron is one of the few elements which exists in minerals in two relatively stable oxidation states, namely Fe(II) and Fe(III). In the crystal structure of clay minerals, Fe may be oxidized or reduced *in situ*, with concomitant changes in a number of physico-chemical properties of the clays. In virtually all of the studies where changes in Fe oxidation state have been investigated, Fe was reduced by chemical reagents. The probability that any of these reducing agents is a significant factor in naturally-occurring processes is extremely low, so one cannot be certain that changes in clay properties due to Fe oxidation state can be invoked by natural redox reactions. Hence, studies of naturally-occurring redox agents were undertaken.

The reduction of Fe(III) to Fe(II) by microorganisms has been reported with Fe in solutions, chelates, and oxides, but not with Fe in clay mineral structures until only very recently (Stucki and Getty, Agronomy Abstracts 1986:279; Stucki, Komadel, and Wilkinson, in review; and Wu, Roth, and Low, in review). In the present study, Fe(III) was successfully reduced to Fe(II) within the crystal structure of smectites by two isolated microorganisms and by unclassified organisms from rice paddy soils.

Smectites used in this study were the < 2 μm fractions of Upton (API 25), Wyoming, USA (U); Jelsový Potok, Czechoslovakia (JP); Kadan-Rokle, Czechoslovakia (KR); and SWa-1, Washington, USA (ferruginous smectite from the Source Clay Minerals Repository). The clays were Na-saturated, dialyzed to < 10^{-3} M NaCl, and freeze-dried.

Bacterium 13-79 was isolated from Ritzville silt loam soil near Moses Lake, Washington, USA; and PI, from SWa-1 smectite after Na-saturation, dialysis, and freeze-drying. Each bacterium was stored either on nutrient agar or in

sterile H₂O at room temperature, or in 5% DMSO at -80 °C.

Bacterial growth rates and the effect of microbial activity on the oxidation state of structural Fe in smectites were determined by incubating samples in sealed 40 ml tubes. Into each tube was placed a 25 ml portion of nutrient broth (NB), consisting of peptone and beef extract, or modified Thornton's (MT) medium (Thornton's medium without FeCl₃ and agar) then seeded with the bacterium and 5 ml of clay suspension in water (4 mg/ml). In the control tubes, medium without bacteria and/or water without clay were used. Both P1 and 13-79 bacteria are gram negative.

Isolated 13-79 grew rapidly in both NB and MT media -- the bacterial population doubled approximately every 10-12 hr. Isolated P1 multiplied about once every 20 hr in NB, but grew very slowly in the MT medium. Components of both NB and bacteria contributed to clay reduction. In the NB medium, both 13-79 and P1 bacteria reduced more than 10% of the total Fe in SWa-1 after 7 days. But in MT medium, P1 reduced only 1.7% whereas 13-79 reduced 15.2% of the Fe after 5 days.

Bacterial growth and Fe reduction in SWa-1, using MT medium, were also investigated in the presence of flowing O₂ or N₂ gas. Both bacteria grew slowly in N₂ in the absence of clay, and showed only a small increase in growth rate when clay was added. The bacterial population was insufficient in both cases to produce measureable Fe reduction in the clay. Bubbling O₂ through the system supported great populations of both 13-79 and P1, and the addition of SWa-1 had no measureable effect on the growth. The Fe(II) content in the clay, however, was low because of reoxidation of the reduced smectite by O₂.

The reduction of Fe(III) in the crystal structures of smectites by 13-79 in MT medium was extended to three additional clay minerals with various levels of total Fe (see Table). Reported in the Table are the Fe(II) and total Fe contents of the four smectites before treatment (expressed as % mass of clay), and the extent of Fe reduction (expressed as Fe(II)/Total Fe ratio and in absolute units of mg Fe(II)/g clay) after 7-days incubation in MT medium with and without seeding with the 13-79 bacterium.

In the clays with low Fe content (U and JP), a greater fraction of the total Fe was reduced by 13-79 than in the high-Fe clays (KR and SWa-1). But bacterial populations and the absolute level of reduction were higher in KR and

SWa-1. Bacterial growth apparently is affected by the total Fe content of the clay, and the amount of Fe reduced increases with increasing bacterial populations.

High levels of Fe reduction (13 - 20% after 12 days) were observed in SWa-1 in MT medium when seeded with bacteria from three different paddy soils from Arkansas. The Fe-reducing microorganisms in these soils have yet to be isolated and classified.

In summary, two bacteria which reduce Fe(III) to Fe(II) in the structure of clay minerals were classified. Bacterial growth rates were higher under aerobic than under anaerobic conditions, but dissolved O₂ in the robustly aerobic system reoxidized the Fe which had been reduced by the organism. The amount of Fe reduced depends on the total Fe content of the clay and on the bacterial population.

Table. Effect of 7-day treatment with 13-79 bacterium in modified Thornton's (MT) medium on the oxidation of structural Fe in four smectites.

Clay	Untreated		Treated 7 days		
	Fe(II) [% mass]	Fe(tot)	Fe(II)/Fe(tot) [%] No Bacteria	13-79	mg Fe(II)/g clay 13-79
U	0.20	2.66	2.4	23.9	6.4
JP	<0.05	2.07	0.0	25.2	5.2
KR	<0.05	10.05	0.0	15.5	15.6
SWa-1	0.09	16.21	0.2	17.8	28.8



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

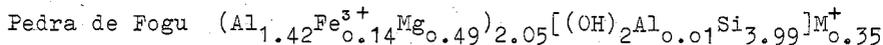
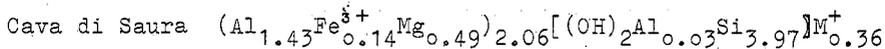
MINERALOGICAL INVESTIGATIONS ON BENTONITES FROM SARDINIA

H.M. KÖSTER

Lehrstuhl für Angewandte Mineralogie und Geochemie,
Technische Universität München, Lichtenbergstrasse 4,
D-8046 Garching, Federal Republic of Germany, FRG.

Bentonite samples from Sardinia are treated with 0.1 M EDTA-solution and 1 M NaCl-solution for decomposition of carbonates and to exchange the naturally adsorbed cations by sodium and for destruction of clay aggregates. Size fractions are prepared from the treated bentonites by settling and centrifugation of the clay suspensions. The size fractions coarser 0.63 μm ϕ from seven bentonites consist of quartz and sandine and the size fractions of one bentonite of quartz and plagioclase. Different amounts of magnetite, or magnetite and haematite, or haematite only are admixt to the size fractions. The parent rocks of the investigated bentonites are rhyolitic and dacitic tuffs as shown by the relictic minerals.

Montmorillonite is concentrated in the finest clay <0.2 μm ϕ of the dressed bentonite samples. Small amounts of "amorphous" silica and alumina are removed from the fine clay fractions by treatment with 0.5 M NaOH-solution and small amounts of iron oxides are resolved by reduction with Na-dithionite. Structural formulas of the purified montmorillonites are calculated taking into account the directly measured interlayer charge. For example:



The trace elements Cr, Cu, and Li are constituents of the montmorillonites. Ti, Mn, Zn, Pb, Sr, and P are removed largely from the montmorillonites with the coarser size fractions and/or by cation exchange treatment. The behaviour of the trace elements Co, Ni, and Rb is indifferent.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS AND AGE OF KAOLINS: THE WESTERN CARPATHIANS

I. KRAUS

Faculty of Sciences, Comenius University, Bratislava,
Czechoslovakia.

A comprehensive account of the given problem represents the first synthetic outlook on the formation of kaolins in the Western Carpathians. The following three genetic types of kaolin deposits may be distinguished in this region: weathering, hydrothermal and sedimentary.

WEATHERING KAOLINS

Contrary to classical deposits in the Bohemian Massif, these weathering kaolins have different parent rocks and morphological-tectonic development, and they have developed in different time stages. The presence of kaolin weathering crusts was stated in all units of the inner Western Carpathian Mts., where they arose on granitoids or Paleozoic metamorphites, respectively, and on neovolcanites.

Kaolin weathering crusts on granitoids are not economically significant, and preserved relics represent the transition type between the bisialic and monosialic weathering in the sense of Pedro /1971/. Kaolinite did not develop on these rocks by the weathering of K-feldspars, but by that of only plagioclases and biotite. The illite transformation into kaolinite has not been recorded during the whole weathering.

The economically significant kaolin deposits in the Western Carpathians have originated by the weathering of metarhyolites, where kaolinite was formed through the transformation of albite. In advanced kaolinization of metarhyolites, Na-mica /brammalite/ originates by Na^+ release during the decomposition of albite into kaolinite. In such

case, the relict muscovite/sericite, or authigenic illite have been subjected to total transformation into kaolinite. The most extensive kaolin weathering crusts have been preserved on sericitic metaquartzites and sericitic-chloritic phyllites, nevertheless, they are not considered economically significant so far. Kaolinite was formed here by the transformation of muscovite, or chlorite respectively.

In neovolcanic rocks /rhyolites, andesites, basalts and their volcanoclastics/, kaolinite with frequent admixture of halloysite, sometimes also allophane, originates mainly by the weathering of feldspars, volcanic glass, sporadically also biotite.

HYDROTHERMAL KAOLINS

Neovolcanic formations seem to be the potential occurrences of kaolin deposits of hydrothermal origin. The model of metasomatic zoning in the sense of Volostnykh /1972/ was confirmed. The stages of synchronous and topochronous zonings were distinguished in this model.

During the synchronous stage, kaolinite was formed in direct environment of ore veins while montmorillonite originated in a more distant part.

Total metasomatosis of kaolinite - relict mineral of synchronous stage, is testified by hydromuscovite of polytype modification $2M_1$ in veiny gold bearing quartz in topochronous stage. The topochronous phase witnesses, at the same time, to an extensive transformation of montmorillonite into mixed layer mineral illite-montmorillonite.

SEDIMENTARY KAOLINS

These have the character of kaolinite sands and gravels. They constitute a part of the sedimentary filling in Neogene basins of river and lake facies. They have been formed by the redeposition of the upper part of kaolin weathering crusts. Sedimentary kaolins register reliably presence of source areas, the intensity and extent of pri-

mary kaolinization. Smaller part of kaolinite in sedimentary kaolins is of authigenic origin. A substantial part is represented by allothigenic kaolinite which has formed in original kaolin weathering crust.

DISTRIBUTION OF MICROELEMENTS IN KAOLINS

It was observed in the fraction below 2 micrometers. It is primarily determined by the character of parent rocks. In kaolin weathering, the majority of observed microelements concentrate in the clay fraction, which is in particular evident in the case of B, Cu, Sn, Ni and Co. Adverse tendency is manifested only by Ba and Sr.

As opposed to weathering kaolins, the hydrothermal ones are more or less deficient in the presence of Cu, Ni, Co, V, Cr, Ti, Zr and Ba. The B, V contents increase and that of Zr decreases during the redeposition of kaolins from the weathering crusts into sedimentation basins.

KAOLINIZATION AGE

In Tertiary, the oldest, reliably confirmed kaolinization took place before Egerian and during, or before Oligocene. The main stage of hypogene kaolinization took place only after the Styrian folding phase from Badenian to Pontian, when all significant kaolin weathering crusts have formed and constituted. It is mainly rhyolite volcanism of Sarmatian-Panonian age that is significant for the hydrothermal kaolinization.

REFERENCES

- PEDRO, G. /1971/: Eksperimentalnye issledovaniya geokhemi-cheskogo vyvetrivaniya kristallicheskih porod. Mir, Moskva, 1-251.
- VOLOSTNYKH, G.T. /1972/: Argillizatsiya i orudneniye. Nedra, Moskva, 1-240.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FORMATION OF MINERALPHASES OF VARIOUS MAGNESIUM LAYER-SILICATES DURING FIRING

H. KROMER*), D. ROSE*), K. H. SCHÜLLER**)

*) Staatl. Forschungsinstitut für Angewandte Mineralogie bei der TU-München, D-8400 Regensburg, West-Germany

**) Georg-Simon-Ohm-Fachhochschule, D-8500 Nürnberg, West-Germany

Magnesium layer-silicates like talcs and steatites are used for various industrial applications. Their technological applicability as ceramic raw materials is controlled by the structure which is developed during firing. This again depends on certain features of the raw material like chemical and mineralogical composition and crystal size. In order to get a better knowledge of the relationships between the composition of the raw materials and the fired products a series of talcs and steatites was examined as received and after firing to 1300 °C.

Three groups of raw materials are considered. They concern increasing contents of iron oxide, alumina and calcia respectively.

Group 1 is characterized by increasing iron contents. Iron is partly incorporated in the talc structure, partly in accessory minerals like chlorite and hematite. The amounts of nickel and chromium indicate that those samples having total iron oxide contents of more than 4 % generated from ultra mafic rocks. During firing the iron oxide promotes the formation of cristobalite, protoenstatite is the pyroxene phase formed from these materials. The occurrence of further pyroxene phases is uncertain but spinels and some olivine could be identified by x-ray diffraction and by scanning electron micrographs.

The increasing contents of alumina of group 2 is caused by an increasing amount of chlorite in the samples. Calcia is rather low in the samples under consideration. As the iron oxide contents are below 1 % in all samples of this group it is confirmed that the chlorites associated with talcs are predominantly of the magnesium-aluminium type. The alumina has a considerable effect on the phase formation during firing. It causes the formation of cordierite. But the type of pyroxene is also affected by

the alumina; clinopyroxene occurs besides protoenstatite in the fired product.

The third group is characterized by increasing calcia contents whereas alumina and iron oxide are remarkably low. The calcia is incorporated in dolomite. Some quartz was found in the samples having higher contents of dolomite. The calcia causes the formation of diopside. Protoenstatite decreases the more the higher the calcia contents of the sample are. The excessive silica is consumed by the formation of diopside and thus cristobalite disappears in the fired product with increasing calcia contents. However, quartz is partly preserved under the firing conditions applied in our investigations which indicates a retarded reaction with the other phases. Indeed quartz is present in a rather coarse grain size.

Other samples high in iron oxide, alumina and calcia are extremely impure and contain various accessory minerals. The reaction sequences during firing of these materials are rather complicated and need further studies.

The results indicate the significance of chemical impurities and accessory minerals for the reaction running during firing of ceramic ware. They explain why only certain steatites with low impurity levels can be considered reasonably for an application in ceramics.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FORMATION OF CLAY MINERALS BY MECHANOCHEMICAL
REACTIONS DURING GRINDING OF BASALT UNDER WATER

R.A. Kühnel¹ and S.J. van der Gaast²

1. Delft University of Technology/Institute for Aerial Survey - I.T.C.
Delft, The Netherlands
2. Netherlands Institute for Sea Research, Texel, The Netherlands

Durability of basalt is essential for its utilization as construction material for roads and water works. According to their composition some basalts show tendencies for fast weathering and/or mechanical decay. In such degrading processes, clay minerals and in particular smectites play an important role.

Some clay minerals are always present in basaltic rocks, however, they are of different origin: 1) Hydrothermal clay minerals which were formed in the early postvolcanic stage. Hot solutions which have saturated just solidified rocks cause alteration of some constituents; e.g. glass, zeolites, feldspathoids and feldspars. Hydrothermal clay minerals also occur along frissures, fractures, faults and other discontinuity planes due to the attack of migrating hydrothermal solutions on the host rock. 2) Hypergeneous clay minerals which were formed by weathering processes under subaerial or subaquatic conditions at the surface of lithosphere in contact with atmosphere and hydrosphere respectively. 3) Neoformed clay minerals (artefacts) have been observed on basalts ground in water under laboratory conditions.

By grinding - a large, new and active surface is generated and numerous ions have been liberated from the rock - water interaction. Dissolved alkali metals and alkali earths control the pH which on basalt suspensions was higher than eight in all cases. Under such conditions, when the silica and alumina are present, the precipitation of poorly crystalline aluminosilicates is favored. With ageing of such quasiamorph, precursor, clay minerals can crystallize in time. If hydrothermal clay minerals are present, they act as

nuclei for neoformed crystallites.

A series of X-ray diffraction analyses (humidity diffractometry) has been carried out on basalts ground in water and in cyclohexane. The second agent has been applied in order to discriminate mechanical process of diminution under dry conditions from mechanochemical reactions which accompany the water - rock interaction. Basalt samples (1-2 mm fragments) were ground in a vibration mill in the presence of a liquid (at solid: liquid ratio 1:10) for one minute. After milling, the surface area of about 18 m^2 was reached. X-ray diffraction analyses were carried out on oriented preparations ($\sim 4 \text{ }\mu\text{m}$) with an internal standard of 1% MoS_2 for the checking of the degree of preferred orientation and for the correction of intensities.

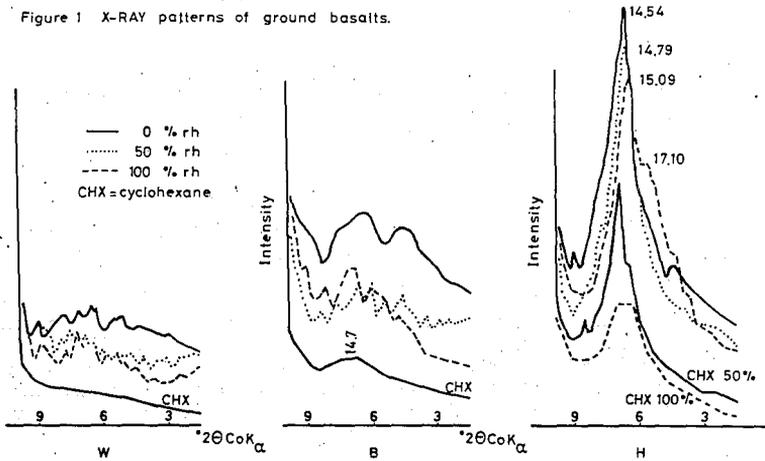
By means of step scanning and subsequent smoothing, X-ray diffraction patterns have been recorded within the range of $1.5\text{-}10^\circ 2\theta$. Oriented preparations were later exposed to a flow of wetted helium directly in the diffractometer. After a period of conditioning, X-ray patterns were carried out at 100, 50 and 0% relative humidities.

The major differences of X-ray patterns on basalt ground in cyclohexane and in water can be summarized as follows:

- 1) On basalt ground in water it was always substantially a higher background due to a higher amount of quasisamorphous substances.
- 2) Basalts ground in cyclohexane showed only limited sensitivity to the humidity unless some smectite were already present in the rock.
- 3) A diffuse, humidity sensitive 001 reflection $14\text{-}17 \text{ \AA}$ has been observed on basalts ground in water. The "bulge" is differently modulated at 0, 50 and 100% relative humidity. A shift toward lower 2θ angles indicates lattice expansion due to hydration.
- 4) Already existing peaks of clay minerals in basalts generally become more intensive after grinding in water.

The above mentioned changes of X-ray patterns show that during the grinding in water, amorphous or poorly crystalline aluminosilicates are generated by mechanochemical reactions. From these quasisamorphous precursors smectites can crystallize in time either by ageing or by

Figure 1 X-RAY patterns of ground basalts.



overtaking already existing crystallites of clay minerals. In such cases, intensities of reflections substantially increases.

Examples of three basalts are demonstrated in figure 1. Basalt W is the most stable one. Its background after grinding in cyclohexane is low and not sensitive for humidity. Grinding in water has caused an increase of background which varies in shape at different humidities. Basalt B is an intermediate case and basalt H shows the highest tendency to decay. It shows distinct smectite 001 reflection 14-15A shifted to 17A at higher humidities.

Swelling effects of smectite present and/or generated by grinding accelerate the process of chemical weathering. Simultaneously a weakening of mechanical properties takes place. From the behavior of basalts during milling in water and cyclohexane chemical and mechanical stability of the rock can be predicted.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**IMPACT OF EOLIAN INPUTS ON CENOZOIC CLAY SEDIMENTATION
IN NE ATLANTIC**

C. Latouche and N. Maillet
Institut de Géologie du Bassin d'Aquitaine - 351 cours de la Libération
33405-Talence Cédex (France)

The Deep Sea Drilling Project (DSDP) is an international partnership of scientists that have joined together to explore the structure of the Earth between the Ocean basins under the sponsorship of six governmental Oceanographic Institutions. DSDP brings scientists from all over the World to retrieve core samples from the Ocean floor. These cores help scientists to understand better the age of Ocean basins and their development, the rearrangements of continents, the structure of the earth crust, and the history of World wide climatic changes. Among the numerous parameters from core samples considered by scientists, clay minerals contribute greatly to the reconstruction of paleoenvironmental deposition. For this reason we have been involved in all clay mineral DSDP studies in the NE Atlantic Basin.

Cenozoic sediments, samples of which were recovered during Leg 94, are spread out over a large part of the North Atlantic (37°N to 53°N).

A mineralogical analysis of the clay phase of these samples showed the following succession: a predominance of smectites from the base of the Tertiary until the middle Miocene; A progressive replacement by illites and chlorites in the late Miocene and the base of the Pliocene. An abundance of illite and chlorite in the upper Pliocene and Quaternary. This evolution is similar to that observed in previous sediments from North-East Atlantic legs, that is to say:

- at the base of the Tertiary the marine sedimentation depends largely upon the immediate geological environment and climate;
- from the middle Miocene to the lower Pliocene the clay phases becomes more uniform (with dominance of illite on smectites) respect to the increase in North-South hydrosedimentary exchanges;
- from the upper Pliocene onwards there is a simultaneous important increase in illites and chlorites, associated with ice-derived inputs.

In addition to these well-established processes, Leg 94 sediments revealed a specific mode of sediment transport (the studies carried out at Site 608 (King's Trough). At this site, there exists within a mono-mineral clay sedimentation (smectite from the middle Eocene to the middle Miocene) a specific Oligocene episode, the dominant characteristic of which is an assemblage composed of illite, chlorite, kaolinite and fine quartz (< 2 µm). Given the topographic situation of the zone, these minerals could not have been transported by bottom currents but only by wind. Eolian transport is also thought to have carried sediments of the same age to site 558 (Leg 82, southern Azores). This would imply the existence of relatively arid conditions in the second half of the Oligocene.

The results of this study are of particular interest given the exceptional sedimentary conditions in the Oligocene, as already evidenced in previous DSDP cores in the NE Atlantic. During this period, numerous sedimentary gaps have been observed. The occurrence of eolian deposits associated with arid climatic conditions are in good agreement with the scarcity of sedimentation in the Oligocene.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**EVOLUTION OF PALEOSOILS WITH SEPIOLITE DEVELOPMENT IN
THE MADRID BASIN (SPAIN).**

S. LEGUEY, M. POZO, J.A. MEDINA and R. VIGIL.

Department of Agrochemistry, Geology and Geochemistry. Autonoma University of Madrid. (Spain).

The evolution of the mineral components of sepiolite predominant rocks is analyzed according to: geological characteristics, textural features and spatial distribution. The analysis was made in samples of seriate profiles in which the mineralogical composition had previously been determined by X-ray analysis. The texture, micro-fabric and accurate analysis were determined using thin lamina sections and scanning electron microscopy (S.E.M.) with an incorporated EDAX system.

The materials studied belong to exploited deposits in the Neogene basin of Madrid. These deposits are associated with two types of material, separated by an erosive-type sedimentary contact:

- a) Green clays, principally containing magnesian smectites, from the intermediate Miocene, with deposits over an area of approximately 25 Km and an average potential of 6-8 m. Sepiolite and/or palygorskite content ranged from 40-90%, and carbonates, illite and aluminium smectites towards the upper limit.
- b) Brown, sandy clays, of clay origin belonging to the transition between the middle and upper Miocene in which sepiolite levels appear, with a potential of 1-5 m over almost 50 Km. Average sepiolite proportions range between 60-85%, together with 5-20% of quartz, and decreasing amounts of smectites, mica and feldspars (0-10%), and traces of dolomite, C-T opal, palygorskite, kaolinite and sometimes zeolites.

On a field scale, the materials present vertic features (prismatic disjunctions, slickensides, etc.) Fe and Mn oxide tinctures, nodule formation and scattered organic material. In thin section

there appeared reticular, granular, banded and nodular textures, of a generally translucent material, presenting gradation phenomena in the interstices, in the clay predominating areas, and of pore lining and pore-filling, in sandy areas.

The sepiolite in both units is generated on paleosurfaces on which the formation of vertic, hydromorphous or calcimorphous soils takes place, which develop in the distal zones of alluvial fans. These materials of the intermediate unit come mainly from metamorphic rocks (schists and gneisses), rich in biotite, and from granites and gneisses in the intermediate-upper transition unit.

Smectite formation is favoured during flooding periods. Associated with this are plant residues and organic matter, which can reach up to 4.5% in some areas.

Sepiolite formation would take place in the intermediate unit, by hypergenesis of magnesium smectites, and in the upper intermediate unit, due to alteration of clay materials by water rich in Mg, that come from the washing of magnesium clays and dolomite materials, in the S-SE of the basin, which emerge due to tectonic action. In a climate of contrasts, with wet and dry periods, and an absence of sedimentation, desiccation phenomena abound, resulting in the formation of lattices and nodules. Neof ormation of sepiolite mainly occurs in pores and cracks, closely related to the progress on the water table. Fibrous aggregate development depends on the presence of free spaces.

A lacustrine régime settled in the lower paleosurface after the formation of vertic paleosoils. This regime contained expansive and retractive episodes with development of biomicrites detrital sheet flows and calcimorphous paleosoils. Tilting of the insular shelf created an uneven surface, with elevated zones, in which circulation of carbonate-rich waters is activated, causing mobilization of Mg from levels containing sepiolite, producing residual silcretes, with sepiolite and dolomites, as well as diagenetic palygorskite, when there is a significant proportion of terrigenous deposits among carbonated layers.

Sepiolitic materials of the upper paleosurface are covered and protected by clay sediments from alluvial fans. Only a general increase in silification is noted, as is the calcrete development

towards the NE of the basin.

Evidence of various sepiolite generations is found in the micro-fabric. A primary generation develops in irregular or squashed glomerules and a secondary generation develops in the interglomerular pores (secondary porosity).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MODE OF FORMATION OF Mg-BEARING CLAY MINERALS

F. LIPPMANN

Mineralogisches Institut der Universität, D-7400 Tübingen

In Germany, Triassic sedimentation includes at least three phases of restricted conditions characterized by the deposition of gypsum (anhydrite) and, in places, rocksalt. These evaporative events occur in the Röt (at the transition from Buntsandstein to Muschelkalk), in the Middle Muschelkalk, and in the Keuper. The clay fractions in all these formations are distinguished from other Mesozoic sediments by the occurrence of corrensite. A recent study of the Middle Muschelkalk has shown that certain beds are rich in a thermostable chlorite, which represents another neof ormation of a Mg-bearing silicate besides corrensite. Comparison with clay-mineral suites from non-evaporitic Triassic and Jurassic sediments leads to the conclusion that the Mg-bearing minerals must have formed largely at the expense of kaolinite in brines rich in Mg^{2+} . In the pertinent chemical reaction, not only Mg^{2+} but also equivalent amounts of OH^- are consumed.

These anions, or generally speaking alkalinity, are generated by weathering in continental environments under warm climates. When discharged into a normal marine basin, the alkalinity is consumed entirely by carbonate precipitation. Only in a restricted basin can part of the OH^- ions become active in the transformation of silicates, notably clay minerals.

The Mg-bearing minerals corrensite and chlorite are thus not indicators of evaporation as are gypsum (anhydrite), rocksalt and other salt minerals. Rather they point to another aspect of a restricted basin, viz., that of collecting alkaline waters derived from adjacent continents.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

DETERMINATION OF LEAD IN CLAYS AS A METHOD OF PROSPECTING FOR LEAD ORES.

M.J. LISO, J. LISO, J. LOPEZ and M. BIGERIEGO

Departamento de Cristalografía y Mineralogía. Facultad de Ciencias.
Universidad de Extremadura. BADAJOZ. (Spain).

Lead was determined in sericitic shales and in clay fractions of different soils close to galena deposits in the province of Badajoz (SW Spain). The aim of this paper is to attain a geochemical method for lead prospecting. Lead determination was carried out by atomic absorption spectrometry and clay mineralogy was characterized by X-ray diffraction. Samples were collected according to their proximity to galena deposits.

The results for lead in soils and in sericites are given in Tables I and II, respectively. The values for the sericite samples range from 0.012 to 0.086, while in soils near galena outcrops they range from 0.10 to 1.23% of lead content. We consider this lead to have replaced the interlayering potassium in the phyllosilicates due to the similarity of ionic diameter.

In the case of the sericitic shales, principally muscovite 2M, with small proportions of kaolinite or chlorite, pyrophyllite, quartz, feldspars, the samples with a more silky sheen (A12-1) have a slightly higher PbO content, and, with respect to colour, the more greyish tones (LCBr3) have higher values than the white or reddish tones (ZA1).

As was to be expected, in clay from the soil samples, proximity to the deposit of galena means a higher lead content, and there is also a dependence on the direction from the mineral vein. Regarding the mineralogy and cation exchange capacity, lead content is greater for the montmorillonite rich soils than for the illite soils, and these in turn greater than for the kaolinite ones.

We would conclude that PbO values above 1.00% in clays may well be a significant parameter in mineral prospecting.

TABLE-I

PbO content of clay-soil samples

<u>Samples</u>	<u>Distance from mineral deposit</u>				<u>Location</u>
	<u>50m</u>	<u>100m</u>	<u>150m</u>	<u>200m</u>	
Aa	1.20	1.16	1.08	0.38	Azuaga
Ab	1.18	0.81	0.96	0.22	
Ac	1.23	0.98	1.10	0.97	
SMa	1.11	0.72	0.41	0.32	Santa Marta
SMb	1.13	0.60	0.52	0.18	
SMc	1.12	0.52	0.81	0.10	
LRa	0.90	0.63	0.42	0.42	La Roca de
LRb	0.81	0.57	0.21	0.12	la Sierra
LRc	0.92	0.81	0.65	0.41	

TABLE-II

PbO content of sericites

<u>Samples</u>	<u>%PbO</u>	<u>Location</u>
A11-1	0.024	Alange 1
A11-2	0.012	
A11-3	0.019	
A11-4	0.030	
A12-1	0.081	Alange 2
A12-2	0.036	
A12-3	0.086	
A12-4	0.025	
A12-5	0.041	
A12-6	0.038	
A12-7	0.046	
ZA1	0.018	Zarza de Alange
ZA2	0.031	
ZA3	0.029	
ZA4	0.021	
LCBa1	0.049	La Codosera 1
LCBa2	0.028	
LCBr1	0.034	La Codosera 2
LCBr2	0.043	
LCBr3	0.060	
LCBr4	0.041	
CR1-1	0.019	Cristina
CR1-2	0.023	
CR1-3	0.028	
CR1-4	0.034	



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SUBBETIC, MIDDLE-CRETACEOUS, DARK MUDSTONES ON THE SOUTHERN IBERIAN PALAEO-MARGIN: ANALYSIS OF THE CLAYS AND THEIR PALAEOGEOGRAPHIC IMPLICATIONS

LOPEZ GALINDO, A. ^(1,2); COMAS MINONDO, M.C. ⁽²⁾ & FENOLL HACH-ALI, P. ^(1,2)

(1) Departamento de Mineralogía y Petrología. (2) Instituto Andaluz de Geología Mediterránea, C.S.I.C. Facultad de Ciencias. Universidad de Granada. 18071 Granada (Spain).

A problem of considerable interest at the present moment is an understanding of the palaeogeographical and environmental significance of the anaerobic black-shale type facies which were deposited during the Aptian-Coniacian both on the continental margins and in the ocean troughs.

In the palaeogeographical domain known as the Subbetic Zone, which formed part of the Southern Iberian Mesozoic Palaeomargin, this type of facies is well represented. The sediments of this zone are similar to those of other Tethyan margins with alternate sequences of hemipelagic and turbiditic facies, the principal component of which is by and large bentonitic clay.

In this work we intend to analyse the mineralogical and geochemical characteristics of these Subbetic Cretaceous facies in an attempt to distinguish or corroborate already identified palaeogeographical subdivisions in the Zone and also to throw light on the environmental conditions that controlled the sedimentation in this part of the Tethys during the Aptian-Coniacian age.

METHODOLOGY

We took samples from the clay-rich levels and also from the organic-matter-rich beds in all the successions studied. In the turbiditic sequences we took further samples from some pelite levels genetically associated with them. The mineralogical analysis of the samples was carried out mainly by X-ray diffraction and electron microscope studies. For the former we used a Philips PW 1710 diffractometer, $\text{CuK}\alpha$ radiation and a scanning speed of between 1° to 6° per minute. The types of samples used were untreated dry-powder specimens and orientated aggregates of <2 microns and 2-20 microns (normal, saturated with ethylene-glycol, dimethyl-sulphoxide, and heated to 550°C for one hour).

The morphological study of the clays and associated minerals was carried out with a Philips 400T transmission electron microscope. The microscope was equipped with a Si(Li) detector and a EDAX 707A multichannel analyser, which permitted punctual chemical analysis.

MINERAL ASSOCIATIONS AND THEIR PALAEOGEOGRAPHICAL DISTRIBUTION

The mineral associations to be found in the different sequences studied belong to three main groups and point to the existence of three palaeogeographical sub-domains (Figure 1).

1. Northern Sequences

The typical association in these sequences is phyllosilicates (illite-kaolinite-chlorite-mixed-layers-smectite)-calcite-quartz-feldspar. Illite is the dominant clay in all the samples taken, accounting for up to 90% of the material at times. Kaolinite and chlorite are always present, although together they never amount to more than 20%. Their concentration does increase significantly, however, in the turbiditic pelites of the sequences found nearest to the Cretaceous palaeocontinent. The mixed-layers and the smectites only occur in minor quantities.

2. Central Sequences

These sequences are characterised by the phyllosilicates (smectites-illite-palygorskite-kaolinite)-quartz-calcite-feldspar association. In the hemipelagic samples the phyllosilicates are dominant while calcite is more abundant in the turbiditic pelites. The most frequent clay mineral to be found in both types of sample are smectites, normally accounting for more than 50% of the material, followed by illite, in quantities ranging from 10% to 40%. In the westernmost outcrops palygorskite is abundant in about the same quantities and kaolinite is absent, while in the eastern outcrops kaolinite is to be found in quantities of about 10% and palygorskite is absent. Chlorite and mixed-layers are sometimes represented but to a minor degree.

3. Southern Sequences

In these sequences two different associations may be identified, depending on the amount of calcite present. Thus, in the Internal Subbetic sequences a phyllosilicate (smectites-illite-kaolinite-palygorskite)-quartz-opal CT-calcite-clinoptilolite-feldspar association is to be found, with mineral proportions similar to those of the central sequences, while in the Penibetic sequences a calcite-phyllosilicates association occurs, made up of calcite-(smectites-illite-palygorskite-kaolinite-mixed-layers)-quartz.

Bearing in mind the disposition of the various sequences encountered in the Southern Iberian Paleomargin, together with the distribution of the gravitational sediments and the mineralogical characteristics of all the facies involved, we suggest that two main trough environments existed in this domain during the Middle-Cretaceous:

THE SEPTENTRIONAL TROUGH. In this trough our "northern" sequences were deposited and the hemipelagic and turbiditic contributions came mainly from the continent.

THE MERIDIONAL TROUGH. The sediments in this trough include our "central" and "southern" sequences and are clearly different from those in the other. The frequent absence of calcite in the pelagic levels would indicate a deeper sedimentary environment, probably below the calcite compensation depth. The distribution of the clay minerals suggests that, in this trough, bottom and/or contour currents played an important role in transporting the clays. This would explain the compositional uniformity of the Subbetic samples and also their similarity to coetaneous Atlantic facies. Both the chemical composition and the crystallinity of the smectites and their association with clinoptilolite and palygorskite appear to suggest that they derive in great part from the submarine alteration of basic volcanic rocks (López Galindo, 1986).

REFERENCES

López Galindo, A. (1986). Las facies oscuras del Cretácico Medio en la Zona Subbética. *Mineralogía y Sedimentación*. Doctoral Thesis. Univ. Granada.

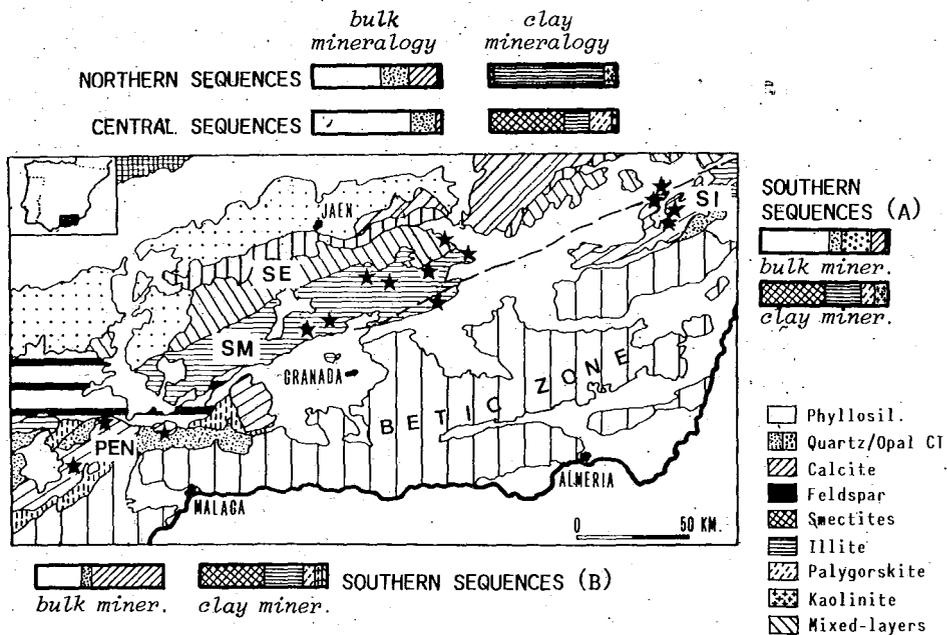


FIGURE 1. Geological map of the Betic Cordillera, showing a simplified scheme of the various mineral associations. SE = Intermediate Units and External Subbetic. SM = Median Subbetic. SI = Internal Subbetic. PEN = Penibetic.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE DISTRIBUTION OF RARE-EARTH ELEMENTS IN THE CRETACEOUS DARK MUDSTONES OF THE SUBBETIC ZONE (BETIC CORDILLERA, SPAIN)

LOPEZ GALINDO, A.⁽¹⁾; MELONI, S.⁽²⁾ & ODDONE, M.⁽³⁾

(1) Departamento de Mineralogía y Petrología. Instituto Andaluz de Geología Mediterránea. Facultad de Ciencias. Universidad de Granada. (2) Centro C.N.R. per la Radiochimica e l'Analisi per Attivazione, Dipartimento di Chimica Generale, Università di Pavia. (3) Dipartimento di Chimica Generale, Università di Pavia, Italia.

One of the authors of this paper has recently carried out a detailed study of the mineralogy and geochemistry of the Cretaceous, anaerobic, black-shale facies which are to be found in abundance in the Subbetic Zone (López Galindo, 1986). These sediments are believed to have accumulated in some of the trough realms that existed in the Cretaceous, Southern Iberian Paleomargin from the Aptian to the Lower Senonian under extensive-regime conditions (García-Dueñas and Comas, 1983).

The mineralogy of these sediments has revealed the existence of two main troughs in which different types of pelagic and turbiditic materials, containing distinct mineral associations, accumulated (cf. López, Comas and Fenoll, this volume).

In this paper we intend to show how the distribution of the rare earths can be a useful pointer when attempting to characterise the environments that prevailed in these two troughs. To this end we have selected some of the most characteristic samples of the sequences which represent this palaeomargin.

METHODOLOGY

The analyses were carried out at the University of Pavia (Italy), using a Triga Mark II reactor (250 Kw). 300 grs of sample and also of standard rocks (G-1, GSP-1 and BUVO-1) were irradiated for 15 hours at a thermal flux of about $1 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, followed by a second irradiation of 5 minutes at a thermal flux of about $2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in order to determine the short-lived radionuclides. After the first irradiation the samples were left in solution for 3 days before being processed and after the second it was necessary to leave them in solution for 30 minutes before analysing them by gamma spectrometry. To this end a Ge(Li) detector (1.71 KeV FWHM for the 1332 KeV gamma ray of ^{60}Co) was used. The elements analysed were La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

RESULTS

In the presentation of our results (cf. fig. 1) we have grouped the sequences studied into the three domains usually recognized within the Subbetic Zone as a whole: from North to South, the External, Median and Internal Subbetic. Although in general the distribution pattern for all three domains is very much the same, with three important negative anomalies in Ce, Eu and Yb similar to those observed in seawater, there are several phenomena worth noting:

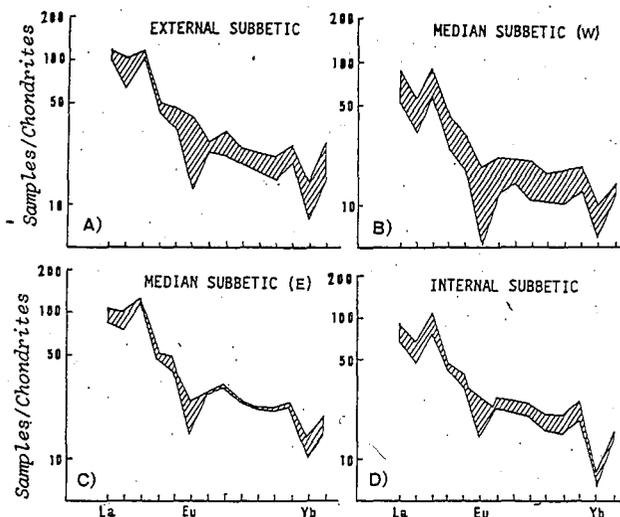


FIGURE 1. Chondrite-normalized REE distribution in the Cretaceous, dark mudstones of the Subbetic Zone. A) External Subbetic; B) Westernmost sequences of the Median Subbetic; C) Easternmost sequences of the Median Subbetic; D) Internal Subbetic.

- the highest concentrations of rare earths are to be found in the Septentrional trough (External Subbetic) (cf. figure 1A). This characteristic is tied to a massive presence of typically detrital minerals, such as illite, kaolinite and chlorite.

- within the Meridional trough, which roughly covers both the Median and the Internal Subbetic, the lowest values of RE are reached in those sequences showing a smectite-illite-palygorskite association (cf. fig. 1B and 1D).

A study of the Ce/Ce^* (as proposed by Courtois and Hoffert, 1977) and the Yb/Yb^* ratio, as indicators to the extent of the negative anomalies in these elements, reveals a clear lessening of the detritic influence from North to

South (Ce/Ce* : 0.61 in the Internal Subbetic, 0.7 in the Median Subbetic and 0.81 in the External Subbetic; Yb/Yb* : 0.45, 0.50 and 0.53, respectively) and thus a concomitant increase in the oceanic nature of the sedimentation, as evidenced in the high quantities of smectites present in the southernmost sequences.

REFERENCES

COURTOIS; C. & HOFFERT, M. (1977). Distribution des terres rares dans les sédiments superficiels du Pacifique sud-est. Bull. Soc. Geol. France, 19, 1245-1251.

GARCIA-DUEÑAS, V. & COMAS, M.C. (1983). Paleogeografía mesozoica de las Zonas Externas Béticas como borde de la Placa Ibérica entre el Atlántico y la Mesogea. Act. Congr. Nac. Sedim., Menorca.

LOPEZ GALINDO, A. (1986). Las facies oscuras del Cretácico Medio en la Zona Subbética. Mineralogía y Sedimentación. Tesis Doctoral, Univ. Granada.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE CLAY MINERALOGY AND GEOTECHNICAL PROPERTIES OF THE LANDSLIP AT OLIVARES
(MOCLIN, PROVINCE OF GRANADA, SOUTHERN SPAIN)

LOPEZ GALINDO, A. (1,3) & CHACON MONTERO, J. (2,3)

(1) Departamento de Mineralogía y Petrología. (2) Departamento de Geodinámica. (3) Instituto Andaluz de Geología Mediterránea, C.S.I.C. Facultad de Ciencias. Universidad de Granada. 18071 Granada.

On 12 April 1986 the village of Olivares in the municipality of Moclin was overtaken by a dramatic event. The "Barranco del Hundidero" began to move and the existence of the village itself appeared to be imperilled. The barranco, or narrow ravine, is notorious for small slides that occur during the rainy season, but this time some 180.000 square metres (5 million metric tonnes) of earth and rock started to descend at about 2 ms per hour. This landslip was due to a rotational slump in the barranco, producing an earth flow which threatened to dam the nearby river Velillos (cf. figure 1) and flood the village of Olivares. Emergency work managed to keep the river free and drain the earth flow of water, until it was finally stopped on 25 April 1986, thus averting the danger for the present. The Junta de Andalucía (The Regional Government) has asked the University of Granada to produce a geological report on this phenomenon, and some of the initial findings are presented below.

GEOLOGICAL SETTING

The village of Olivares is situated adjacent to the Liassic dolostones and limestones of the Moclin Unit, which, in this area, thrust over the Cretaceous and Tertiary materials of the Median Subbetic Domain.

The materials which have begun to slump belong geologically to the Fardes Formation (Comas, 1978), a unit which crops out extensively in the Mid-Subbetic Zone along a 200 Km belt from Puerto Lopez in the Province of Granada to Zarcilla de Ramos in Murcia. The facies include several kinds of carbonate turbidites and olistostromes together with hemipelagic sediments rich in smectites, all typical of the Albian-Turonian age in this area. An analysis of the turbiditic associations shows that the clastic sediments were deposited by deep-sea fans existing in the Cretaceous basins and also that large quantities of material were carried from submerged swells down the slopes of these basins by gravitational processes, thus transporting pelagic and hemipelagic sediments to the deepest parts of the troughs.

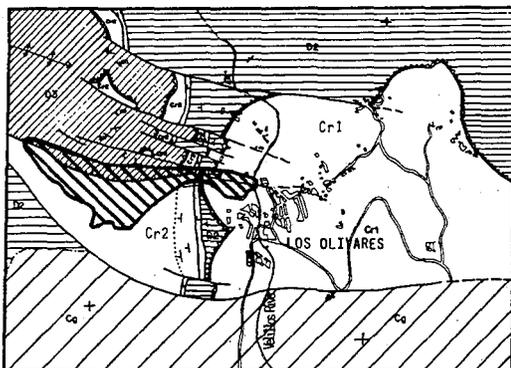


FIGURE 1. Generalized geologic scheme of the area around Los Olivares. D2-D3 = Moelin Unit. Cr1-Cr2 = Cretaceous of the Median Subbetic. Cg = Quaternary. The landslide is indicated by means of gross lines.

METHODOLOGY

Atterberg limits of both undisturbed and remoulded samples of the Olivares slide were established in order to plot the liquid limits and the plasticity index on a Casagrande Plasticity Chart. The standard Unified Soil Classification System of the samples was determined according to the D 2487-83 ASTM designation. The lithology of the samples was divided into four groups and their consistency and mineralogy were compared. The mineralogical analysis was carried out by X-ray diffraction, using a Philips PW 1710 diffractometer; $\text{CuK}\alpha$ radiation and a scanning speed of between 1° to 6° in dry powder specimens and orientated aggregates.

MINERALOGY

Four main lithologies can be identified in the landslide. The outcrops and core evidence show that the upper part of the moving material consists mainly of black and dark green claystones. Grey and green marls and clayey marls can also be seen in the Hundidero barranco cropping out along the main scarp at the southern side of the crown of the slide. Interbedded in the sequence are levels of red marls, while within the barranco itself are altered marls and quaternary soils.

On the whole the most important minerals in all the samples taken are phyllosilicates, quartz, calcite and feldspars with minor quantities of gypsum, dolomite and opal CT. The proportions in which these minerals occur are shown in Table I.

The quantities of several of the clay minerals have been determined both for fractions of <2 microns and 2-20 microns. The character and proportions of these are shown in Table II. It can be seen that smectites are the dominant facies, reaching at times proportions of up to 90% of the material sampled. Illite and palygorskite are also abundant, although their proportions do not usually exceed 40%. Chlorite and kaolinite, although not always present, represent between 5% and 15% of the total, occurring normally in the 2-20 microns fraction.

Crystallographic analysis shows a high degree of crystallinity in the smectites (0.8-0.9) which diminishes significantly in the silt fraction of the soil samples (0.25-0.45). The b_0 of the smectites indicates that they are dioctahedral with values of around 9.025-9.045, which points to an Fe + Mg content in octahedral positions of about 0.7-0.9 atoms per half-unit cell.

TABLE I. Bulk mineralogy and U.S.S. Classification of the several lithologies distinguished in the landslide at Olivares.

MINERAL	Dark clays	Grey marls	Red marls	Soils
Phyllosilic.	60-85	25-60	30-45	35-40
Quartz	10-20	5-25	3-6	5-10
Calcite	0-15	25-70	50-65	35-50
Dolomite	0-2	0-2	0-3	0-20
Feldspar	0-4	0-2	---	0-2
Gypsum	0-5	---	0-5	---
Opal CT	0-2	---	---	---
U.S.C.S.	CH, MH	CL, CL-ML, (ML)	CH, MH, CL	CL, ML

TABLE II. Clay mineralogy (%) of the 2 micron and 2-20 micron fractions and parameters determined in the samples from Olivares.

MINERAL	Dark clays		Grey marls		Red marls		Soils	
	<2 μ	2-20 μ	<2 μ	2-20 μ	<2 μ	2-20 μ	<2 μ	2-20 μ
Smectites	65-90	60-85	60-80	40-75	65-75	45-75	40-75	10-40
Illite	10-30	15-35	15-30	15-50	10-15	10-30	15-35	50-60
Kaolinite	0-5	0-8	2-7	2-6	7-15	8-15	3-18	5-25
Chlorite	0-5	0-7	---	0-3	2-8	2-8	4-8	6-12
Palygorskite	2-16	0-12	2-20	3-30	0-6	0-10	---	---
PARAMETERS								
Biscayé Index	0.7-0.95	0.6-0.9	0.8-0.9	0.6-0.9	0.7-0.9	0.6-0.8	0.6-0.8	0.2-0.4
Illite crystallin.	0.4-0.5	0.2-0.4	0.35-0.5	0.2-0.4	0.25-0.45	0.3-0.4	0.45	0.25
b_0 smectites	9.025-9.041		9.035-9.048		9.033-9.048		9.044	

REFERENCES

COMAS MINONDO, M.C. (1978). Sobre la geología de los Montes Orientales. Sedimentación y evolución paleogeográfica desde el Jurásico al Mioceno inferior (Zona Subbética, Andalucía). Ph. D. Thesis, University of Bilbao.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CHARACTERIZATION OF THE PHYLLOSILICATES IN METAMORPHIC ROCKS OF THE SOUTHERN HESPERIAN MASSIF (OSSA-MORENA AND CENTRAL-IBERIAN ZONES)

A. LOPEZ MUNGUIRA and E. SEBASTIAN PARDO⁺

Dpto. Geología. Facultad de Ciencias. 06071 BADAJOZ. (Spain)

Dpto. Min. y Petrol. Facultad de Ciencias. 18002 GRANADA. (Spain)

INTRODUCTION

The metamorphic precambrian rocks that include the Ossa-Morena Zone (OMZ) are a series of biotite schist, amphibolytes, shales, and black-quartzites, with a high organic content and major contribution from volcanic-type materials.

The characteristic series of the Central-Iberian Zone (CIZ) are made-up of conglomerates, sandstones, greywackes and lutites also having a high organic content (Complejo Esquisto Grauváquico). The age of this complex is middle upper Vendian-lower Cambrian /1/.

MINERALOGY

Rocks from the OMZ have phyllosilicates in varying proportions, whereas quartz and feldspar retain a relatively uniform distribution (fig. 1a).

The phyllosilicates found are mainly micas. Chlorite occurs in highly variable proportions, and others such as kaolinite, smectite, or mixed-layer minerals appear sporadically.

The micas are generally dioctahedral, although there exist trioctahedral types. The average value of the parameter b_o is 9.015 \AA for the former and 9.173 \AA for the latter. They all show a clear phengite tendency (fig. 1b) /2/. Crystallinity index (CI) ranges from 0.18 to 0.25^o of 2θ , measured at the 004 reflection, indicating a high degree of crystallinity. The iron content (% of Fe_2O_3), calculated from the intensities of the basal reflections I_{004}/I_{002} /3/, varies widely from 1 to 7%, the upper value being characteristic of the biotites.

On the other hand, the chlorites show quite homogeneous crystallochemical parameters (fig. 1c; calculated following /4/, and may be classified as ferric clinoclinoes /5/. The average value of parameter b_o is 9.290 \AA .

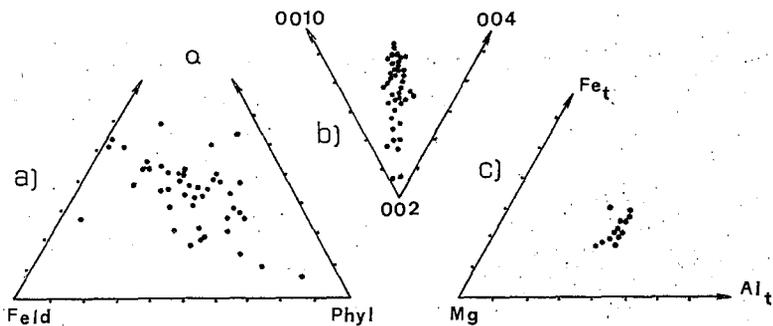


Figure 1. Triangular Diagrams corresponding to the Ossa-Morena Zone.

The remaining phyllosilicates, kaolinite, smectites, and mixed-layer chlorite-vermiculites, appear in amounts of little significance and are interpreted as forming in the weathering of feldspar and phyllosilicates.

In the CIZ (Complejo Esquisto Grauváquico), the feldspar content is relatively constant, except for certain samples which might be considered to be feldspar-greywackes. Quartz and phyllosilicates are found in varying proportions, with the latter always predominant (fig. 2a). The proportion of mica is greater than 50%. Its phengitic character /2/ can be seen from the basal intensities (fig. 2b). A fairly low iron content, -- between 0.4 and 2.5 (% of Fe_2O_3) also indicates that we are dealing with aluminous micas. The CI is high, 0.19^o of 2θ . The average value of the parameter b_0 is 9.009 Å.

The chlorites, which, with an average value for b_0 of 9.289 Å, are -- trioctahedral, present similar values for the Fe and Mg contents /4/, and may be classified as being stages halfway between chamosite and clinochlore /5/. (fig. 2c).

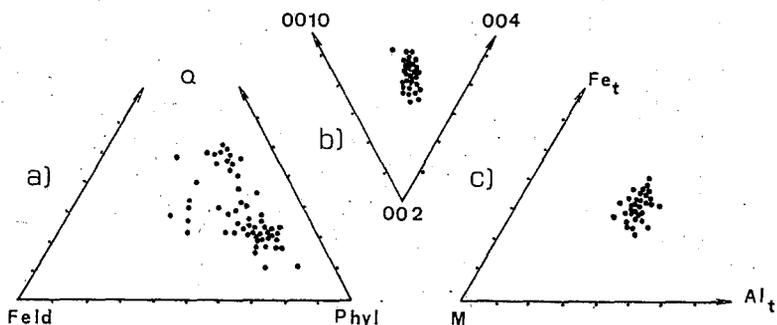


Figure 2. Triangular Diagrams corresponding to the Central-Iberian Zone.

The existence of ordered mixed-layer chlorite-vermiculite in appreciable proportions is worthy of note. This could be interpreted as originating in an altering of chlorites. Kaolinite is always present.

CONCLUSIONS

Even though both zones appear similar in overall mineralogy, we saw in the section on mineralogy that this is not case when one looks at detailed phyllosilicate composition either qualitatively or quantitatively.

One can take the phengites of the CIZ to be essentially detrital. The chlorites would be formed from other phyllosilicates present in the sediments by transformation during a very low-grade metamorphic process. In the OMZ, on the other hand, the micas, with very nearly a trioctahedral nature, would not have been inherited as such, but formed possibly from more illitic or phengitic stages by a metamorphic process of greater intensity (according to the geological data, of medium grade).

The basins in which these materials were originally deposited before undergoing the aforementioned metamorphism had to have quite different features. In the CIZ, the greater Al content of the micas, together with the presence of other aluminium-rich phyllosilicates (i.e. the kaolinites, although these have been considered to be products of soil formation or of weathering, well after metamorphism), makes us believe that the detrital contribution together with the influence of nearby emerged relief, was far more important than in the case of the OMZ, where the existence of magnesium chlorites, and the lower proportion of Al in the micas, would indicate a basin which may have been subsiding more quickly or at any rate, influenced much less by continent.

REFERENCES

- /1/. PALACIOS, T. (1986). Tesis Doctoral.
- /2/. REY, J.Ph. et KUBLER, B. (1983). Schweiz. Min. Petr. Mitt. 63,13-36.
- /3/. MARTIN RAMOS, J.D. y RODRIGUEZ GALLEGO, M. (1978). Anal. Quim. Real Soc. Esp. Fis. Quim. 74, 235-241.
- /4/. NIETO, F. y RODRIGUEZ GALLEGO, M. (1982). Soc. Ital. Min. Petr. 38, 1429-1436.
- /5/. BAILEY, S.W. (1980). Can. Mineral. 18, 143-150.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE COMPLEXITY OF KAOLINITE

R.C. MACKENZIE AND L. HELLER-KALLAI*

Dept. of Chemistry, University of Aberdeen, Old Aberdeen, B9 2UE (UK)

* Dept. of Geology, The Hebrew University, Jerusalem 91904 (Israel)

Kaolinite is usually regarded as one of the simplest of clay minerals, the composition being near theoretical, isomorphous substitutions being limited essentially to the surface layers of crystals and the main complexity arising from the mode of stacking of the layers. In view of recent observations, however, this simple picture must now be questioned. Thus, Heller-Kallai et al. (1986) noted that the "water" released on the dehydroxylation of kaolinite and other clay minerals affected calcite in a peculiar manner and Keller (1986) and Heller-Kallai et al. (1987) showed that the dehydroxylation of kaolinite resulted in the liberation of volatiles containing a wide variety of species (F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , NH_4^+ , Si^{4+} , Al^{3+} , traces of various metal ions and even gases) in addition to water. Moreover, Mackenzie and Rahman (1987) and Mackenzie et al. (1987) demonstrated that the calcite dissociation endotherm on DTA curves for mixtures with a Cornish kaolinite was considerably distorted in atmospheres of air, nitrogen and carbon dioxide. The configuration of the calcite peak depended on various instrumental and procedural factors, as well as on particle size, and was not due to the superposition on the calcite endotherm of exotherms caused by solid-state reactions - although such reactions do appear to modify the peak at the higher temperatures induced by a CO_2 atmosphere.

The present paper presents new evidence in the form of detailed analyses of dehydroxylation volatiles, the composition of which is sensitive to experimental conditions and impurities (including other clay minerals), and of DTA curves for mixtures of different kaolinites with calcite. For nine such mixtures, examined in static air and with dry and moist nitrogen flowing through the samples, no two sets of DTA curves were identical, although moist nitrogen always tended

to enhance a low-temperature component of the calcite endotherm. These variations must be related in some way to the volatiles released on dehydroxylation and the fact that even samples from the same general locality gave widely diverse results suggests that considerable variation can occur within one deposit.

It appears likely, as Keller (1986) postulates, that the species volatilized during dehydroxylation occur either chemisorbed or within the kaolinite crystal lattice rather than in accessories, but the most urgent task is to determine their location. For this purpose, kaolinite, even if it proves more complex than currently envisaged, seems the best subject for study.

REFERENCES

- Heller-Kallai, L., Miloslavski, I. and Aizenshtat, Z. (1986). Naturwiss., 73, 615-617.
- Heller-Kallai, L., Miloslavski, I. and Aizenshtat, Z. (1987). Clay Miner., in press.
- Keller, W.D. (1986). Am. Miner., 71, 1420-1425.
- Mackenzie, R.C. and Rahman, A.A. (1987). Thermochem. Acta, in press.
- Mackenzie, R.C., Rahman, A.A. and Moir, H.M. (1987). Thermochem. Acta, in press.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MODELLING TITRATION CURVES OF MIXED MATERIALS WITH VARIABLE AND PERMANENT SURFACE CHARGE: THEORY.

L. MADRID AND E. DIAZ-BARRIENTOS

Instituto de Recursos Naturales y Agrobiología. Sevilla.

The adsorption of potential-determining ions by variable charge surfaces has been extensively studied, and various mathematical models have been applied to the data. However, only two of these models have proved to be highly successful, those given by Bowden et al. (1977) and by Davis et al. (1978). The former considers the interface divided in various planes of electric potential, and supposes the adsorption of p.d.i. to happen in the inner plane, while the electrolyte ions are adsorbed in a second, outer plane. A third plane defines the beginning of the Gouy diffuse layer. The amount of charge in each of the first two planes is calculated by a Stern-type equation, and two electric capacitances are defined between each pair of planes. Instead, the Davis model considers the adsorption of each p.d.i. to happen at a particular surface site, which becomes charged, and each electrolyte ion adsorbed is associated with one of those charged sites.

Madrid et al. (1984) studied titration curves of mixtures of an iron oxide and a clay mineral and suggested some points for modelling the behaviour of such mixed materials. In this communication, the suggestions of Madrid et al. are developed.

As a basis for a model of adsorption of p.d.i. by mixed materials we have chosen the theory of Bowden et al. (1977), as their model is more versatile and does not need any previous assumption about the nature of the bond with the surface. We have considered two kinds of surfaces able to adsorb p.d.i., and we will call them 'oxide' and 'clay' for the sake of simplicity. The clay surface bears a given permanent charge, and each surface adsorbs p.d.i. according to

a Stern-type equation to calculate the charge conveyed by such adsorption. Each equation includes a different value of the electric potential. Another Stern equation describes the adsorption of electrolyte ions by the oxide. We have simplified the model by neglecting the adsorption of these ions by the clay surface, as it is generally admitted that no specific affinity is expected to occur if the main electrolyte ions are Na^+ and Cl^- . Three capacitors are defined in the interface, one between the plane of adsorption of p.d.i. and that of electrolyte ions by the oxide, another between the latter and the beginning of the diffuse (Gouy) layer, and another, in parallel with the other two, between the clay surface and the diffuse layer, which is considered common for both kinds of surfaces. A Gouy-type equation gives the charge in the diffuse layer. A system of capacitors similar to that described here has been suggested by Smit(1986) for non-uniform variable charge surfaces.

$$\sigma_{\text{ox}} = \frac{N_{\text{ox}}(1-R) \{ K_{\text{Hox}} a_{\text{H}} \exp(-0.039 \psi_{\text{ox}}) - K_{\text{OHox}} a_{\text{OH}} \exp(0.039 \psi_{\text{ox}}) \}}{1 + K_{\text{Hox}} a_{\text{H}} \exp(-0.039 \psi_{\text{ox}}) + K_{\text{OHox}} a_{\text{OH}} \exp(0.039 \psi_{\text{ox}})}$$

$$\sigma_{\text{cl}} = \frac{N_{\text{cl}} R \{ K_{\text{Hcl}} a_{\text{H}} \exp(-0.039 \psi_{\text{cl}}) - K_{\text{OHcl}} a_{\text{OH}} \exp(0.039 \psi_{\text{cl}}) \}}{1 + K_{\text{Hcl}} a_{\text{H}} \exp(-0.039 \psi_{\text{cl}}) + K_{\text{OHcl}} a_{\text{OH}} \exp(0.039 \psi_{\text{cl}})}$$

$$\sigma_{\text{p}} = \frac{N_{\text{ox}}(1-R) \{ K_{+} a_{+} \exp(-0.039 \psi_{\text{p}}) - K_{-} a_{-} \exp(0.039 \psi_{\text{p}}) \}}{1 + K_{+} a_{+} \exp(-0.039 \psi_{\text{p}}) + K_{-} a_{-} \exp(0.039 \psi_{\text{p}})}$$

$$\sigma_{\text{d}} = -1.22 \times 10^{-10} \cdot c^{1/2} \cdot \sinh(0.0195 \psi_{\text{d}})$$

$$\psi_{\text{ox}} - \psi_{\text{p}} = \sigma_{\text{ox}} / [G_{\text{ox}}(1-R)]$$

$$\psi_{\text{p}} - \psi_{\text{d}} = (\sigma_{\text{ox}} + \sigma_{\text{p}}) / [G_{\text{d}}(1-R)]$$

$$\psi_{\text{cl}} - \psi_{\text{d}} = (\sigma_{\text{cl}} + \sigma_{\text{p}} R) / (G_{\text{cl}} R)$$

$$\sigma_{\text{ox}} + \sigma_{\text{cl}} + \sigma_{\text{p}} R + \sigma_{\text{d}} = 0$$

The various $K_{i\text{cl}}$ and $K_{i\text{ox}}$ are the binding constants of each ion i to the clay or oxide surface respectively, N_{cl} and N_{ox} are the maximum charge on each surface, the various

G are the capacitances of the capacitors described above, σ_p is the permanent charge on the clay surface, and R the proportion, in terms of the surface area, of clay in the mixture. These 13 parameters have to be estimated in order to solve the system for the various ψ (potentials) and σ (charges). Some of them can be independently estimated if the pure components are available. The experimentally accessible variables are the concentrations of each ion, a_i , and the total electrolyte concentration, c, and the adsorption of p.d.i. is a measure of $\sigma_{ox}^+ + \sigma_{cl}^-$.

A computer program has been designed to solve the system for a set of values of the parameters. Another program, based on that given by Barrow (1979), was developed to estimate the best fit of some of the parameters to a given set of experimental data of adsorption of p.d.ions. Both programs are written in FORTRAN.

Theoretical curves have been calculated for different values of the parameters, and it was concluded that the model reproduced very well the qualitative behaviour observed by Madrid et al. (1984) for mixtures of lepidocrocite and illite. Other data, to be published, corresponding to mixtures of various oxides and montmorillonite are also explained by the present model.

REFERENCES

- Barrow, N.J. 1979. CSIRO Div. of Land Res. Develop. Tech. Rep. 79/3.
- Bowden, J.W., et al.: 1977. Aust. J. Soil Res. 15, 121-136.
- Davis, J. A. et al. 1978. J. Coll. Interface Sci. 63, 480-499.
- Madrid, L. et al. 1984. J. Soil Sci. 35, 373-380.
- Smit, W. 1986. J. Coll. Interface Sci. 113, 288-291.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

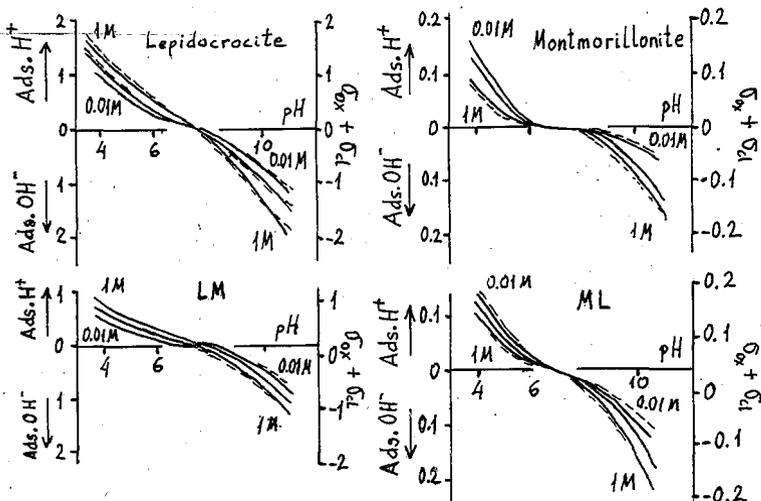
MODELLING TITRATION CURVES OF MIXED MATERIALS WITH VARIABLE AND PERMANENT SURFACE CHARGE: APPLICATION TO MIXTURES OF AN IRON OXIDE AND MONTMORILLONITE.

L. MADRID AND E. DIAZ-BARRIENTOS

Instituto de Recursos Naturales y Agrobiología. Sevilla.

Two well-known materials, lepidocrocite (specific surface area $116 \text{ m}^2\text{g}^{-1}$) and montmorillonite (internal surface area $700 \text{ m}^2\text{g}^{-1}$), can be useful to test the mathematical model described in the preceding communication. With this purpose, acid and base titration curves of both minerals and of mixtures containing 80% (w/w) of lepidocrocite (sample LM) and 80% montmorillonite (sample ML) were obtained at three ionic strengths (0.01, 0.1 and 1 M NaCl). The amounts of titrant consumed by the suspensions at each pH were corrected for the amount consumed by the corresponding solution at the same pH. The resulting graphs are shown in next page. Dashed lines will be explained later.

It is readily evident that the curves corresponding to pure lepidocrocite and LM are very similar to those observed in the literature for oxides and many variable charge soils, with a crossover point (point of zero salt effect, PZSE) approximately corresponding to the zero point of titration. Sposito (1984) concluded that the point of zero net charge (PZNC) and the PZSE are equal for solids with no specific affinity for the electrolyte ions, so that in the PZSE $\sigma_{\text{ox}} + \sigma_{\text{cl}}$ (σ_{H} of Sposito, 1984) equals $-\sigma_{\text{pR}}$ as long as $\sigma_{\text{p}} = 0$. A study of a wide variety of outputs of the model (Madrid and Diaz-Barrientos, in press) showed that when a crossover point was apparent in $\sigma_{\text{ox}} + \sigma_{\text{cl}}$ vs. pH plots it happened at $\sigma_{\text{ox}} + \sigma_{\text{cl}} = -\sigma_{\text{pR}}$, in agreement with the conclusion of Sposito (1984). This result provides a tool to con-



All ordinates are given in $\text{eq.cm}^{-2} \times 10^{10}$.

vert experimental ordinates to an absolute scale of $\sigma_{\text{ox}} + \sigma_{\text{cl}}$ when a crossover point is present. This is the case of the curves for lepidocrocite, $R=0$, and sample LM, $R=0.6$ (60% of the surface area of the mixture is calculated to correspond to montmorillonite). When $R \neq 0$, the correction term, $-\sigma_{\text{p}}R$, must be included in the optimization routine of the computer program if σ_{p} is one of the adjustable parameters. When $R=0$ the correction is obviously unnecessary.

For montmorillonite and ML, the crossover point no longer appears within the pH range studied, but there is an inflexion point near the initial point of titration, where the curves obtained at different ionic strengths run very close to one another. A similar point of inflexion appears in outputs of the model when R is close to 1 (data to be published) and its ordinate is always $\approx N_{\text{ox}}(1-R)$. The reason for this behaviour of the model is not clear, but can be used to convert the p.d.i. adsorption axis to $\sigma_{\text{ox}} + \sigma_{\text{cl}}$ when no crossover is apparent. For a pure clay, the $\sigma_{\text{ox}} + \sigma_{\text{cl}}$ values must be the same as those for p.d.i. adsorption, as

1-R=0. In the case of ML (R=0.95) the correction was also included in the program, as N_{ox} is one of the adjustable parameters.

The dashed lines show the results of the best fit of the model for each material (they are visible only in those regions where they can be distinguished from the experimental curves at the scale of the drawing). Pure lepidocrocite gave the values $N_{ox}=3 \times 10^{-9} \text{ eq.cm}^{-2}$, $G_{ox}=9 \times 10^{-13} \text{ eq.cm}^{-2} \cdot \text{mV}^{-1}$, G_d^{-1} , $K_{Hox}=1.2 \times 10^8$, $K_{OHox}=2.6 \times 10^6$, $K_+=0.09$, $K_-=0.01$, and montmorillonite $N_{cl}=3.5 \times 10^{-11}$, $K_{Hcl}=2.0 \times 10^3$, $K_{OHcl}=8.0 \times 10^3$, $G_{cl}=10^{-8}$, $\sigma_p=-2.5 \times 10^{-11}$. The significance was high ($P < 0.01$) in both cases.

The best fit for LM and ML gave very similar values of most parameters except N_{ox} , which resulted considerably smaller in both mixtures (1.9×10^{-10} for LM and 8.2×10^{-11} for ML). This unexpected result could suggest that the clay, with a much higher surface area than the oxide, interacts with the latter in such a way that it is able to block in a considerable degree the access of the adsorbing ions to the oxide. This assumption is supported by the fact that the value of N_{ox} is smaller the higher the value of R. More information is necessary to confirm this hypothesis, so that it should be taken carefully.

REFERENCES

- Madrid, L. and Diaz-Barrientos, E. J. Soil Sci. (in press).
Sposito, G. 1984. The surface Chemistry of Soils. Oxford University Press.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**ELEMENT CHARACTERIZATION AND SITE OCCUPANCY IN CLAY MINERALS:
AN APPROACH BY X-RAY ABSORPTION SPECTROSCOPY**

A. MANCEAU¹, G. CALAS¹ AND D. BONNIN²

1-Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et 7 et CNRS
UA09, Tour 16, 4 place Jussieu, Paris 75252, France.

2-Laboratoire de Physique Quantique, Ecole Supérieure de Physique et de Chimie,
10 rue Vauquelin, 75231 Paris Cedex 05.

The determination of site occupancy and intracrystalline distribution of elements in mineral lattice is a clue for understanding geochemical processes governing mineral formation and trace element behaviour. In clay mineralogy, a selective crystal chemical approach is thus needed to prove whether or not an element is incorporated in the mineral framework and what kind of distribution it exhibits among the different sites available. In spite of the great variety of physical techniques used in clay mineralogy, few of them give a structural and chemically selective information.

X-ray Absorption Spectroscopy (XAS) is a *structural* method possessing two main advantages: an *atomic selectivity* and *sensitivity* to diluted systems. This atomic selectivity arises from x-ray absorption discontinuities attached to a given element in the material. Because x-ray absorption edges of the different elements are well separated in energy, this type of spectroscopy is a unique method for probing the local environment of specific elements in a multicomponent sample. The detection limit for first row transition elements is as low as a few hundred ppm. XAS data comprise both absorption edge structure and EXAFS.

X-RAY ABSORPTION EDGE

The energy and intensities of absorption edge features contain information about the oxidation state, site symmetry and electronic structure of the atom under study. Edge spectroscopy has been used to determine the oxidation states of chromium in chlorite¹ and copper in vermiculite². The former mineral exhibits optical spectroscopic properties: the presence of hexavalent Cr was then suggested in the literature. However no chromate groups are found from edge structure analysis and Cr is proven to be trivalent. The structure of the Cu K-edge of vermiculite indicates that copper atoms are divalent. A last example is provided by Co-bearing Mn oxides where it is shown that Co is trivalent in these supergene ore minerals³.

EXAFS

The long-range oscillation above the absorption edge, or EXAFS, is due to the interference between the outgoing and the backscattered photoelectron waves. EXAFS provides information about the local structure of the x-ray absorbing atom. Typically, three nearest atomic shells surrounding the central x-ray absorber can be quantitatively studied: interatomic distances, nature and number of surrounding atoms are determined. One of the main interest of EXAFS for clay mineralogy and associated oxides is its capability to recognize the host mineral for a given element. Furthermore it provides an unique way to study the reality of solid solutions by distinguishing 3d elements from Mg and Al. Three series of minerals will serve to illustrate the influence of the chemical composition of the second atomic shell on EXAFS spectra: the phlogopite-annite series, the lizardite-nepouite series and the kerolite-pimelite series⁴⁻⁵.

In the phlogopite-annite series, Fe atoms are known to be almost randomly distributed over sites of the octahedral sheet. As a consequence each Fe atom is surrounded by Fe and Mg second-nearest neighbours at about 3.05Å. Furthermore 4 (Si,Al) atoms are located in the vicinity of this (Fe-Mg) coordination shell ($d(\text{Fe-Si,Al})=3.27\text{Å}$). This structurally well known series offer a unique case to decipher how interfere the photoelectron wave propagating from the x-ray absorbing Fe atom and waves backscattered by Mg, Fe and Si atoms in phyllosilicates. It is shown that waves backscattered by Mg and Fe atoms are out of phase whereas waves backscattered by Si and Fe are almost in phase in the studied wavevector range.

In Ni-bearing lizardite and kerolite, EXAFS spectra recorded at the Ni K-edge are mainly independent of the Ni content. A detailed analysis of EXAFS spectra shows that the intracrystalline distribution of nickel within the Mg octahedral sheet is never random. Such a clustering of Ni atoms indicates non-equilibria processes during the formation of these low-temperature minerals. It is thus expected that an increasing formation temperature and the subsequent faster cation exchange kinetics will favour ideal mixing of mineral components as for biotites. EXAFS could be an unique tool providing information about the temperature during the crystallization of these minerals.

REFERENCES

- 1- Calas G., Manceau A., Novikoff A. and Boukili H. (1984). *Bull. Miner.* 107, 755-766.
- 2- Ildefonse P., Manceau A. and Prost D. (1986). *Clay and Clay Minerals.* 34, 3, 338-345.
- 3- Manceau A., Llorca S. and Calas G. (1987). *Geochim. Cosmochim. Acta.* 51, 105-113.
- 4- Manceau A. and Calas G. (1985). *American Mineralogist.* 70, 549-558.
- 5- Manceau A. and Calas G. (1986). *Clay Minerals.* 21, 341-360.

MINERALOGICAL CHARACTERISTICS OF OLIVE-GROWING SOILS IN JAEN (S. SPAIN) IN RELATION TO THEIR PRODUCTIVITY.

MARAÑES, A. ⁽¹⁾; ORTEGA HUERTAS, M. ^(2,3) & SIMON, M. ⁽¹⁾

(1) Dpto. Edafología y Química Agrícola. Universidad de Granada (Spain)

(2) Dpto. Mineralogía y Petrología. Universidad de Granada (Spain).

(3) Instituto Andaluz de Geología Mediterránea. C.S.I.C.-Univ. de Granada (Spain).

INTRODUCTION

In this paper we intend to relate the mineralogical, physical and chemical characteristics of the soil to their productivity.

The area studied lies in the region of "La Loma", in the province of Jaén. All the soils are cultivated in the same manner, both with regard to the way they are harrowed and to the way they are fertilised. Furthermore, as they are closely situated, the climatic conditions are the same. For this reason, the manifest differences in their yield must be put down to variations in their mineralogical, physical and chemical properties.

TYPES OF SOILS AND THEIR RESPECTIVE PRODUCTIVITY.

The soils studied have developed upon old remains of glacis (profile L-4), sandstones (profile L-19) and marls (profiles L-5 and L-9).

The soils formed on the glacis and sandstones are calcic Cambisols with two Ap horizons (Fig. 1 a and b). Horizon Ap1 is developed as a direct consequence of harrowing and has a crumb structure, while horizon Ap2, with a thickness of some 10 cm. to 20 cm., corresponds to a compact horizon and has an agglomerate structure split into prismatic units by small vertical cracks.

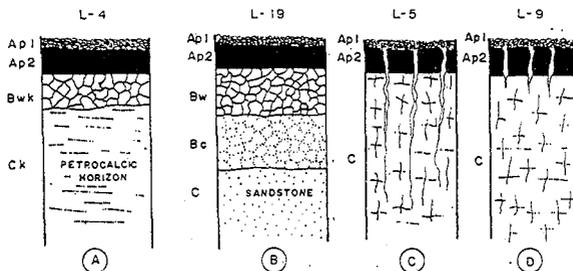


Fig. 1. The soils studied

The fundamental difference between the two kinds of soil, however, is to be found in the subsoil: in the case of profile L-4 there is a thick petrocalcic horizon beneath the topsoil at a depth of 46 cm., while in profile L-19 a fresh, damp sandstone appears.

With regard to profiles L-5 and L-9 (Fig. 1 c and d), soils developed on marls, the former has a slope of some 12%, while the latter is almost flat (1%) and receives eroded materials from roundabout. These soils also have two Ap horizons, genetically similar to those already described, although the Ap₂ horizon differs morphologically in that during the dry season it fragments into wide, deep cracks. They show no cambic horizons and thus can be classified as calcic Vertisols in the case of profile L-5 and calcareous Regosols in the case of profile L-9.

As far as yield is concerned, profile 4 is that which has the lowest average productivity index (36 kg per olive tree p.a.) and also an enormous fluctuation in crop from year to year. It is noteworthy that the olives grown on this soil dehydrate considerably during the summer, pointing to a lack of water in the subsoil. Profiles L-5 and L-19 show an average yield of 50 kg per olive tree p.a., with little annual fluctuation, and the olives do not shrink in the summer. The characteristics of the crop produced on profile 9 are similar to the latter, except that the annual yield reaches some 78 kg per olive tree

MINERALOGICAL AND TEXTURAL CHARACTERISTICS.

As can be seen in Table I the textures of the soils vary from clayey to clayey loams in those developed on marls and from loams to sandy loams in those developed on glaucis or sandstone. As for the mineral content, it is worth noting that the smectite content of the clay fraction in the soils developed on marls is much higher (30%-45%) than in the other soils (10%-20%).

Table I. Mineralogical and textural characteristics.

Horizon	TOTAL SAMPLE					< 2 μ m				Texture
	C	D	Q	Fd	CM	I	Sm	Ch	K	
L4-Ap ₁	25	-	18	t	57	70	18	7	5	l
L4-Ap ₂	22	-	22	<5	56	72	10	10	8	l
L4-Bwk	22	-	14	5	59	61	24	9	6	l
L5-Ap ₁	21	-	10	<5	65	58	32	5	5	cl
L5-Ap ₂	22	-	13	<5	61	51	37	7	5	cl
L5-C	37	-	10	5	48	49	40	5	6	cl
L9-Ap ₁	25	-	10	<5	61	53	36	11	t	cl
L9-Ap ₂	26	-	11	t	63	39	46	10	5	c
L9-C	26	-	10	t	64	59	29	10	5	c
L19-Ap ₁	18	11	13	<5	54	90	5	5	t	l
L19-Ap ₂	41	5	21	<5	29	85	10	5	t	scl
L19-Bw	32	<5	19	t	46	76	19	5	t	scl
L19-BC	41	<5	12	-	43	85	11	<5	t	sl
L19-C	39	16	22	t	23	71	21	5	5	sl

C = calcite; D = dolomite; Q = quartz; Fd = feldspars; CM = clay minerals; I = illite; Sm = smectites; Ch = chlorite; K = kaolinite; l = loam; cl = clay loam; c = clay; scl = sandy clay loam; sl = sandy loam.

CONCLUSIONS

In all of the soils studied harrowing produces a more or less compact lower horizon which reduces the permeability and thus the deep drainage of the soil. Nevertheless, the effects of this compact horizon on the moisture reserves of the soil in any particular instance depend largely on its morphology in the dry season and also on the characteristics of the subsoil.

The high smectite content of the clayey soils encourages fierce cracking in the summer which breaks up the Ap₂ compact horizon and allows moisture to penetrate to the subsoil during the rainy season, providing the trees with a moisture reservoir during times of drought.

The contrary applies to the soils developed on glaci^s and sandstone, which, being scarce in clay and smectites, remain compacted and do not allow deep drainage. This effect may be counterbalanced to some extent by the nature of the subsoil itself, as in the case of profile L-19, where the fresh, humid sandstone provides the trees with a certain amount of moisture during the dry season.

The least productive of the profiles studied is affected by a combination of a compact Ap₂ horizon and beneath it a thick petrocalcic crust that provides no moisture for the tree roots. The yield of this soil, therefore, depends directly on the rainfall in any one year, as it has little moisture-harbouring capacity.

(This work forms part of the "Capacidad de uso de los suelos de olivar de la provincia de Jaén" project. Diputación Provincial de Jaén).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE ARRANGEMENT OF SILICATE LAYERS IN PHASE BOUNDARIES DURING THE MICA-VERMICULITE TRANSFORMATION AS REVEALED BY HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

CH. MARCKS, H. WACHSMUTH AND H. GRAF VON REICHENBACH

Institut für Bodenkunde und Sonderforschungsbereich 173
Universität Hannover, FRG

A definite phase boundary can be seen with light or scanning electron microscopy in mica particles during their transformation to vermiculite by interlayer cation exchange. The interface separates the expanded from the still contracted zone and moves from particle edge to particle center during the reaction. The phase transition obviously imposes considerable strain on the structure. The spacial arrangement of silicate layers within the interface should reflect the structural mechanisms by which the internal strain is minimized. These mechanisms are believed to correspond with cooperative phenomena observed at interlayer cation exchange in micas.

The paper reports on preliminary observations made by inspecting layer arrangements in ultramicrotome sections of mica-vermiculite with HRTEM. Special emphasis is given to methods of sample preparation.

By repeatedly treating particle size fractions of natural biotite (Miask, Ural) with $BaCl_2$ solutions samples were prepared representing different states of mica vermiculite transformation. Since the hydrated state of Ba-vermiculite is not maintained under the conditions in the electron microscope (high vacuum, heating in the electron beam), the structure of the expanded phase was stabilized by introducing n-alkylammonium ions into the interlayers. This was done either by reexchanging barium from the vermiculitic part of the structures or by treating micas directly with alkylammonium ions. However, the stability of alkylammonium vermiculite was found to be also limited. X-ray diffraction measurements on preheated samples revealed a significant decrease of basal spacings already in the range of temperatures between 100° and 200°C.

Alkylammonium treated minerals were embedded in SPURR-resin. Parallel orientation of the platy particles was achieved by centrifugation. Ultramicrotome sections were prepared by cutting parallel to the c-axis. The thickness of the sections was in order of 20 - 200 nm. Sections with well preserved structures were obtained from minerals with a particle size of up to 25 μm in diameter.

Selected area electron diffraction was used for aligning the sample to the electron beam. Clear electron diffraction patterns and highly resolved lattice images could thus be obtained from ultra thin sections of the original biotite as well as of dehydrated Ba-vermiculites.

Using published structural data of biotite, a simulation of the lattice images of biotite and of dehydrated Ba-vermiculite could be calculated for comparison with the experimentally obtained images. Due to their similarity in layer distance, dehydrated Ba-vermiculite could not be distinguished from the biotite.

For several reasons the investigation of alkylammonium saturated vermiculites is more difficult. Instability of the structures in the electron beam admits only a short time for inspecting the sample, adjusting its orientation and taking photographs of lattice images. Due to damage caused by the electron beam definite layer distances can not be expected. Variation of layer distances was observed for samples saturated with alkylammonium ions of identical chain length.

With the reservation required by these limitations examples of partially expanded biotites, of contracted or expanded structural domains and of interstratification are presented in the paper.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

RELATION BETWEEN MUDSTONES COMPOSITION, SOURCE ROCK AND ENVIRONMENTAL AND DIAGENETIC CONDITONS IN THE MIDDLE MUSCHELKALK OF CATALANIDES RANGE (N.E. OF SPAIN).

R. MARFIL*, R.M. CASTAÑO* and F.X. CASTELLTORT**

*Dpto. de Petrología y Geoquímica, F.C. Geológicas, Universidad Complutense. 28040 Madrid.

**Dpto. de Geología Dinámica. Universidad Central. Barcelona.

The middle Muschelkalk sediments in the Catalanides Range have been interpreted as alluvial deposits similar to the terminal fans formed under arid-semiarid climatic conditions. The sedimentary basin is controlled by a system of longitudinal and transversal faults which delimit two basins separated by the Prades threshold (Fig. 1). The first basin is located to the North (central and northern domain) and is mainly filled with red sandstones alternating with subordinated red siltstones (alluvial-sand flat deposits). The southern basin (meridional domain) is fundamentally characterized by evaporites and red mudstones being dolostones very scarce, deposited in a playa lake or coastal sabkha (CASTELLTORT, 1986).

The composition of the associated sandstones, in both areas, includes fine to medium-grained arkoses. They are mainly composed by subrounded monocrystalline quartz grains, in which the content of k-Feldspar is higher than the content of plagioclase. Low contents of volcanic and schist fragments are present, and micas (muscovite, biotite, chlorite) and micritic ooids are accessory minerals. (CASTELLTORT, et al., 1987).

The sandstone composition is related to the granitic source rocks. According to DICKINSON's and SUCZEK's model (1979), these arkoses are derived from continental blocks in an uplifted basement.

The sandstones show around the grains abundant montmorillonitic and chloritic clay films but scarce illitic and ferric coatings. Other important cementing minerals

are K-feldspar, quartz, analcime, anhydrite, dolomite, calcite and baritine. This association of cements and the characteristic sequence of neof ormation and replacement indicates a brackish to evaporitic diagenetic environment. This condition is more intense to the southern basin and toward the top of the stratigraphic columns (CASTELLTORT et al., 1987).

All those samples, as well as the $<20\mu\text{m}$ and the $<2\mu\text{m}$ fractions from mudstones and siltstones beds were analyzed in eleven stratigraphic columns. X-ray diffraction methods, optical microscopy and scanning electron microscopy were applied. The S.E.M. was fitted with an energy-dispersive X-ray analyzer. The illite crystallinity of KUBLER (1969) (IC) and the I(002)/I(001) relation after ESQUEVIN (1969) was measured. Likewise, the chlorite crystallinity, the content of mixed-layers chlorite/smectite and the % of expandible layers were obtained by comparison with theoretical X-ray patterns of RUIZ AMIL et al., (1967).

The bulk composition of the studied samples shows a highly homogeneous quartz and K-feldspar content, with minor amounts of albite for the southern basin. The calcite tends to be associated with the red sandstone facies in the northern basin. On the other hand, the dolomite is present in the evaporitic facies of the southern basin. The amounts of hematites are similar in both areas. The gypsum is characteristic of the southern and central domains. The analcime cement is present only in sandstone and siltstone facies, whereas the anhydrite cement shows a similar tendency in all the stratigraphic columns.

The clay minerals of the $<20\mu\text{m}$ and $<2\mu\text{m}$ fractions are formed by illite with subordinated chlorite. However, the samples taken near the Prades threshold, present a notable increase of chlorite. In the southern basin, smectites and $^{14}\text{Ch}-^{14}\text{Sm}$ mixed layers are also present, although small amounts of these clay minerals sometimes occur in the northern siltstones.

Generally, the illites associates with carbonates and sulphates have less crystallinity in the $<20\mu\text{m}$ fraction as well as in the $<2\mu\text{m}$ one. This characteristic is influenced by two principal factors: first, because illite is highly degraded upon its arrival to the distal zone of the basins, and second, because illite in the fine-grained sediments is less affected by diagenesis (GARCIA PALACIOS, et al., 1977). In relation to the illite composition, illites associated with most evaporitic environments, show a lower Al/Mg+Fe value than those associated with fluvial environments. Likewise, the latter have a trioctahedral trend, which is more noticeable in the $<2\mu\text{m}$ fraction. This fact is probably due to the closeness of the fluvial illites to granitic and metamorphic (muscovite and biotite) source areas. At the same time, the illites from evaporitic facies, show a Fe+Mg deficit, partly due to a loss by hydrolyzation, and partly because Mg was used in the structure of carbonates.

Chlorite tends to have small amounts of smectite expanding layers, similar to those occasionally shown by some illites. We have also observed that the percentage of expanding layers increases toward the marine-influenced areas, where true ^{14}ch - ^{14}sm mixed layers exist.

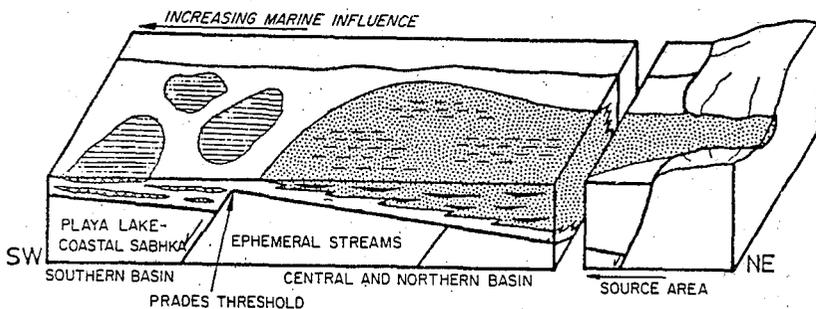


Fig. 1.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PREVENTING PHOTOCHEMICAL REACTIONS ON A CLAY SURFACE

L. Margulies,^a H. Rozen,^a L.O. Ruzo^{a,b} and E. Cohen^b

Departments of (a) Soil and Water and (b) Entomology,
Faculty of Agriculture, The Hebrew University,
Rehovot 76-100, Israel.

Coadsorption of two different organic compounds at the surface of a clay leads to systems in which energy transfer processes between the two types of organic molecules may take place. If the efficiency of these processes is high enough, other deactivation pathways such as photochemical reactions may be quenched. Thus, photolabile compounds can be stabilized on the clay surface provided that an adequate chromophore, which can act as energy acceptor, is also adsorbed. This method has been suggested for the photostabilization of agrochemicals <1> and was applied to prevent photochemical degradation of a pyrethroid insecticide exposed to solar radiation <2>.

Another group of insecticides which suffer from instability in sunlight and which therefore have not been used in agriculture in spite of their favorable toxicological properties are the nitromethylene heterocycles. Preliminary experiments carried out on a compound of this group showed that some photostabilization can be achieved using the method described above.

Since the efficiency of energy transfer processes depends on the spectroscopic characteristics of the donor and the acceptor, on the distance between them and on their relative orientations, the clay and chromophore to be used should be chosen according to the chemical and spectroscopic properties of the pesticide to be photoprotected.

Montmorillonite was used as a clay support and three different cationic dyes were used as potential chromophores for protecting the insecticidal nitromethylene heterocycle. The dyes and the pesticide were adsorbed on the clay and the clay-organic interactions were investigated using uv-vis absorption and differential FTIR spectroscopies. In all cases more information was obtained by means of the FTIR technique.

Bioassays using the flour beetle *Tribolium castaneum* were carried out in order to test the insecticidal power of prepared clay-dye and clay-dye-pesticide complexes. Unirradiated complexes retained the biological activity of the pesticide molecules indicating that adsorption to the clay surface did not affect their insecticidal activity.

The bioassays were repeated on samples which were exposed to sunlight for various periods of time. A considerable decrease in insecticidal activity was observed in almost all irradiated samples. However, this photodeactivation was slower in some clay-dye-pesticide complexes than in the isolated pesticide. The degree of protection achieved depended on the absorption characteristics of the chromophores. Best results were obtained using dyes which have strong absorption bands around 400 nm.

References

1. Margulies, L., Rozen, H. and Cohen, E., *Nature*, 315:658-659 (1985).
2. Margulies, L., Cohen, E. and Rozen, H., *Pest. Sci.*, 18:79-87 (1987).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**REACTION OF HYDRATED TITANIA GEL WITH AQUEOUS SOLUTIONS OF LITHIUM
HYDROXIDE.**

O. MARINO AND G. MASCOLO

Dipartimento di Ingegneria dei Materiali e della Produzione. Univer-
sità di Napoli. Piazzale Tecchio, 80125 Napoli - ITALY.

Hydrolysis of titanium (IV) - salts in aqueous solutions easily yields colloidal products. However several studies have shown that no stable crystalline titanium (IV) hydroxides or oxyhydroxides exist (1-2).

On the other hand it is known that lithium ion is characterized by high mobility in crystal lattice of its oxides, even though this mobility does not depend on the presence of tunnels, vacancies or layers in their structures (3-4), what is of considerable interest in the field of solid electrolytes. On the ground of this considerations and keeping in mind the possibility of isomorphous substitution between Li and Ti (5), it has been thought interesting to study the reaction of hydrated titania gel with aqueous solutions of LiOH.

TiO₂ of R.C. grade was dissolved in hot concentrated H₂SO₄ and precipitated as hydrated TiO₂ gel with ammonia in cold solution. The precipitate was filtered, washed with distilled water and treated with LiOH solutions. The different suspensions, with X_{Li} (molar ratio) ranging between 0.6 and 0.9, were kept in sealed Teflon con-

tainers and rotated for a week at constant temperatures of 60, 80, 100 and 120°C. After the hydrothermal treatment the products were washed to eliminate excess LiOH and dried in air.

Li₂O was determined by atomic absorption spectrophotometry after dissolution of the solid into acid solution. While TiO₂ was determined gravimetrically. The heat-induced weight loss was determined through simultaneous TG and DTA measurements. X-ray powder patterns (XRD) were obtained using a Guinier de Wolff camera with CuK radiation. Pb(NO₃)₂ was chosen as internal standard.

The crystalline phases obtained by hydrothermal treatment in the Li₂O-TiO₂-H₂O system are summarized in fig. 1. Li₂TiO₃ formation is favoured by temperature and concentration of LiOH (6). The X-ray pattern of this phase is characterized by two reflections at 0.207 nm and 0.145 nm (7).

At lower temperature a microcrystalline phase with a considerable line broadening forms. Table 1 reports the X-ray powder data of this phase.

The Li-Ti ratio of this phase is 1:2, while the weight loss due to water release from OH⁻ is three times the content of Li. Therefore the chemical formula should be represented as LiTi₂O₃(OH)₃, corresponding to an oxyhydroxide. This formula resembles that of the oxyhydroxide of trivalent metals of the type MOOH.

The lattice constant were calculated in the orthorhombic system with a=0.380 nm, b=1.690 nm and c=0.290 nm. A further refinement should be done when the crystallinity of the product will be enhanced. The X-ray pattern remains unchanged even though the sample is thermally treated for many hours at 200°C, breakdown occurs at temperatures of 250°C or higher, giving rise to an amorphous product.

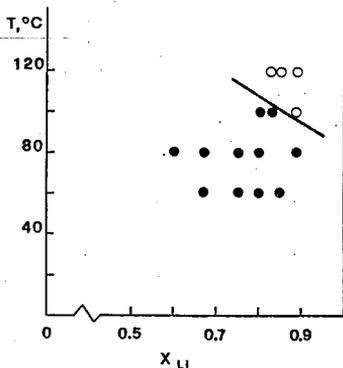


Fig. 1 Crystallization field in the $\text{Li}_2\text{O}-\text{TiO}_2-\text{H}_2\text{O}$ system after removing excess $\text{LiOH}:\text{LiTi}_2\text{O}_3(\text{O})$, $\text{LiTi}_2\text{O}_3(\text{OH})_3$ (●).

TABLE 1. X-ray powder data for $\text{LiTi}_2\text{O}_3(\text{OH})_3$.

$d(\text{nm})$	Intensity
0.850	VVS (b)
0.369	W
0.314	VS (b)
0.281	m (b)
0.243	VS (b)
0.203	S (vb)
0.190	S
0.185	W (b)
0.168	m (b)

References

- 1) W.B. BLUMENTAL, *The Chemical Behaviour of Zirconium*, Von Nostrand, Princeton, N.J. 1958 p. 181.
- 2) S. KOMARNENI, E. BREVAL and R. ROY, *Journal of Non-Crystalline Solids* 79 (1986) 195.
- 3) R.J. CAVA, A. SANTORO, D.W. MARPHY, S.M. ZAHURAK and R.S. ROTH, *J. Solid State Chem.* 50 (1983) 121.
- 4) M.H. THACKEROY, W.I.F. DAVID and J.B. GOODENOUGH, *Mat. Res. Bull.* 17 (1982) 785.
- 5) A.R. WEST, *Journal of Materials Science-Letters* 16 (1981) 202.
- 6) P.E.D. MORGAN, *J. Amer. Ceram. Soc.* 57 (1974) 499.
- 7) JCPDS Inorgan. Comp. File 8-249.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

WEATHERING PRODUCTS OF VOLCANIC ROCKS FROM CAMPO DE CALATRAVA
(CIUDAD REAL, CENTRAL SPAIN).

Martín de Vidales, J.L.*; Casas, J.**; Galván, J.**;
Herrero, F.* and Hoyos, M.A.*

* Departamento de Química Agrícola, Geología y Geoquímica. Facultad de Ciencias. Universidad Autónoma de Madrid. Cantoblanco. 28049 MADRID. Spain.

** Instituto de Edafología y Biología Vegetal. Serrano, 115 bis. 28006 MADRID. Spain.

Mineralogical analysis of weathering products from four soil profiles were made by transmission electron microscopy, X-ray diffraction and chemical methods. The underlying volcanic rocks were studied by petrographic microscopy and X.R.D.

RESULTS.

The underlying volcanic rocks are olivinic basalts and olivinic nephelinites.

The chemical analysis (C.D.B.) show high contents in amorphous SiO_2 , Al_2O_3 and Fe_2O_3 concerning to the $< 2 \mu\text{m}$ fractions. These fractions display high C.E.C. (70-100 meq/100 gr) and the chemical analysis show Al_2O_3 percentages ranging from 15 to 22%, low contents in K_2O , CaO , MgO and Na_2O so as variable quantities in TiO_2 (0.5 to 2.5 %). These fractions show high loss after fusion to 1000°C ($\text{H}_2\text{O}^- + \text{H}_2\text{O}^+ = 17-25 \%$). In all the instances, clay fraction show positive reaction to the allophane test (Fielde and Claridge, 1966) with values 9.4 to 10.2 after two minutes contact.

The whole of the Mg-saturated oriented samples, show a strong reflection to 14.6 \AA and an asymmetric peak to 7.2 \AA with variable relative intensities. After ethylene-glycol solvation the 14 \AA peak displaces to 18 \AA ratifies the smectite presence. The 7.2 \AA peak remains

in this spacing with a greater asymmetry and partially swells, giving rise to a broad line diffraction between 7.2 and 11 Å. After heating to 300 °C, 14 Å peak collapses to 10 Å. The 7.2 Å peak remains and a new reflection to 8.2 Å appears. After heating to 550°C only a 10 Å sharp reflection is detectable.

The Li⁺ test (Lim and Jackson, 1986), swelling to 18 Å indicates the beidellitic character of the smectite, corroborated by d₀₆₀ reflection to 1.50 Å in the randomly powder diffractogram. The 7.2 Å peak shows an anomalous behaviour after formamide test (Churchman et al. 1984) because it does not swell at all.

The study of clay fraction with T.E.M. confirms the presence of beidellite with sizes between 2 to 1 µm, so as spheroidal halloysites in rolling phases with sizes < 0.1 µm and diatom debris.

DISCUSSION AND CONCLUSIONS.

The main weathering products of volcanic rocks in the semiarid climatic conditions in the Central Spain volcanic region are:

1. Beidellites, previously described and studied by us (Martín de Vidales et al. 1985 and 1986).
2. Allophanes, confirmed by the NaF test. This component has been already outlined in wet climatic conditions. In this case, its presence in semiarid climatic conditions can be justified by constituting the core of halloysites rolling.
3. 7Å halloysites with spheroidal morphology that could influence perhaps in its anomalous behaviour after formamide test.
4. The diffuse reflections between 7.2 and 11 Å in O.A. + E.G. which are defined to 8.2 Å after heating up to 300 °C. We think that these reflections are due to a randomly mixed layer phyllosilicate 1:1 - - beidellite. A mineral with similar behaviour was characterized as interstratified kaolinite-smectite by Yerima et al. (1985). Quantification curves for the X-ray powder diffraction analysis of mixed-layer kaolinite-smectite (Tomita and Takahashi, 1986), allow appraise to 70% 1:1 phyllosilicate - 30% beidellite proportions.

REFERENCES

- CHURCHMAN, G.J.; WHITTON, J.S.; CLARIDGE, G.G.C. and THENG, B.K.G. (1984). Clays and Clay Minerals 32, 241-248.
- FIEDES, M. and PERROT, W. (1966). N.Z.J.Sci. 9, 623-629.
- LIM, C.H. and JACKSON, M.L. (1986). Clays and Clay Minerals, 34, 346-352.
- MARTIN DE VIDALES, J.L.; SANZ, J.; GUIJARRO, J.; HOYOS, M.A. and CASAS, J. (1985). Proceeding 5th. Meeting of the European Clay Groups, Pragne. J. Konta Editor. 465-470.
- MARTIN DE VIDALES, J.L.; CASAS, J. and SANZ, J. (1986). Clay Minerals 21, 389-400.
- TOMITA, K. and TAKAHASHI, H. (1986). Clays and Clay Minerals 34, 323-329.
- YERIMA, B.P.K.; CALHOUN, F.G.; SENKAYI, A.L. and DIXON, J.B. (1985). Soil Sci. Soc. Am. J. 49, 462-466.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

STUDY OF THE KAOLINITE FIRST EXOTHERMIC REACTION USING SINGLE CRYSTALS

R. MARTINEZ, M.P. CORRAL, S. DE AZA, J.S. MOYA, T.A. BIELICKI*, G. THOMAS*

Instituto de Cerámica y Vidrio, C.S.I.C., Arganda del Rey,
Madrid (Spain).

*Dept. of Materials Science and Mineral Engineering. Univer
sity of California, Berkeley, CA. 94720 (USA).

Despite of abundant studies, disagreement still exists
on the mechanisms of the transformacion and the cause of the
~ 980°C exothermic reaction of kaolinite.

The main reasons for the different results already pu
blished in the scientific literature (1-3), deal with a) ty
pe of impurities present and b) the ordered-disordered natu
re of the starting kaolinite.

In the present work, single crystals ~ 5-10 mm size of
kaolinite quoted from a Colombian deposit (4) have been se
lected.

The kaolinite single crystals were completely characte
rized by XRD, SEM and EDX (figure 1).

Samples were heat treated up to 1020°C in a Mettler DTA-
TGA equipment as shown in figure 2.

In order to improve the TEM observation of the heat treat
ed samples, these were chemically etched by NaOH 10% solu
tion with the aim to remove the exolved silica during the
980°C exothermic reaction (figure 2).

Samples for TEM observation were prepared by cleaving
along the basal planes of the layer structure. The slices
were ion-thinned to produce electron transparent regions at
the edges. A Philips EM400 Transmission Electron Microscope
was used. Bright field and dark field images and selected
area diffraction (SAD) patterns were obtained (figure 3).

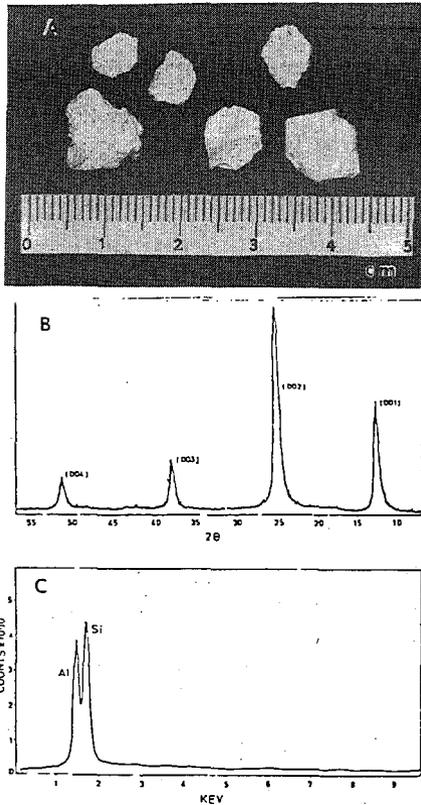


Fig. 1.- (A). Kaolinite crystals, (B) XRD pattern quoted on the surface of a kaolinite crystal. (C) EDX microanalysis.

As observed, the samples show a finely grained microstructure. The SAD patterns showed several discontinuous rings, indicating the presence of both polycrystalline and amorphous materials.

A dark field image using part of a ring reflection showed that the crystallites are very small (~ 10 nm) and uniformly dispersed along the plates.

After etching the microstructure was now visible with

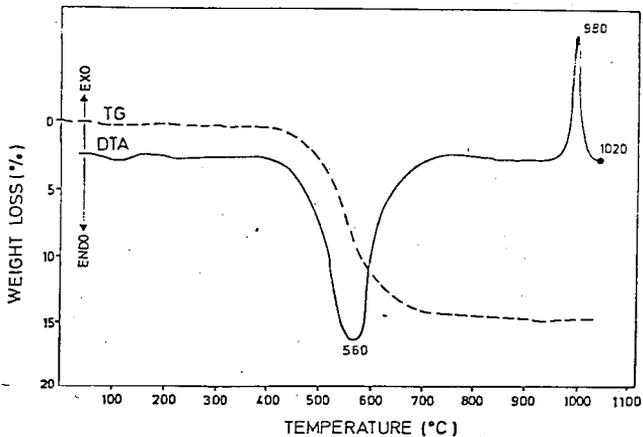


Fig. 2.- DTA-TGA curves of the kaolinite crystals.

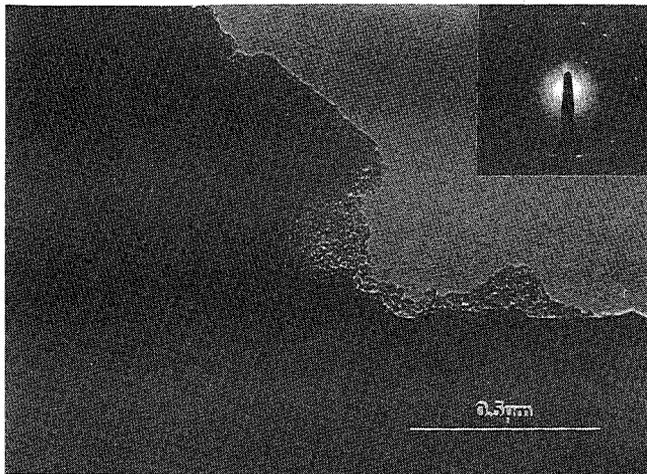


Fig. 3.- (A) Bright field TEM image of a kaolinite single crystals edge after heat treatment at 1020°C and NaOH solution attack, and the corresponding SAD pattern.

strong contrast slightly defocused to emphasize the boundaries between different regions.

Indexing the SAD patterns in both cases shows rings consistent with the interplanar spaces of mullite. No cubic patterns was observed in any case.

These results clearly show that the first exothermic peak of kaolinite is actually due to an homogeneous nucleation of mullite crystallites on the original kaolinite plates rather than to the formation of Si-Al spinel as claimed by several authors.

REFERENCES

- (1)- G.W. BRINDLEY and M. NAKAHIRA. J.Am.Ceram.Soc. 47 (1959) 311-324.
- (2)- A.K. CHAKRABORTY and D.K. GHOSH. J.Am.Ceram.Soc. 61 (1978) 170-173.
- (3)- S.M. JOHNSON, J.A. PASK and J.S. MOYA. J.Am.Ceram.Soc. 65 (1982) 31-35.
- (4)- D. PAETSCH, K. FELTKAMP and G. SCHIMMEL. Ber.Dtsch.Keram. Ges. 40 (1963) 386-391.

ACKNOWLEDGEMENTS

One of the authors (M.P. Corral) wishes to thank Explosivos Riotinto for financial support.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE REFRACTORY CLAYS IN ITALY

P.MATTIAS (*), E.BARRESE(**), E.PARIS(***) , G.DE CASA(*)

- (*) - Dip. Idraul. Trasp. e Strade - Area Geologia, Univ. di Roma
- Centro di Studio per la Geologia Tecnica del CNR
- (**) - Dip. Scienze della Terra, Univ. della Calabria
- (***) - Dip. di Scienze della Terra, Univ. di Camerino

The most important deposits of refractory clays in Italy are located essentially in the Sardinia and Piemonte regions. In general these materials show very homogeneous mineralogical-petrographic compositions and are related to different geologic and paleoclimatic environments. Age and genetic conditions are also very dissimilar.

In Sardinia, refractory clays are mostly of Bajocian-Bathonian age (Dogger) and lie at the base of a calcareous-dolomitic formation called "Tacchi" which limits their exploitation. They result from the alteration of a basement constituted by gneiss, micaschists, and granitic rocks. The deposition of these argillaceous products (kaolinite, illite prevailing on smectite, and mixed-layers) occurred in a lacustrine-lagoon or deltaic environment.

The clays from Piemonte, on the other hand, are mostly of Pliocene-Pleistocene age and are present with large outcrops. These clays derive from the chemical-physical alteration of clastic rocks (especially conglomerates) from the last Pleistocene Alpine glaciations. While the components

of the conglomeratic rocks are very variable (i.e., ranging from acidic to ultramaphic igneous rocks, and metamorphites with highly variable metamorphic grades, the final products are nearly homogeneous with kaolinite, halloysite, and micaceous minerals (illite) as newly formed minerals and quartz and, sometimes, feldspars as residual.

The mining conditions seem favorable at a first sight, but the presence of iron hydroxides on the technical side and ecological problems often put severe constraints on the normal running of the operations.

Geochemical and geotechnics studies along with TEM and SEM observations complete the present investigation and confirm that the two areas under study are characterized by considerably different geologic histories and conditions of formation.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

A STUDY OF CERAMICS FROM PICO BUITRE (Guadalajada, Spain) (Shelters: Transition period Bronze and Iron Age).

P.Menéndez Aparicio*, J.M. Palacios**, A. de Andrés Gómez de Barreda

*Instituto de Química Inorgánica 'Elhuyar', C.S.I.C., Serrano 113, 28006 Madrid.

**Instituto de Química Física 'Rocasolano', C.S.I.C., Serrano 119, 28006 Madrid.

INTRODUCTION

The settlement of Pico Buitre is situated on a small hill adjacent to the Tejer mountain close to Henares river and town of Espinosa, province of Guadalajara. Its exact location is defined by the coordinates $0^{\circ} 38'5''$ EM/ $40^{\circ} 53'55''$ N in the chart 486 'Jadraque' of the Geographical and Statistical Institute. This site has been studied in (1-2).

The Archaeological materials were distributed on a rather oval gray-colour area, 6m in diameter approximately, attributed to small cottages belonging to the transition period between the Bronze and Iron Age, approximately 950 BC.

From an archaeological standpoint the materials selected in the study have been classified in three groups as follows:

1. Ceramics with burnished surface (samples 27, 46, 55, 97) of ultra Pyrennean influences.
2. Ceramics with excise and incise designs of the Late Bronze Age Period (samples 72, 73, 74, 76 and 2, 65, 67, 69).
3. Graphited painted Ceramics belonging to a period beyond the Late Bronze Age II and II that corresponds to a cultural level prior to that of the Meseta (the latter being adscribed to by the presence of fields of urns) (samples 93, 94, 96).

EXPERIMENTAL

The samples were studied by the techniques used by previous researchers, such as XRD, TG, petrographic analysis and SEM with EDX.

RESULTS AND DISCUSSION

The finish surface in ceramics from group 1 is relatively smooth but there is no evidence of any slip, simply it seems the result of solid rubbing. In group 2 two thick layers appear clearly well defined. In group 3 carbonaceous material seems to have been intentionally deposited. Excluding samples from group 3 that present a higher content in Fe and lower content in Si, all of other are similar in chemical composition.

From the mineralogical analysis is deduced that all of samples have the same minerals too: quartz, feldspars and plagioclases, mica and aluminium and iron oxides. It is important to observe the almost absence of calcite (ceramics are no calcareous) and the presence of clay minerals, especially kaolinite, sepiolite and montmorillonite. Samples 94, 67 and 96 show, however, peculiarities consisting in the enrichment in feldspars and mica.

The two layers in samples from group 2 are similar in composition and minerals. It seems that they appear differentiated due to light changes in colour and porosity. Nevertheless the surface in samples from group 3 are clearly enriched in K as compared with bulk, probably due to the increasing concentration of mica. The brilliant and smooth black aspect of the surface is achieved through the presence of mica and carbonaceous material.

CONCLUSIONS

-From TG analysis, refiring treatment and mineralogical studies it has been possible to set up that the firing temperature of all analyzed samples is below 800°C.

-Because the composition of samples is not very different between them the raw materials used in manufacturing have been probably the same, except samples from group 3. The main differences appear in the techniques used in achieving the final product: burnishing, slip, etc.

REFERENCES

- (1) Valiente Malla J. Pico Buitre (Espinosa de Henares. Guadalajara). La transición del Broze al Hierro en el Alto Henares. Wad-Al-Hayara 11, (1984) (9-57).
- (2) Valiente Malla, J., Crespo Cáno, M.L., Espinosa Gimeno, C. Un aspecto de la celtización en el Alto y Medio Henares. Los poblados de ribera. Wad-Al-Hayara, 13 (1986).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

INFLUENCE OF THE TEXTURAL AND STRUCTURAL PROPERTIES OF FIBROUS CLAY
MINERALS ON THE ACTIVITY AND SELECTIVITY OF SUPPORTED-NiMo-HYDROHEATING
CATALYSTS.

A. MIFSUD*, A. CORMA, F. MELO and E. SANZ

* Instituto de Ciencia de Materiales C.S.I.C. Serrano, 115 dpdo.
28006-MADRID (Spain)
Instituto de Catálisis y Petroleoquímica C.S.I.C., Serrano, 119.
28006-MADRID (Spain)

The hydrotreating of the heavy fractions of petroleum is becoming the more and more a necessity. This is due not only to economical reasons which impose a better use of the bottom of the barril, but also to an ecological necessity which is claiming for a decrease in SO_x and NO_x emission. This process results in a rapid deactivation of the catalysts used due to an irreversible adsorption of metal impurities, mainly nickel and vanadium. The utilization of unexpensive catalysts is an attractive way in competence with the noncatalytic methods.

The fibrous clay minerals are relative abundant materials and by different treatments it is possible to obtain textural and acid properties comparables to those of the Al_2O_3 and SiO_2 supports.

In this work a series of NiMo catalysts supported on sepiolite and palygorskite in their natural states and modified by acid leaching have been prepared. The preparation variables studied were: method of metal deposition, amount of active phase, support pretreatment and sulfuration conditions.

The NiMo catalysts, in both oxide and sulfided forms, have been characterized by X-ray diffraction, TEM, BET surface area and adsorption of pyridine. The catalytic activity has been measured in a fixed bed reactor at 300°C and 400°C and 20 Kg.cm⁻² of total pressure using a mixture of cyclohexene, cyclohexane and thiophene. In this way, the activity of the catalysts for hydrogenation, isomerization and hydrodesulfurization reactions have been simultaneously estimated.

In catalysts supported on sepiolite, an optimum for HDS and hydrogenation activity is found for a 12%, 5% wt MoO_3 , NiO respectively prepared by simultaneous impregnation by the pore volume method at pH = 5. 400°C and 3 hours of sulfuration are the optimum conditions with these catalysts. The isomerization activity is very sensitive to the support acidity. For the catalysts supported on palygorskite the HDS and hydrogenation activities are lower than the corresponding catalysts supported on sepiolite but the isomerization activity is higher, probably due to the support acidity.

By relating the catalytic activity of NiMo/sepiolite with the characterization results it is found that the precursor active phase in HDS is formed by a non-stoichiometric solid solution of nickel and molybdenum oxides. After sulfuration this phase is transformed in a molybdenum sulfide phase while the other oxides phases present are not sensibly affected. The origin of this sulfided phase and the broad of the diffraction peak seems to indicate the presence of nickel in molybdenum positions in the crystals similar to the related active phases found in catalysts supported on alumina.

For the NiMo/palygorskite catalysts the mixed oxide phase is not clearly observed. The molybdenum sulfide formed could proceed from a molybdate phase present in the oxide samples. The lower activity of the NiMo/palygorskite catalysts can be due to the lower BET surface area of these samples in comparison with the catalysts supported on sepiolite.

Finally, the activity of the sepiolite catalysts is comparable to the NiMo/ γ -alumina prepared following the same procedure.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THERMAL STABILITY AND TEXTURAL PROPERTIES OF EXCHANGED SEPIOLITES

A. MIFSUD, I. GARCIA and A. CORMA*

Instituto de Ciencia de Materiales C.S.I.C., Serrano, 115 dpdo.
28006 MADRID (Spain).

*Instituto de Catálisis y Petroleoquímica C.S.I.C., Serrano, 119.
28006 MADRID (Spain).

Sepiolite is a crystalline magnesium silicate whose structure consists of flat laths (2:1) joined together at their edges (1). In its natural state, the sepiolite does not show ionexchange capacity. However, the Mg^{2+} located at the border of the octahedral sheet could be made exchangeable, so an exchange capacity of ~ 300 meq. $100 g^{-1}$ could be achieved. Besides that potential, and the existence of channels of $10.8 \times 4.0 \text{ \AA}$ run the whole length of the fibre, the structure of the sepiolite resembles that of the zeolites, and could, therefore, present shape selectivity for adsorption and catalytic reactions.

In the present work, a natural sepiolite (Vallecás type) was used as the starting material. Procedures for exchanging part of the cations located in the octahedral layer have been reported (2,3) and in our case we have introduced by ion exchange for the corresponding Mg^{2+} located at the edges of the octahedral sheet, ~ 150 meq. $100 g^{-1}$ of monovalent and divalent cations such as Li^+ , Na^+ , K^+ , Cs^+ , Ca^{2+} and Ba^{2+} . The resultant materials have structural, textural and thermal characteristics quite different from the natural sepiolite. They are suited to show interesting adsorption and catalytic properties.

The materials are studied by different physicochemical techniques i.e., i.r., X-ray diffraction, BET surface, pore volume distribution and T.G. It has been observed that the specific surface of the exchanged samples decreases with respect to the original sepiolite being the decrease stronger in the case of monovalent cations (Table I).

TABLE I

Specific surface area of natural and exchanged sepiolite.

SAMPLE	Nat-Sep	Ca ²⁺ -Sep	Ba ²⁺ -Sep	Li ⁺ -Sep	Na ⁺ -Sep	K ⁺ -Sep	Cs ⁺ -Sep.
S_{BET} m ² /gr	295	205	196	170	108	165	155

On the other hand, the water molecules, coordinated to the ions located at the borders of the octahedral sheet, are lost at temperatures different that in the case of the purely magnesium sepiolite. Moreover in most of the exchanged samples the structure is not completely folded even after heating the samples at 600°C in vacuum of 10^{-2} torr (Fig. 1).

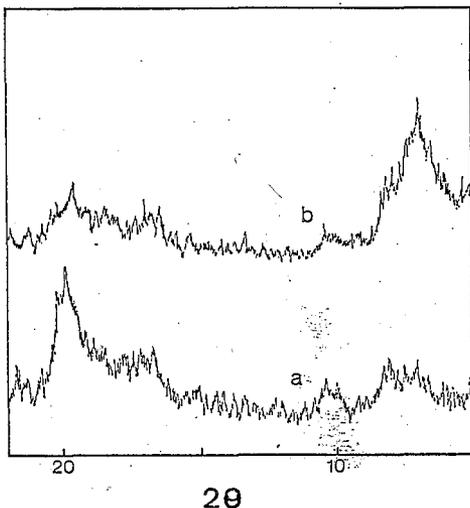


Figure 1.- XRD pattern of a) natural sepiolite, b) Li-sepiolite, heated at 600°C. in vacuum of 10^{-2} torr.

In other words, some of the exchanged samples present still the channel structure when heating at high temperatures.

The properties of the new materials have been explained on the basis of the ion composition of octahedral sheet. In this way the electric field and the void space available for adsorption are explained on the basis of the charge to radio of the exchanged cations.

REFERENCES

- (1) BRAUNER K & PREISINGER A (1956) *Tschermaks Miner. u. Petrogr. Mitt.* 6, 120.
- (2) YOKA M OKKUCHI Y (1978) Supporting metal on sepiolite in catalyst manufacture. *Japan Kokai* 53, 7592-7594
- (3) CORMA A, FORNES V, MIFSUD A, PEREZ PARIENTE J (1983) Procedimiento para la obtención de un silicato derivado de silicatos magnésicos cristalinos del tipo de la sepiolita. *Sp. Pat.* 527-756



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGY AND UTILIZATION OF "POTTERY STONE" AS RAW MATERIAL FOR
WHITE PORCELAIN IN JAPAN

H. MINATO

Hyogo University of Teacher Education (Japan).

White porcelain or china ware has been manufactured from "Pottery Stone" in Eastern Asia, Japan, China, Korea and etc., originally from ancient. The pottery stone is white colour, coarsely apperant and not earthy and also not clayey, is formed by hydrothermal reaction, is composed of fine grains of quartz and clay minerals, and is used for the raw material of white porcelain. Five to ten quarries are worked in Japan. In this report, the mineral assemblages and their characteristics of procelain of different production localities in Japan are compared.

Main quarries developed in our country are Hattori, Kawai, Izushi, Tobe, Izumiyama and Amakusa, from northeast to southwest. The pottery stone is formed from acidic igneous rocks such as rhyolite, quartz porphry, etc. by hydrothermal alterations. Mineral composition and its properties in each quarries are shown as follows:

Amakusa Toseki*: This is a main pottery stone in Japan, and is occurred at Shimojima Island, Amakusa Islands, west of Kumamoto Prefecture, Kyushu. Two or three groups of rhyolite dykes, which are altered to pottery stone, are developed in western side of the Shimojima. The direction of the dykes are NNE - SSW and NE - SE and their length are 15 km and 5 km, respectively and their width are 10 to 30 m. Pottery stone of high quality is mainly composed of sericite of 1M and 2M₁ type, kaolinite, fine grained quartz, and small amounts of feldspar, sericite/montmorillonite and sericite/chlorite mixed layer clay minerals. They have been used for raw material of ceramics such as the mixing materials of china wares and fire brick and main raw material for white porcelain named 'Arita

* Toseki is a Japanese name of pottery stone.

Yaki' - 'Arita Porcelain' or 'Imari Yaki' - 'Imari Porcelain', which are famous porcelain from old time in the world.

Izumiyama Toseki: It had been worked at Izumiyama, eastern part of the Arita city, where has been a manufacturing place of 'Arita Porcelain', since 17th century, as the first period of the manufacturing. The pottery stone is mainly composed with sericite and fine-grained quartz.

Tobe Toseki: It has been worked southern area of Matsuyama city, Ehime Prefecture, Shikoku Island, and is raw material of 'Tobe Yaki' - 'Tobe Porcelain'. It is composed of sericite and fine grained quartz and with a small amounts of sericite/montmorillonite mixed layer clay mineral, in some case. The sericite has some NH_4^+ ion instead of K^+ ion, which will be one of the defects of the 'Tobe Porcelain'.

Izushi Toseki: It has been worked for raw material of 'Izushi Yaki' - 'Izushi Porcelain', at the eastern part of Izushi-cho, manufacturing place of the Izushi Porcelain, northern part of Hyogo Prefecture. The pottery stone was formed from glassy rhyolite dykes by hydrothermal alteration, and is composed mainly of Al-chlorite, sericite, sericite/chlorite and sericite/montmorillonite mixed layer clay minerals, fine-grained quartz and with a small amounts of kaolinite. It has characteristic mineral composition and has special property for the porcelain.

Hattori and Kawai Toseki: They are worked from Hattori and Kawai deposits and are situated about 20 km south of Kanazawa city, Ishikawa Prefecture. It is composed with sericite and fine-grained quartz.

Utilization.

The utirizations of pottery stone are devided into the following two methods, one is the mixing materil for ceramic production, such as fire brick, sanitary wears, an insulator, and porcelain wears, etc., and the second is main raw material for fine porcelain. The origin of the porcelain was produced in China from about 7th century, and one of the famous manufacturing place is Ching-te-chen. Main raw material of the Ching-te-chen porcelain is "Peitongzu" which is treated pottery stone by means of water washed methods. Techniques of manufacturing procelain, including raw material of pottery stone were derived to Japan from China. We have many kinds of porcelain, Arita Yaki, Kutani Yaki, Tobe Yaki, Izushi Yaki, etc., and each products has their specialities and they are derived from their raw materials which is its special character of pottery stone.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FORMATION PROCESSES OF HALLOYSITE FROM ACIDIC VOLCANIC GLASS BY WEATHERING REACTIONS

H. Minato and M. Otsu

Hyogo University of Teacher Education (Japan).

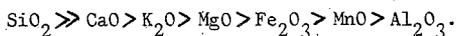
Field observations on the dacitic volcanic glass, so called "Shirasu bed", developed in the Kagoshima Prefecture, Southwest Kyushu, Japan, are carried out in order to trace the weathering processes. The "Shirasu bed" was formed about 22,000 years before present when the climate of the area was relatively high in temperature and humidity. Moreover, the experiments on the chemical weathering of the "Shirasu bed" are also carried out in order to trace the behavior of the major elements during the weathering.

Field observations revealed the following points:

1; Well weathered "Shirasu bed" is observed in the uppermost level of the bed at the Ryugamizu district, northern part of the Kagoshima city. There is a yellow soil bed which is composed of halloysite, allophane, and iron hydroxides. At the Magome, northern part of the Kagoshima Prefecture, there is a "Shirasu bed" which was welded and is not capable of percolation. In the bed, montmorillonite and calcite are found. Thin segregation veins of calcite are found in the montmorillonized bed. At these two localities, weathering profiles are well observed.

2; Exuded waters of fallout from the ceiling of the cave formed in the "Shirasu bed" were collected. Each waters have different pass in the bed. The chemical compositions of each water shows the differences of the pass of the circulation and the reaction with pumice.

The concentrations of the dissolved species decrease in the following sequence:



Chemical compositions of the weathered "Shirasu bed" of the

halloysite and montmorillonite zones are compared with those of the fresh "Shirasu bed". Dissolved components in the two zones are as follows:

Halloysite zone; $\text{SiO}_2 \gg \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{CaO} > \text{MgO} > \text{MnO}$ and no Al_2O_3 .

Montmorillonite zone; $\text{SiO}_2 \gg \text{K}_2\text{O} > \text{Na}_2\text{O} > \text{CaO} > \text{Fe}_2\text{O}_3 > \text{MgO} > \text{MnO}$
and no Al_2O_3 .

Leaching experiments of the "Shirasu" glassy rock are performed in order to trace the behavior of the elements during the weathering process. Fresh pumice of the "Shirasu bed" at the Takeoka, western part of the Kagoshima city was used for this experiment. The pumice was pulverized to 60 - 100 mesh. The pulverized samples were reacted with artificial rain water, which was the water saturated with air and CO_2 . Dissolved species were analyzed by means of gravimetry and atomic absorption spectrometry. Duration of the experiments were 300 hours. Dissolved species after the interaction are as follows: $\text{CaO} \gg \text{SiO}_2 > \text{K}_2\text{O} > \text{Na}_2\text{O} \gg \text{MgO} > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{MnO}$.

The differences in the concentration of the dissolved constituents in the four sequences can be ascribed to the different reactions during the weathering processes of the glassy volcanic materials.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SIGNIFICANCE OF Ba RICH ZEOLITIC SEDIMENTS OF THE OLIGOMIOCENIC SEQUENCES NEAR VOGHERA (PV-AL PROVINCES), ITALY.

V. MINGUZZI, N. MORANDI, F. TATEO

Dipartimento di Scienze Mineralogiche, Università di Bologna (Italy).

Thirty zeolitic sediments, sampled from some oligomiocenic sequences, outcropping in the northern Apennines near Voghera (PV and AL Provinces), Italy, were examined. The sediments are thick from a minimum of 2 cm to a maximum of 180 cm with average values about 30-40 cm and affect the pelitic-arenaceous sequences for a thickness of 80-100 m. The zeolitic layers are normally grey pink coloured and clearly distinct from the pelites by both the higher hardness and the defined boundary. They show many sedimentary textures as fine bedding, bio-turbations, slumps, cylindrical concentrations of pure green smectite and dispersed hexagonal crystals of biotite.

The prevailing mineral in the examined samples results to be a Ba rich phillipsite with BaO ranging in the sediment between 2% and 12%. The X-ray powder diffraction patterns of those phillipsites is largely correlated to BaO content: in particular the intensity of 10-1 and 011 peaks at 8.1Å and 6.4Å increases and that of 120 at 5.4Å decreases proportionally to BaO% values. The TG and DTG curves show the water loss reactions distributed in a wide range of temperature proving the presence of different phillipsitic frameworks characterized by variable BaO content and mixed in the same sample. The phillipsitic mineral is associated with small quantity of heulandite (four samples), analcime (two samples), smectite (most samples), calcite, authigenic quartz and clastic feldspars and biotite.

The chemical analyses (major and trace elements) of the whole samples were recalculated to 100 percent after removing calcite, quartz and other impurities, estimated by X-ray diffraction. The corrected chemical data are coherent with the principal mineralogical composition. The minor-element values show an anomalous enrichment of Zr, Nb, La and Ce and a content reduction of Zn, Cu, V, Cr, Co, Ni, Rb and Li that are normally rich in pelitic rocks of the examined sequences.

This exceptional finding is peculiar from the mineralogical, petrographic and geological point of view. In fact, the mineralogical and chemical composition and the observed sedimentary textures lead to attribute a volcanic origin to the examined samples. During a sequence of extrusive cycles into the basin could be occurred immediate hydrothermal reactions silica glass → zeolites and/or smectites. The Ba enrichment would be due to a "capture" mechanism of the element, released during the reactions, by the phillipsitic framework. The turbulent flows formed into the heated sea water would favour the distribution of the reaction products (zeolites and smectites) in a large space (other zeolitic sediments in the northern Apennines between Reggio Em. and Bologna are correlated with those from Voghera), in rapid subsequent phases and with typical structural features (cylindrical smectitic concentrations). The obtained chemical and mineralogical data might be a good suggestion to define the type of magmatism that characterized the Oligo-Miocene boundary in a large area of the northern Apennines.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

RELATIONSHIPS BETWEEN TERRA ROSSA AND NON CARBONATIC RESIDUE FROM CRETACIC LIMESTONES (PUGLIA-SOUTHERN ITALY).

M. MORESI AND G. MONGELLI

Dipartimento Geomineralogico - Università di Bari.
Trav. al N. 200 di Via Re David. BARI, (Italy).

The compositional pattern of terra rossa from Puglia has been examined both to evaluate the possibility of its origin from weathering of underlying cretacic limestones and to define the nature of the processes that have governed its evolution.

The statistical treatment of chemical data shows that the terra rossa carbonate free (82 samples), compared with the cretacic limestone residue (69 samples), is richer in SiO_2 and Al_2O_3 , and poorer in MgO , CaO , K_2O , Na_2O ; no differences exist in the contents of TiO_2 , Fe_2O_3 , H_2O .

The main mineralogical components both of terra rossa and of limestone residue are kaolinite, illite, Fe-oxides and hydroxides; minor components are quartz, feldspars, micas, Al-oxides and hydroxides.

According to the nature of main clay minerals and to the chemical differences between terra rossa and limestone residue, the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio has been assumed as an "weathering index" related to the plausible degradation from illite to kaolinite.

The pattern of chemical components in the limestone residue shows that as decreases the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio (namely as increases the weathering), increases Al_2O_3 , decrease MgO , CaO , K_2O , Na_2O , whereas no changes exist in the contents of SiO_2 , TiO_2 , Fe_2O_3 , H_2O .

Thus the trends of all components, SiO_2 excepted, well agree the chemical changes observed in the transition from

limestone residue to terra rossa. Only some quantities of SiO_2 , that no belong to limestone residue, seem to be added to terra rossa.

On this basis there is not any difficulty in believing that terra rossa may be originated from the weathering of cretacic limestone residue.

Nevertheless, it is necessary to remark that the evolution of terra rossa has not been only governed by chemical weathering because the pattern of chemical components of terra rossa shows that as decreases the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio, increase TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , H_2O , whereas decrease SiO_2 , Na_2O , K_2O , CaO . Thus the trends of some chemical components (namely SiO_2 , TiO_2 , Fe_2O_3 , MgO , H_2O) are changed in the terra rossa with respect to those observed in the limestone residue.

To explain these differences one can remark that the pattern of chemical components in terra rossa is quite similar to this found, as consequence of the grain size distribution, in several clay sediments from Southern Italy.

Thus, also in the terra rossa such as in the clay sediments, the pattern of chemical components appear to be governed by a gravitative selection of mineralogical components.

Moreover, the marked re-mixing of mineralogical components of terra rossa suggest that its evolution has been influenced by several stages of transport and deposition mainly developed in aqueous environment.

To sum up, the terra rossa from Puglia may be regarded as the weathering product of residue from underlying cretacic limestones. Nevertheless, the evolutive environment of terra rossa, at last in the mechanical respect, is very different to one of parent-residue from limestones.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

EXPLORATION AND EVALUATION OF KAOLIN DEPOSITS

Haydn H. Murray

Department of Geology, Indiana University, Bloomington,
Indiana 47405 (USA)

Kaolin production and utilization continues to grow annually. Because transportation and handling costs continue to escalate, more exploration and evaluation of kaolin deposits is being done in many areas of the world. The largest user of the industrial mineral kaolin is the paper industry where it is used both as a filler and a coater. These two applications require some different specifications, the more stringent being those required for utilization as a coating grade kaolin.

Geologically, kaolins occur as either primary or secondary deposits, the most common being those that are primary in their origin. Exploration techniques differ dependent upon whether the kaolin deposit is either primary or secondary. Some physical characteristics such as percent grit, particle size distribution, brightness, viscosity, abrasion, and mineralogy may differ in primary versus secondary deposits.

Exploration methods, particularly drilling patterns, are different for primary and secondary kaolin deposits. Evaluation may also differ dependent primarily on the eventual end use of the kaolin.

Processing techniques continually evolve so that many deposits that heretofore would have been considered unusable can be beneficiated into usable products. This is particularly true for making filler grade kaolins where brightness is a most important specification. There are several ways to improve brightness including gravity separations, oxidation and reduction reactions, high intensity magnetic separation and flotation.

Examples of the exploration and evaluation techniques that have been used for some deposits will be described in this paper.



THE Palygorskite Deposit of Bercimuel (Segovia, Spain)

I. NAVARRETE, M. PERALTA, M. SUAREZ, J. MARTIN-POZAS and I. ARMEN-
TEROS *

Department of Geology, University of Salamanca, Spain

* Department of Stratigraphy, University of Salamanca, Spain

The present work studies a deposit of palygorskite of economic importance situated in the small village of Bercimuel (N. of the province of Segovia, Spain).

Geologically, the deposit is situated in the area of confluence of two miocene alluvial fan systems (Fig. 1) and above the level of caliche layers that demarcate the joining of the two systems. The level of caliche changes distally (towards the NE) to carbonated levels of paludal/lacustrine origin.

The outcrop studied has an approximate thickness of five meters and a lateral width quite possibly greater than 100 m.

The rocks of the outcrop are fairly homogeneous in aspect and no significant structure can be observed; the only important feature is a slight change in colouring, possibly due to edaphic processes.

From the XRD study, it may be inferred that the major component of the rocks is palygorskite accompanied by smaller amounts of illite, smectite sepiolite and quartz.

The content in quartz does not surpass 15% in any of the samples studied and within the clay components palygorskite is the major mineral, reaching values close to 75%.

Regarding the conditions of the formation of the deposit, the magnesium character of the sepiolite and palygorskite point to the existence of a medium with a high Mg content.

It seems evident that the source area of the Mg must have been situated both in the paleozoic metamorphic rocks and in the mesozoic dolomitic formations of the Sierra de Honrubia-Pradales and the Sierra de

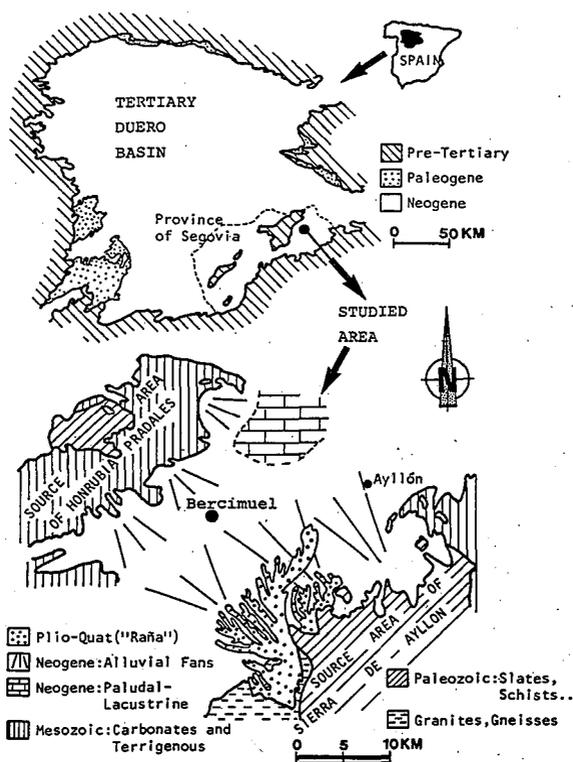


Fig. 1.- Location of the Bercimuel deposit.

Ayllón (Fig. 1) and, in view of its proximity to the zone studied, the provision of Mg must have been direct, although the possibility that it might have been the result of post-sedimentary processes cannot be ruled out.

The work here also reports on other results obtained both regarding mineralogy (chemical analysis, DTA, electron microscopy) and the determination of some properties useful for technical applications (absorption capacity, decolouring potential, rheological properties).

This work forms part of a project of geological prospection for special clays in the Duero basin subsidized by the Conserjería de Energía y Trabajo of the Junta of Castilla and León.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE DEVELOPING OF CRISTOBALITE IN KAOLINIZED VOLCANIC ROCKS IN SAN ANDRES MOUNTAINS IN MICHOACAN (MEXICO)

J. NEUŽIL and J. SERRATO RODRIGUEZ

Department of petrology, Faculty of Nat. Sciences, Praha (Czechoslovakia).

Instituto de investigaciones metalúrgicas, Universidad Michoacana de San Nicolas de Hidalgo Morelia, Mich. Mexico.

The Sierra Vulcanica mountain range is situated in the central part of Mexico. It consists of acid, intermediate and basic volcanic rocks with their pyroclastic equivalents. The volcanic activity started in Tertiary and lasted during Quaternary sporadically up to now. In some places there are the so called postvolcanic phenomena like exhalations, of hot gases water vapor and liquids. These agents have altered mainly acid and intermediate volcanic rocks and their pyroclastics to kaolin and alunite under hydrothermal conditions. An example of these processes presented in Sierra San Andrés (Los Azufres) near Ciudad Hidalgo and Ciudad Zinapécuaro in the Nord-West part of the Michoacan State. One of the highest hills Cerro del Gallo (3060 m) in these mountains built from rhyolite and trachyandesite with their pyroclastics and volcanic glasses (obsidian, perlite) is completely altered to kaolin of pure white colour. During hydrothermal alteration kaolinite, halloysite (endellite), partly montmorillonite, alunite and zeolite are originated with high bulk of silica. Free silica changes from amorphous hydrated opal A to more stable opal CT and to cristobalite as the final product of hydrothermal kaolinization. This succession was studied in the field and in laboratory by following methods: XRD, IRAS, DTA, SEM, chemical anal. and microscopy.

Chemical composition of fresh and kaolinized rocks:

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O
A.)	71.95	0.06	18.18	0.86	0.96	0.65	4.02	1.26	1.70
B.)	44.88	2.74	34.63	0.18	0.12	0.02	0.06	0.00	13.37
C.)	52.08	1.54	32.62	0.40	0.10	0.02	0.06	0.16	12.39

A.) relatively fresh volcanic parent rock (Keller, Hanson, Huang and Cervantes, 1971)

B.) kaolin from the hillside

C.) kaolin at the foot of the hill Cerro del Gallo

About 20% of differences of silica between fresh and kaolinized rock give the reasons of a high amount of free silica in the forms opal A opal CT and cristobalite.

At the beginning of the kaolinization process, silica is very finely dispersed in kaolin. After dehydration and lithification of kaolin due to diagenesis the hard rock is formed on the surface of that kaolin deposit with very pure cristobalite tiny cavities structure. It protects the kaolin deposit against to erosion. The cavities may originate through the washing out of clay minerals on the hillsides by rain water. At the foot of the hill the washed out clayey substance was deposited almost without cristobalite and other form of free silica admixtures.

In Sierra San Andres mountains the kaolinization lasted since Late Tertiary time up to the present and could serve as a good example of uniformitarianism as far as hydrothermal alteration is concerned.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SOME CRYSTALLOCHEMICAL AND PETROGRAPHIC CRITERIA FOR THE DETERMINATION OF THE SOURCE ROCKS IN SEDIMENTARY PROCESSES: THE NEOGENE SEDIMENTS OF THE BETIC CORDILLERA (SE SPAIN).

F. NIETO, M. ORTEGA HUERTAS & N. VELILLA

Dpto. Mineralogía y Petrología. Universidad de Granada (Spain).
Instituto Andaluz de Geología Mediterránea. C.S.I.C.-Univ. de Granada.

INTRODUCTION

The study of sedimentary rocks normally involves some sort of knowledge of their precedence, the source rocks, which in turn implies the application of a combination of mineralogical, petrological and stratigraphical techniques. In this paper we propose a methodology which includes all these aspects of the problem, with special emphasis on the mineralogical and petrological approach. While describing our methodology we intend also to apply it to the Neogene sediments of the Betic Cordillera, in order to determine: a) whether the deposits originated from a single or various source areas, b) in the latter eventuality, the relative importance of each source area, c) discover the types and the intensity of the sedimentary and post-sedimentary processes through a comparative study of certain crystallochemical parameters to do with phyllosilicates.

THE AREA STUDIED

We selected for study the Neogene materials from the "Alpujarran Corridor", which forms part of the eastern Betic Depressions. The mineralogy-petrology (Ortega Huertas et al., 1985), the stratigraphy (Rodríguez, 1982) and the sedimentology-tectonics of the area (Sanz et al., 1985) have already been documented. The zone is especially suitable to our purpose as it is delimited by extensive strike-slip faults which have affected the substratum as well as the Neogene materials (Sanz et al., op.cit.). It is also noteworthy that this narrow fringe is bounded by metamorphic rocks belonging to at least two important tectonic complexes, the Nevada-Filábride (sub-divided into the Veleta nappe and the Mulhacén nappe, from bottom to top respectively) and the Alpujárride complex (Fig.1). The various Neogene materials studied are known stratigraphically, from bottom to top, as the "Cádiar", "marine Ugíjar", "Yátor" and "continental Ugíjar" sequences and are made up of fine detrital sediment such as marls, sands and clays, intercalated between much thicker conglomerate levels of up to 600 m.

METHODS

I. X-ray diffraction.

A) Qualitative and quantitative mineralogical study. The mineralogy of the fine detrital sediments was studied both in the clay and silt fractions by O.A., O.A.+E.G., O.A.+D.M.S.O. and O.A.+550°C.

B) Crystallochemical parameters.

1) The phyllosilicate spacings were measured by using the MAX programme of the diffractometer, which searches the maximum intensity of a reflection through step scan measurements at regular angular intervals during equal periods of time. The experimental conditions were the following: size of step between points = $0.005^\circ 2\theta$, measuring time at each point = 1 second, number of points on each side of start angle=40.

As an internal standard quartz was used.

1.a: b_0 measurements. The (006) reflection of phengites and chlorites was measured using uncovered, thin sections and with fine, detrital sediments it was carried out using a side-loading sample holder in order to obtain the most favourable orientation of the reflection.

1.b: Measurement of the basal spacings of phengites, paragonite and chlorites in O.A. For the first two the (0,0,10) reflection was measured and for the latter the (004) reflection.

2) Intensity ratios of the (003), (004) and (005) chlorite reflections were measured by graphic recording under the following experimental conditions: speed of scan = $1^\circ/\text{min.}$, time constant = 2, recorder speed paper = $20 \text{ mm}/^\circ 2\theta$, recorder full scale = 2.10^3 . The final data represents the arithmetic mean of five measurements. The iron content of this mineral was determined from its b_0 parameter and/or the intensity ratios of the basal reflections, according to the method proposed by Nieto and Rodríguez Gallego (1983).

3) Crystallinity. This was measured from the (004) reflections of illite and paragonite and the (003) reflection of chlorite under the following conditions: speed of scan = $2^\circ/\text{min.}$, time constant = 1, speed paper = $50 \text{ mm}/^\circ 2\theta$.

II. Optical petrographic study.

This consisted essentially in a characterisation of the various metamorphic parageneses and an analysis of the textural criteria.

A HYPOTHESIS CONCERNING THE SOURCE AREAS AND THEIR TEMPORAL EVOLUTION

The materials to be found in the "Cádiar" sequence bear witness to the influence of rocks belonging to the Alpujárride complex, and specifically those nappes with a higher thermal gradient, the Contraviesa group (Aldaya et al., 1981). This assignation is supported by petrographic evidence and the b_0 values of the phengites. Furthermore, the scarcity and/or absence of paragonite and chlorite can be explained by the high-temperature conditions of this group of nappes. The fine detrital sediments and the pebbles of the "Yátor" sequence point to several source areas. At the bottom, the rock types (phyllites), the b_0 values of the phengites ($>9.00 \text{ \AA}$) and the $\Delta 2\theta$ muscovite-paragonite ($>1.7^\circ 2\theta$) all suggest an Alpujárride origin, specifically the rocks belonging to the Lújar and Guadalfeo nappes and the Contraviesa group (op.cit.). Towards the top of this sequence, however, there is clear influence both from the Alpujárride materials and from the Nevado-Filábride complex as shown by crystallochemical analyses (Mulhacén: b_0 phengite $>9.00 \text{ \AA}$, $d_{(0,0,10)}$ phengite $>1.996 \text{ \AA}$, $d_{(001)}$ chlorite $<14.16 \text{ \AA}$, Fe chlorite <2.00 atoms), and also for metamorphic parageneses of various grades (medium and high thermal gradient in the Mulhacén nappe and low thermal gradient in the Veleta nappe). The highest stratigraphical sequence, "continental Ugíjar", completes the evolution begun in the lower ones. At the bottom there is clear influence from both the Mulhacén and Veleta nappes of the Nevado-Filábride complex, while at the top only material from the Veleta is evident (Fig. 1).

Fig. 1. Temporal and spatial evolution of the source areas.
GR:Granada, AL:Almería. A: Nevado-Filábride complex; B: Alpujárride complex; C: Neogene sediments. Alpujárride complex:
1. Contraviesa group, Lújar and Guadalfeo nappes. Nevado-Filábride complex: 3. Mulhacén nappe, 4. Veleta nappe. (Structural scheme of Sanz et al., 1985).

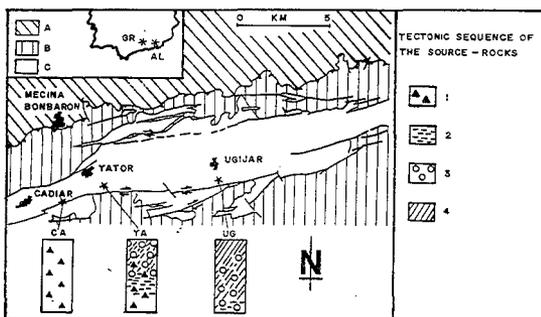


Fig. 1. Temporal and spatial evolution of the source areas. GR:Granada, AL:Almería
 A. Nevado-Filábride complex; B: Alpujárride complex; C: Neogene sediments.
 Alpujárride complex: 1. Contraviesa group,
 2. Lújar and Guadalfeo nappes.
 Nevado-Filábride complex: 3. Mulhacén nappe,
 4. Veleta nappe.
 (Structural scheme of Sanz et al., 1985)

SOME CONSIDERATIONS CONCERNING THE SEDIMENTARY PROCESS

A study of the clay-mineral associations leads to several conclusions. The "Cádiar" sequence was deposited in a marine environment with sporadic influence from the continent (Ortega Huertas et al., 1985). The "Yátor" and "continental Ugijar" sequences correspond to alluvial-fan deposits (op.cit.). In this kind of environment, in which physical factors are the prime movers, certain crystallochemical parameters, such as basal spacing, are remarkably constant. Basically, the most notable differences can be seen in the crystallinity values of illite and chlorite, which diminish substantially in the clay fraction compared to the silt fraction and the pebbles and rocks of the source areas. Also noteworthy is the slight drop in the iron content of the chlorites in the "Yátor" and "continental Ugijar" sequences, probably due to the sedimentation having taken place under energetic conditions, as suggested by Liebling and Sharp (1980) and Nieto y Rodríguez Gallego (1981).

REFERENCES

- Aldaya, F.; García, V. y Navarro, F. (1981). *Acta Geol. Hisp.* 14, 154-166.
 Liebling, R.S. and Sharp, H.S. (1976). *Bull. Geol. Soc. Am.* 87, 513-514.
 Nieto, F. and Rodríguez Gallego, M. (1981). *Acad. C. Mat. Fís.-Quím. y Nat. Granada*, 1, 108-124
 Nieto, F. and Rodríguez Gallego, M. (1983). *Rend. Soc. Ital. Miner. e Petr.*, 38(3), 1429-1436.
 Ortega Huertas, M.; Nieto, F.; Rodríguez, J. and López, A.C. (1985). *Bol. S.E.M.*, 8, 307-318.
 Rodríguez Fernández, J. (1982). *Tesis Doctoral*. Univ. Granada.
 Sanz, C.; Rodríguez, J. and López, A.C. (1985). *Geol. Rundsch.* 74/3, 641-655.

(This work forms part of "Análisis sedimentológico, mineralógico y evolución tecto-sedimentaria de las Depresiones Béticas Orientales". project. - C.S.I.C.-C.A.I.C.Y.T.).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
 Seville, Spain, 1987. Sociedad Española de Arcillas

INTERLAYER COMPLEXES OF LANTHANIDE VERMICULITES WITH AMINES AND AMIDES

P. OLIVERA PASTOR, E. RODRIGUEZ-CASTELLON AND A. RODRIGUEZ-GARCIA

Departamento de Química Inorgánica, Cristalografía y Mineralogía,
 Facultad de Ciencias, Universidad de Málaga, 29071 Málaga (SPAIN)

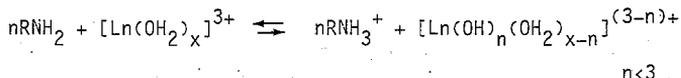
The lanthanide ions are typical "hard" acids in the Pearson sense. Although the majority of the stable complexes contain ligands with oxygen donor sites, complexes containing pure N-atom donor ligands have been obtained, under rigorously anhydrous conditions (1). Little is known about the interaction of such ions with organic substances in the confined space of clays. The objective of this work was to study the interactions of lanthanide ions (Ce(III), Nd(III), Gd(III), Er(III) and Lu(III)) with amines (n-butylamine, n-pentylamine, n-hexylamine, ethylenediamine and 1,3-propylenediamine) and amides (acetamide, N,N-dimethylformamide and N,N-dimethylacetamide), in the vermiculite interlayer space.

The natural sample of vermiculite came from Benahavis, Spain. And the homoionic lanthanide vermiculites were prepared as described elsewhere (2). Interlayer complexes were characterized by X-ray diffraction, infrared spectroscopy and DTA-TG analysis.

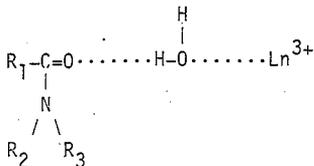
From the composition data of the complexes was observed a decrease of the organic substance content with the lanthanide ion radius. This adsorption order appeared to be inversely related to: a) the degree of contraction of the lanthanide-vermiculite interlayer space, in their dehydrated state, which ranged from 11.85 Å for Ce-vermiculite to 11.66 Å in the case of Lu-vermiculite; and also b) to the hydration energy of the lanthanide ion.

The study of the sorption isotherms of n-butylamine on lanthanide vermiculites revealed a strongly acidic medium, attributed to an increase of the Brønsted acid centers, which are formed from the hydrolysis of the lanthanide ions in the vermiculite interlayer space.

Sorption of molecular amines by lanthanide-vermiculites involved protonation of the amine group and hydrolysis of the interlayer lanthanide cation; suggesting that sorption of certain organic materials by clays, under specific conditions, may cause chloritization of the clays (3).



The amides, less basic than amines, interacted with the interlayer lanthanide cations through hydrogen bonded water-bridges between the directly coordinated water and the amidic carbonyl oxygens.



This suggested mechanism for amine and amide interaction with lanthanide vermiculites can be qualitatively explained in terms of the atomic dielectric theory (4).

The amines and amides molecules can not transmit the high polarizations associated with surface oxygens coordinated to the aluminium ions of the tetrahedral sheets, in which the vermiculite charge predominates, and so they can not substitute for water directly coordinated to the interlayer lanthanide cations. The amides readily displace the water from outer hydration spheres of such ions, because of their strong inherent tendency to form chains. This chain conformation facilitates the transmission of localized charges on the lanthanide cations to the vermiculite layer surface, along the hydrogen bonded chains.

DTA-TG analyses of the complexes suggested that the thermal decomposition of amines and amides depended in part on the interlayer lanthanide cation.

REFERENCES

- 1).- Moeller T. (1972) Lanthanides and Actinides: Butterworths, London, pp. 275-298.
- 2).- Olivera, P., Rodríguez-Castellón, E. and Rodríguez-García A. (1987) Uptake of lanthanides by vermiculite: Clays & Clay Minerals In press.
- 3).- Heller-Kallai, L., Yariv, S. and Reimer, M. (1973) The formation of hydroxy interlayers in smectites under the influence of organic bases: Clay Miner., 10, 35-40.
- 4).- Farmer, V.C. and Russell, J.D. (1971) Interlayer complexes in layer silicates. Structure of water in lamellar ionic solutions: Trans. Faraday Soc., 67, 2737-2749.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

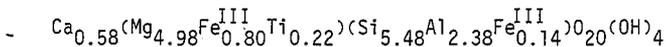
UPTAKE OF LANTHANIDES BY VERMICULITE

P. OLIVERA PASTOR, E. RODRIGUEZ-CASTELLON AND A. RODRIGUEZ GARCIA

Departamento de Química Inorgánica, Cristalografía y Mineralogía,
Facultad de Ciencias, Universidad de Málaga, 29071 Málaga (SPAIN).

Several recently published works have reported that lanthanide ions can hydrolyze on the clay mineral surfaces (1-3). However, no detailed investigations about the relationships between solution pH and ion exchange of such ions on clays have been reported to date. The present work was designed to evaluate the effects of pH on the uptake by vermiculite of five lanthanide ions (Ce(III), Nd(III), Gd(III), Er(III) y Lu(III)) from solutions ranging in composition from $1.5 \cdot 10^{-2} \text{N}$ to $2.5 \cdot 10^{-2} \text{N}$.

The vermiculite used came from Benahavis, Spain. The structural formula of the calcium-exchanged sample is:



The cation-exchange capacity was 150 meq/100g (based on the weight of the sample heated at 900°C).

The ion exchange of the lanthanide ions on vermiculite was studied using cation-exchange measurements, infrared spectroscopy and X-ray diffraction. The ion exchange studies were conducted on the uptake of the lanthanide ions by n-butylammonium vermiculite in relation to lanthanide salt amount added, and pH of the equilibrium solution. The lanthanide ions were taken up by vermiculite in excess of its cation exchange capacity, from addition of a lanthanide salt amount slightly above the CEC value.

Uptake in excess increased with hydration energy of the lanthanide ion and with the pH of the n-butylammonium vermiculite suspension. Under conditions where the pH of the equilibrium solution ranged between 3 and 4.5, the amounts of lanthanide ions taken up were slightly greater than the CEC, while above pH 4.5, uptake increased abruptly. The observed strong adsorption of lanthanide ions by vermiculite, beyond the CEC, appears to be the result of hydrolysis of such ions on the interlayer surface of the vermiculite. The pH is a critical factor in the uptake process of lanthanide ions by vermiculite because it determines the charge of the adsorbed cationic species. High localization of the vermiculite layer charge is believed to be responsible of the observed decrease of three units in pH (4), at which lanthanide ions begin to hydrolyze when vermiculite is present.

The hydrolysis of lanthanide ions in vermiculite is also supported by the fact that hydrated free protons are present

in the homoionic lanthanide samples, as deduced by the appearance of a band at $1715-1720\text{ cm}^{-1}$, in the infrared spectra.

The lanthanide exchanged vermiculites gave X-ray diffraction patterns with 002/001 intensity ratios greater than that of the magnesium-exchanged vermiculite due not only to the greater atomic numbers of the lanthanide ions, but also to the increase in the interlayer cation content (5).

REFERENCES

- 1).- Bruque, S., Mozas, T., and Rodríguez, A. (1980) Factor influencing retention of lanthanide ions by montmorillonite: Clay Miner. 15, 413-420.
- 2).- Miller, S. E., Heat, G. R., and Gonzalez, R. D. (1982) Effect of temperature on the sorption of lanthanide by montmorillonite: Clays & Clay Minerals 30, 111-122.
- 3).- Laufer, F., Yariv, S., and Steinberg, M. (1984) The adsorption of quadrivalent cerium by kaolinite: Clay Miner. 19, 137-149.
- 4).- Baes, C. F. and Mesmer, R. E. (1976) The Hydrolysis of Cations: Wiley-Interscience, New York, p. 1290.
- 5).- Bassett, W. A. (1958) Copper vermiculites from Northern Rhodesia: Amer. Mineral. 43, 1112-1133.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**THERMAL TRANSFORMATION OF AN ATYPICAL KAOLIN CLAY MINERAL.
AN ELECTRON OPTICAL STUDY***

FATIMA PAIS LOPES AND HELENA DE SOUZA SANTOS

Laboratório de Microscopia Eletrônica - Instituto de Física
Universidade de São Paulo. São Paulo, Brazil

The phase transformation of an atypical clay mineral (Piedade, SP) heated to progressively higher temperatures (600°C to 1300°C) was studied by transmission electron microscopy and selected area electron diffraction.

Up to 600°C no detectable morphological changes were observed at the Piedade's tubes. At 600°C, the diffraction diagram, identified as the metakaolin phase reveals the existence of a certain degree of crystalline order. A contraction in the unit cell parameter b and c of the original kaolinite occurs, leading to the metakaolin parameters.

Longitudinal striae were observed on the surface of the Piedade tubes, either in the clay mineral without heat treatment or in the heated tubes up to the temperature of 800°C. These striae are interpreted as favorable nucleation sites for the development of the spinel crystalline phase.

It was possible to follow, morphologically and crystallographically, the development of the spinel phase, whose nucleation occurs between 750°C and 800°C. That phase starts as granules without a preferential orientation, on the surface of the tube pseudomorphs.

The topotactical relationships held by the complete phase transformation series, from the Piedade clay mineral to the final mullite crystalline phase, were established as: $b_p // b_{me} // b_e // c_{mu}$; i.e. the b axis direction remains the same throughout the phases Piedade, metakaolin and spinel, becoming at the last phase, parallel to the mullite c axis.

* Grant from FAPESP



Summaries, - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

QUANTITATIVE ANALYSIS OF CLAY MINERALS IN A MODERN SEDIMENTARY BASIN

A. PALANQUES*, F. PLANA*, J. RIUS**

* Instituto Jaime Almera, c/ Martí i Franqués s/n, 08028 Barcelona (Spain).

**Instituto de Materiales, c/ Martí i Franqués s/n, 08028 Barcelona (Spain).

A standardless X-ray diffraction method for quantitative multi-component analysis of mixtures was designed. This method derives calibration constants only from diffracted intensities and calculated phase absorption coefficients through a least-squares procedure without requiring neither the use of pure phases nor the measurement of the sample absorption coefficient.

The studied area is the Ebro Continental Margin. Bottom and suspended sediment samples were taken in several cruises. Mineralogy, geochemistry and grain size were analyzed systematically. The results agree with the sedimentary environment distribution.

In bottom sediments, the illite and clorite content in muds ranges between 8 and 16%, while kaolinite does between 4 and 6%. Silts and Sands present obviously lower clay content: illite 0-4%, clorite 0-8% and caolinite 0-2%. Illite and kaolinite are well correlated with clay fraction, but clorite is more correlated with silt fraction.

No interstratified clay minerals have been detected in most of the samples as a result of the fact that the material carried by the Ebro River has had a long and complex process of transport that allows its reaching stable phases. Interstratified clay minerals have been detected only in actual litoral sediments coming from near-litoral source areas.

The suspended sediment shows a low concentration mainly due to the anthropogenic action effectuated in the river during the last decades. The clay content is about twice as much as the clay content in bottom muds, and illite predominates over clorite and kaolinite. Illite ranges one between 20 and 40%, clorite between 16 and 28% and kaolinite between 8 and 16%.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Sevilla, Spain, 1987. Sociedad Española de Arcillas

PELAGIC JURASSIC SEDIMENTATION IN THE BETIC CORDILLERA. AN ILLUSTRATION OF THE ROLE OF GEOCHEMISTRY AND THE IMPORTANCE OF CLAY MINERALS IN THE ANALYSIS OF BASIN DEVELOPMENT.

I.PALOMO^(1,2); J.RODRIGUEZ GORDILLO^(1,2); P.RIVAS^(2,3) and M.ORTEGA HUERTAS^(1,2).

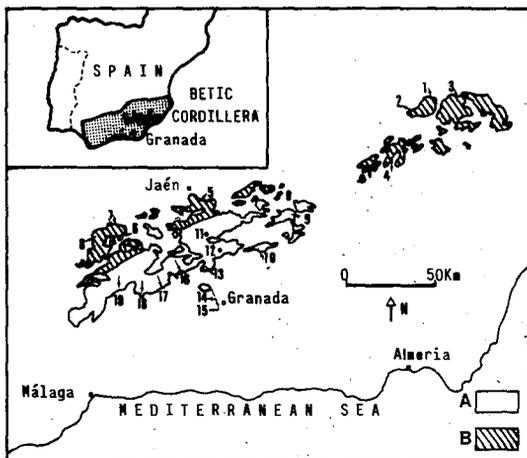
(1) Dpto. Mineralogía y Petrología. (2) Instituto Andaluz de Geología Mediterránea. (3) Dpto. Estratigrafía y Paleontología. Universidad de Granada-C.S.I.C. (España).

INTRODUCTION

This paper follows on from those published by Palomo et al.(1981, 1985) and by Ortega et al.(1985) on the Jurassic pelagic sediments in the Subbetic Zone of the Betic Cordillera and we describe here the most likely palaeogeographical conditions which led to the depositing of the Liassic grey marls and marly limestones facies in this area.

THE GEOLOGICAL SETTING AND AGE OF THE LITHOLOGICAL FACIES

The sequences under study belong to the lithological realms known as the External and Median Subbetic within the Betic Cordillera: a scheme of their geological location can be found in fig.1.



A: Median Subbetic
B: External Subbetic

Fig.1. Location of sequences.

The materials consist mainly of grey marls and marly limestones, although in some sequences various other sediments appear, such as, red and pinky limestones, sandy and grey marls, limestones and marls with chert nodules, nodular limestones, brown marls and "ammonitico rosso" facies. All these sediments date from the upper-Carixian to the Bajocian.

METHODS

We analysed the samples by X-ray diffraction. Several kinds of samples were prepared: untrated dry powder specimens, oriented specimens (AO), AO+EG, AO+DMSO, AO+550°C and AO+H₂SO₄. For the oriented samples we chose to use clay and silt fractions.

The following crystallochemical parameters were determined for the illite: crystallinity (AO+EG), b_c , $d(0,0,10)$, chemical composition (Ernst,1963); Martín Ramos,1976), Na/Na+K (Evans & Guidotti,1966). For the chlorite the basal spacing and the crystallinity were measured (003) and its chemical composition was studied according to the methods of Albee(1962), Nieto & Rodríguez (1983), using the classification of AIPEA (Bailey,1980) in order to establish the chlorite term. Many of the samples were analysed using SEM. The chemical analyses were carried out by means of AAS, and by X-ray fluorescence. We determined the composition of some chlorites and muscovites to be found in the pelitic rocks of the suspected source areas with Electron Microprobe.

MINERALOGY OF THE TOTAL SAMPLE

The sample as a whole consists of varying quantities of calcite (C), dolomite (D), quartz (Q), K-feldspar (Fd) and clay minerals (CM). The average percentage of the various minerals is similar in both realms: Median Subbetic (C+D=50, Q+Fd=12, CM=38), External Subbetic (C+D=52, Q+Fd=9, CM=39). Nevertheless, there are differences in the mean composition of the stratigraphic sequences in each of the palaeogeographical domains. Thus it can be seen in fig.2 that the sequences in the Median Subbetic show a greater dispersion in the triangular compositional diagram, which may be indicative of a diversity of source rocks. In fact, the mean value of the coefficient of variation (V) and the standard deviation of V are: Median Subbetic (C+D:23-10, Q+Fd:31-18, CM:28-17), External Subbetic (C+D:14-7, Q+Fd:22-11, CM:15-16).

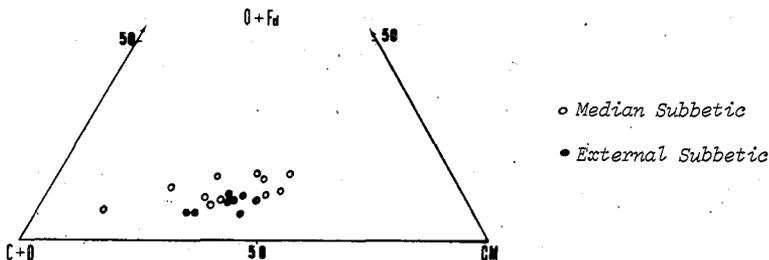


Fig.2. Triangular compositional diagram.

CLAY MINERALS

The clay minerals present are: illite(I), chlorite(chl), kaolinite(K), smectite(Sm) and mixed-layer illite-smectite(I-Sm). We have categorised several associations of clay minerals according to whether or not they

occur and, if so, their relative abundance: Association A:I,chl,K; Association B:I,chl,(Sm); Association C:I,chl,Sm; Association D:I,chl, I-Sm; Association E:I-chl; Association F:I,Sm; Association G:I,Sm,(K). The clay sedimentation is uniform with similar values for standard deviation and V throughout both palaeogeographical realms.

CHEMICAL DATA

We have determined the contents of Si, Al, Fe, Mg, Ca, Ti, K, Na, Mn, Cr, Zn, Co, Cu, Pb, Ni, V, Li, Sr and Rb. A cluster analysis led to the identification of three related groups of samples in the External Subbetic and a much greater diversity in the Median Subbetic. In both domains, however, the chemical compositions are related to either the age, the lithology or the mineralogy of the sediment with geologically co-relatable sequences being geographically far apart. This fact is of particular interest when we come to describe the structure of the palaeoenvironment.

PALAEOGEOGRAPHY AND SOURCE AREAS

The temporal and spatial distribution of the clay minerals associations shows clearly that there is no special relationship between any one lithological facies and a particular mineral association and that the sequences are transgressive towards the top. In general it may be concluded that the palaeogeography was more homogeneous in the External Subbetic, while in the Median Subbetic a varying series of troughs and swell that tended to divide up the basin developed during different periods.

As far as the source rocks for these sediments are concerned the crystallochemistry of both the micas and the chlorites shows that the igneous and metamorphic rocks of the Variscan Massif of the Spanish Plain were the primary source for the deposits in the easternmost areas of the External domain and the greater part of the Median domain. Nevertheless, the presence of kaolinite in the "Cañada del Hornillo, Iznalloz, Zegrí Sur y Cerro Méndez" sequences suggest that a certain times other distinct sources areas may have contributed to the deposits. This hypothesis is supported by the presence of clay-mineral association F in the western sequences of the External Subbetic and in the bottom of some Median sequences and also by the variation in the basal spacing of the chlorite in some of the sequences.

REFERENCES

- Bailey SW (1980) Summary of recommendations of AIPEA nomenclature committee. *Clay Minerals* 15,85-93.
- Ernst WG (1963) Significance of phengite micas from low-grade schists. *Am Mineral* 48:1357-1373.
- Evans BW, Guidotti CV (1966) The sillimanite-potash feldspar isograd in Western Marine, USA. *Contrib Mineral Petrol* 12:26-62.
- Martín Ramos JD (1976) Las micas de las Cordilleras Béticas. Tesis Doctoral Univ Granada.
- Nieto F, Rodríguez Gallego M (1983) Metodología para el estudio de la clorita en rocas metamórficas. *Rend Soc Ital Min Petrol* 38(3):1429-1436.

Ortega Huertas M, Palomo Delgado I, Fenoll Hach-Alí P (1985) Mineral composition of the Jurassic sediments in the Subbetic Zone, Betic Cordillera, SE Spain. Miner Petrogr Acta 29-A: 231-243.

Palomo Delgado I, Ortega Huertas M, Fenoll Hach-Alí P (1981) Los carbonatos de las facies margosas jurásicas en las Zonas Externas de las Cordilleras Béticas (provincias de Granada y Jaén). Bol Soc Esp Min 4: 15-28.

Palomo Delgado I, Ortega Huertas M, Fenoll Hach-Alí P (1985) The significance of clay minerals in studies of the evolution of the Jurassic deposits of the Betic Cordillera SE Spain. Clay Miner 20: 1-14.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ARGILLIC ALTERATION AT BALCARCE DISTRICT, ARGENTINE.

ELDA DI PAOLA*

*CONSEJO NACIONAL DE INVESTIGACIONES CIENTIFICAS Y TECNICAS, (CONICET)
MUSEO ARGENTINO DE CIENCIAS NATURALES. A. Gallardo 470, 1405 Buenos
Aires, ARGENTINE.

The three only clay deposits known at Balcarce district are characterized petrographically and mineralogically, by means of thin sections, XRD, EDAX, SEM and conventional chemical analysis. They are Cerro Segundo and María Eugenia kaolin mines, situated at Sierra de Bachicha and Sierra del Volcán respectively, and the alteration area which stands at the west slope of Sierra La Barrosa, fig. 1.

Balcarce district is located at the south-eastern end of Northern Sierras of Buenos Aires Province, Argentine. The hills are composed of precambrian metamorphic-magmatic basement rocks, overlayers by precambrian-eopaleozoic quarcitic sedimentites and by cenozoic piedmont sediments. The landscape is characterized by the alignment of low ridges and scarps, which determines linear features with N-S and N55°E general strikes.

Argillization have developed only on the metamorphic-magmatic complex constituted by leuco and melano-tonalitic "granitoids" and biotitic-granatiferous gneisses, composed of quartz, mirmequites, oligo-andesine, biotite, amphibols, ortopiroxenes, garnet, apatite, opaque ores, zircon and clinozoicite.

Granitoids display schistosity at random, becoming gneisses with a general N75°E strike and almost vertical dip. These rocks are intruded by pegmatitic veins composed of quartz, micropertthites, microcline and oligoclase. The whole complex is tightly folded. Sedimentary layers cover unconformably and almost horizontally metamorphic folded rocks.

Four alteration zones have been detected at Cerro Segundo kaolin deposit, named on the basis of its mineral assemblage and spatial

disposition: "kaolinitic-smectitic", "sericitic-muscovitic", "lower kaolinitic" -associated with a "hematitic-kaolinitic" subzone-, and "upper kaolinitic", respectively.

The first three zones are of hypogenic origin, being the paragenetic sequence: kaolinite-smectite-illite-sericite-muscovite-hematite. Petrographical features strongly suggest a weathering origin for the "upper kaolinitic" zone, characterized by kaolinite-illite-smectite-14/14Å mixed-layer clay association.

Sierra La Barrosa alteration front, which includes an old quarry located in a neighbouring forest, displays ill-defined, discontinuous "smectite" zones, two well-defined "kaolinitic" zones and a "kaolinitic-10/14Å mixed-layer clay" zone, restricted to the old quarry.

It is considered that the general alteration pattern, roughly coincident with the regional schistosity strike, is due to hydrothermal activity, being the characteristic mineralogical assemblage composed of smectite-kaolinite-illite. On the contrary, smectitic alteration developed at joint planes on granitoid blocks, and the interstratified 10/14Å clay detected on micropore walls in some altered rocks, would be indicative of meteoric water activity, being the mineralogical association smectite-10/14Å mixed-layer clay.

María Eugenia kaolin deposit is composed of an unique "kaolinitic" zone with ferric pigment randomly distributed. A "silica" zone of a few centimeters wide is located at the northern end of the quarry. Hypogenic mineral association is represented by kaolinite-smectite-illite-silica.

Chemical data both of fresh and altered rock samples from the three deposits show similar trends: little mobility of SiO_2 and Al_2O_3 and relative loss of CaO , Na_2O , K_2O and MgO are characteristic of smectitic prevailing zones, while relative gain of Al_2O_3 and TiO_2 are main features of kaolinitic zones. Gain of silica, potassium and iron were locally detected at restricted zones of different quarries.

Among other common features, hypogenic microporosity have been detected by means of SEM, in altered feldspar grains, developed at structural planes, as well as between clivage planes in "swelled" altered biotites. Porosity, detected by means of polarizing

microscope, is characterized by smectitic or interstratified clay films on pore walls, and have been considered of secondary origin, due to the activity of surficial waters.

Breccia zones have been detected at La Barrosa and Cerro Segundo deposits, relating argillic alteration patterns with fault zones, and therefore with the action of thermal waters. The action of meteoric waters have been enhanced by the density of the design of the joints developed in the sedimentary cover, favouring the drainage of the higher zones toward lower altered zones.

The general hypogenic-supergenic paragenetic mineral assemblage and the processes connected with, are considered to be:

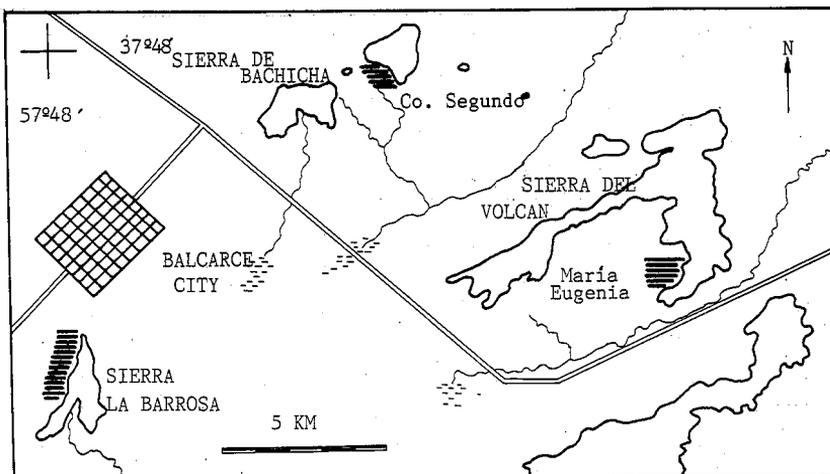
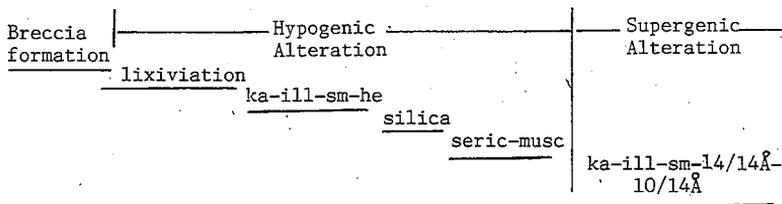


Fig.1. Schematic design of Balcarce district. Striped areas represent argillic alteration zones.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GRINDING OF MUSCOVITE : INFLUENCE OF THE GRINDING MEDIUM

E. PAPIRER

Centre de Recherches sur la Physico-Chimie des Surfaces Solides, C.N.R.S.
24, avenue du Président Kennedy, 68200 MULHOUSE, France

Mica is becoming an important filler for thermoplastics because it imparts interesting mechanical properties to polymeric materials and usually leads to a good surface finish of, for instance, poly(propylene) which is increasingly used in the automotive industry. Optimal performance of filled PP is, however, only achieved when mica platelets of the appropriate size and morphology, but also surface energy, are available.

Fine mica particles are commonly obtained by grinding. In such a process, the grinding medium may play a predominant influence as we already demonstrated it in the case of the comminution of asbestos (1, 2, 3). The object of this paper is to investigate the behavior of muscovite (Bihar, India) when submitted to grinding either in a ball mill or in an attritor, in an aqueous or organic medium and in presence of other additives.

A whole series of analytical methods were employed to follow the grinding process : elemental analysis, X ray diffraction, IR spectroscopy, electron microscopies and determination of the surface properties by inverse gas chromatography (4).

Dramatic changes do occur according to the grinding conditions. For example, attrition of muscovite in water or in methanol, leads to very fine particles which present surface areas as high as $100 \text{ m}^2 \cdot \text{g}^{-1}$. Yet, the structure of muscovite is particularly preserved in methanol. Under identical conditions, but in toluene, the muscovite surface area increases first, up to $30 \text{ m}^2 \cdot \text{g}^{-1}$, but then decreases as amorphization and agglomeration of the particles are taken place.

The influence of the addition of various salts to the grinding medium is also studied. It is observed that Li^+ plays, at first sight, an unexpected role. Indeed, it leads to a rapid and total amorphization of muscovite whereas, K^+ or Na^+ do not have the same influence. Further, when NH_3 is added to methanol, the grinding process is again entirely perturbed and very similar results as previously recorded with Li^+ , are obtained.

Hypotheses are proposed to account for the specific role of the Li^+ ions when grinding is made in water or of NH_3 when the comminution is conducted in methanol. It is postulated that these molecules adopt a peculiar organization on the surface of muscovite, an organization which is highly influenced by agents (Li^+ and NH_3) capable to rupture hydrogen bonds.

REFERENCES

- 1) E. PAPIRER, P. ROLAND, *Clays Clay Min.*, 29 (3), 161-170 (1981)
- 2) E. PAPIRER, *J. Polym. Sci.*, 21, 2833-36 (1983)
- 3) E. PAPIRER in "Composite Interfaces", Vol. I, H. Ishida and J.L. Koenig Ed., Elsevier Sci. Publ. Co, N.Y., 1986, p. 203
- 4) E. PAPIRER, P. ROLAND, M. NARDIN, H. BALARD, *J. Colloid Interface Sci.*, 113 (1), 62-66 (1986)



TEM AND MICROCHEMICAL STUDY OF THE GLAUCONITIZATION PROCESS

C. PARRON AND M. AMOURIC*

Laboratoire de Géologie Dynamique et Pétrologie de la Surface UA CNRS
132. Faculté des Sciences de St-Jérôme, 13397 Marseille Cedex 13, France.

* CRMC2, Campus de Luminy, case 913, 13288 Marseille Cedex 9, France.

To delineate the transformation mechanisms involved during the glauconitization process and with the main aim to give a possible genetical scheme of this process (1) glauconitic peloids the purest in glauconite mineral and (2) glauconitic peloids less rich in glauconite mineral were simultaneously studied with HRTEM, energy-dispersive X-ray microanalysis and electron microprobe. The glauconitic peloids belong to two distinct geographical occurrences of the Paleocene of Ivory Coast. One-dimensional images were mainly analysed, showing the characteristic 001 basal lattice fringes of the main mineral phases present and their relation (Amouric and Parron, 1985).

Structurally, 1 Md, 1M and faulted 2M₁ polytypes of glauconite minerals were observed in both (1) and (2) glauconitic peloids. Also, almost the same microphases were detected in (1) and (2) peloids, the main difference consisting in their relative ratios and their respective size. So a spindle-shaped organization of pure glauconite crystallites ($d(001) \sim 10 \text{ \AA}$) was observed in all the peloids, but numerous very small individual crystallites of pure glauconite may also exist in (2). Inside the spindles, 10 Å glauconite crystallites shown characteristic growth features (Amouric and Parron, 1985) and were generally sandwiched by a layered phase with $d(001) \sim 12.5 \text{ \AA}$. A gel-like material, surrounding the composite glauconite -12.5 Å phase assemblage, always occurred, mainly in peloids (2). It appeared as completely amorphous wide areas with many pores and filaments, locally well contrasted and exhibiting a lot of structurally organized microcenters, or including some layered crystallites.

Chemically, the gel-like material was different in the two occurrences studied. In one case, it was a Si-rich, Fe-poor material and, on the contrary, in the other case a Si-poor, Fe-rich material. Also the 12.5 Å phase revealed a chemical composition respectively close to a Fe-montmorillonite and to a nontronite. In both cases, the 10 Å phase corresponded to a Fe, K-rich mica structure (i.e. glauconite).

According to these results, two geochemical ways for glauconitization process are evidenced :

- Starting from an essentially siliceous gel, a glauconite mica is obtained by increasing Fe and K, after growth and destabilization of a Fe-montmorillonitic phase.
- Starting from an essentially ferriferous gel, a glauconite mica is obtained by decreasing Fe and increasing Si and K, after growth and destabilization of a nontronitic phase.

REFERENCE :

AMOURIC M. and PARRON C. (1985). - Structure and growth mechanism of glauconite as seen by high-resolution transmission electron microscopy. *Clays and Clay Minerals* , 33, 6, p. 473-482.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ASPECTS ON KAOLINIZATION AND KAOLIN POTENTIAL IN FINLAND

Y.O. PEKKALA

Geological Survey of Finland, SF-02150 Espoo, (Finland).

Finland is a major kaolin importing country. In 1981 - 1986 the kaolin import increased from 400 000 tn to 650 000 tn per year and the value of import in 1986 was nearly 400 million FIM (about 85 million US \$). More than 90 % of kaolin is used in paper manufacturing and the demand is still increasing. For these economic reasons the exploration on domestic kaolin occurrences is one of the main objectives of mineral exploration in the Geological Survey of Finland.

KAOLINIZATION

Chemical weathering of the Finnish Precambrian bedrock has increasingly attracted interest during last ten years.

Most findings of kaolin weathering have been made in northern and northeastern Finland where the erosion by continental ice was not as deep as in the other parts of the country. However, a number of weathering indications have also observed in central and southern Finland. In many cases only the topmost part of the bedrock was slightly weathered. Best known are the findings of thin weathering crust on rapakivi granites caused by mechanical disintegration. Kaolinite is generally formed in small amounts even in this kind of weathering.

Observations of more advanced weathering in southern Finland are generally connected to structural basins or fault zones but in most cases they are too small or the quality is poor to be of economic interest. In 1986 one

area in southern Finland was, however, discovered where kaolinization has reached the depth of 30-40 m. Weathering products here are composed mainly of kaolinite and quartz. The host rock of these kaolin occurrences is usually a quartz-felspar gneiss, rich in plagioclase.

In northern and northeastern Finland a great number of findings of kaolin weathering are known. Mostly they are hosted in arkose or sericite quartzites, whose feldspar content is not very high and therefore the kaolin content of weathering products very seldom does meet economic standards. The areas of kaolin weathering are extensive but most of them are poorly investigated. According to drilling results the depth of kaolinization is generally 30-40 m and in one known deposit at least 90 m.

When studying the progress of weathering processes of Finnish bedrock it is obvious that in many cases changes of chemical and mineralogical composition have been slight but there are also a number of occurrences where kaolinite and quartz are the only main minerals left.

According to the present knowledge most major kaolin occurrences seem to be "in situ" deposits formed mainly by chemical weathering. The time of weathering is not exactly known but the Baltic Shield was favourably situated around the Equator during most of the Proterozoic Eon, and through the Paleozoic Era upto the end of the Triassic period. Time correlation will be problematic because almost all rocks younger than early Proterozoic are lacking. However, an occurrence of kaolinized bedrock is known in western Finland underlying the Cambrian sandstone giving evidence of Precambrian kaolinization of Finnish bedrock.

KAOLIN POTENTIAL IN FINLAND

Best known and most investigated kaolin occurrences are located in northern and northeastern Finland.

In Kittilä there is the Lonnakko kaolin occurrence which covers at least an area of 100 x 500 m and kaolinization extends to the depth of 50 m. The bedrock of the area is composed of micaschist and sericite quartzite. Kaolin is mostly pink or yellow and white kaolin is met only occasionally.

The Siurunmaa kaolin deposit in Sodankylä is at least 100 m wide and 500 m long and in places it extends to the depth of 90 m. Kaolinization has occurred in arkose and sericite quartzite producing mostly greyish or yellowish white kaolin. Preliminary dressing tests indicated that Siurunmaa kaolin could meet the requirements for filler material.

In Kainuu, northeastern Finland, much of exploration on kaolin has been carried out since 1979 and a number of occurrences was discovered. The bedrock in kaolinized areas is generally arkose or sericite quartzite. Unfortunately the kaolinite content of weathering products is low. By now the deposits which clearly meet the economic requirements in size and quality are not known, but exploration is still in progress.

In 1986 a great number of kaolin indications were preliminarily sampled in southern Finland. In most cases the weathering layer was too thin to give resources for economic deposits. However, in one exploration area in southeastern Finland several occurrences were discovered where weathering reached 20-30 m depth. Besides in some occurrences kaolinite and quartz were the only main minerals left. Kaolinite content is generally 40-50 %. Preliminary tests indicated that the grainsize distribution is suitable for and the brightness high enough for paper filler. In 1987 an extensive exploration programme with drilling and geophysical measurements will be carried out in the area.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

BEHAVIOUR OF SEPIOLITE, VERMICULITE AND BENTONITE AS SUP-
PORTS IN ANAEROBIC DIGESTERS

J.L. PEREZ RODRIGUEZ, M.I. CARRETERO AND C. MAQUEDA

Instituto de Recursos Naturales y Agrobiología de Sevilla.
Apartado 1052. 41080 Sevilla (Spain).

One of the most important problems in anaerobic processes is the loss of biomass. In order to solve this problem reactors containing supports have been designed with the aim of fixing the biomass and obtaining high loading densities and minimum hydraulic retention (Henze and Harremoës, 1983).

Glass beads, volcanic rocks (Salkinoja-Salonen et al., 1983), needle punched polyester (Harvey et al., 1984), feldspar particles (Lequerica and Toldrá, 1986) etc. are the -- more frequently used supports in anaerobic digesters.

The aim of this paper is to study the effect of some -- clay minerals in anaerobic digestion. The clay minerals used were: natural sepiolite, purified sepiolite, both from Valle cas (Spain), vermiculite from Santa Olalla (Spain) and bentonite from Gador (Spain). Expanded polyuretane and PVC have also been used in order to know possible differences between these materials, frequently used as supports in the anaerobic digesters, and clay minerals.

The reactors used had a capacity of 1 liter and were -- filled up with specific cultures for the development of -- either methanobacteria or methane and sulphate-reducing bac-teria. Blank support free reactors have also been used.

Before and after the process of digestion of the samples were studied by DTA, TGA, electron microscopy, X-ray dif-fraction, IR and atomic absorption.

The study of samples from the reactors containing cultu-

res for methanobacteria shows that purified sepiolite was the best material for the development of these bacteria. This is the only mineral able to fix the bacteria when it is in suspension, and produces easier decantation than --- other materials. This mineral is followed by expanded polyurethane and bentonite in their production of methanobacteria.

In the reactors with specific culture for methane and sulphate-reducing bacteria, the purified sepiolite inhibits the development of sulphate-reducing bacteria and increases methanobacteria production.

Expanded polyurethane produces more sulphate-reducing bacteria and fewer methanobacteria than other materials tested.

In both cultures, when vermiculite is the material used, there is a cation exchange of K^+ for the Mg^{++} ions of the mineral, related with a higher gas production; for this reason we suggest that magnesium might play an important role in the process. The chemical composition of sepiolite and some facility to give up Mg^{++} to solution may also influence the large methane production by this mineral.

CONCLUSIONS

- 1) The purified sepiolite in suspension is the material that produces more methanobacteria, inhibiting the sulphate-reducing bacteria production. The best results for decantation are also obtained with this material.
- 2) The magnesium liberated from the support may play an important role in anaerobic digestion.
- 3) Polyurethane produces methanobacteria, but also many sulphate-reducing bacteria, giving H_2S and thus produces a -- lower quality gas.

REFERENCES

- HARVEY, M.; FORSBERG, C.W.; BEVERIDGE, T.J.; POS, J. and OGILVIE, J.R. 1984. Methanogenic activity and structural characteristics of the microbial biofilm on a needle -- punched polyester support. *Appl. Environm. Microbiol.*, 48, (3), 633-638.
- HENZE, M. and HARREMÖES, P. 1983. Anaerobic treatment of -- wastewater in fixed films reactors. A literature review. *Wat. Sci. Tech.*, 15, 1-101.
- LEQUERICA, J.L. and TOLDRA, F. 1986. Examen microscópico de microorganismos presentes en reactores metanogénicos de lecho fluidizado. *Rev. Agroquím. Tecnol. Aliment.*, 26, (1), 90-100.
- SALKINOJA-SALONEN, M.; HAKULINEN, R.; VALO, R. and APAJALAHTI, S. 1983. Biodegradation of recalcitrant organochlorine compounds in fixed film reactors. Anaerobic treatment of wastewater in fixed film reactors. *Wat. Sci. Tech.*, 15, 309-319.

DECOMPOSITION OF ALKYLAMMONIUM CATIONS INTERCALATED IN VERMICULITE

J.L. PEREZ RODRIGUEZ, E. MORILLO AND C. MAQUEDA

Instituto de Recursos Naturales y Agrobiología de Sevilla. Apartado 1052
41080 Sevilla (Spain).

The phenomenon of alkylammonium decomposition on montmorillonite surfaces has been studied by several researchers. In 1964, Calvet et al. showed that it was possible to transform alkylammonium cations adsorbed on montmorillonite surface at temperatures considerably below the theoretical decomposition temperatures of amines or their chlorhydrates. Above 100°C, in presence of oxygen, the cations decompose into NH_4^+ (which remains on the clay), organic residues and hydrocarbons. The observations were interpreted as the result of catalytic break of the C-N bond. The catalytic effect was attributed to protons of the water adsorbed on the montmorillonite surface.

Durand et al. (1972) have studied in an inert atmosphere the thermal transformation of alkylammonium cations adsorbed on the surface of a montmorillonite in various conditions of hydration. The reactions observed were mainly transalkylations, for which a mechanism of acid catalysis was proposed. A high degree of dissociation of the water remaining on the surface of the clay was required for these processes.

There are some differences between the thermal transformation of alkylammonium montmorillonite in an inert atmosphere and the corresponding transformation in presence of oxygen. In the latter, a faster increase of the NH_4^+ content was observed, and transalkylation processes do not operate.

The aim of this paper is to determine the decomposition of decylammonium cations on vermiculite surface, as a result of the acidity of the medium.

The vermiculite used was obtained from the "Santa Olalla" deposit in Huelva, Spain, and it was saturated in decylammonium cations, according to the method proposed by Lagaly and Weiss (1969).

The decylammonium-vermiculite complex was treated with solutions of HCl in water and butanol, and solutions of N'-(4-chloro-2-methylphenyl)-N,N-dimethyl methanimidamide hydrochloride in butanol, which produces an acidity similar to the HCl solutions.

The treatments were carried out at 60°C in stoppered glass tubes. The solutions were changed weekly up to 100 days of treatment; from that time on, the solutions were left in contact with the samples without further change until a year passed.

The X-ray diffraction pattern and the infrared spectra of alkylammonium-vermiculite complex do not show changes after treatment with deionized water or butanol.

The basal spacing of decylammonium-vermiculite complex changes from 21.21 Å to 12.8 Å after several treatments with HCl solution in water or butanol. The latter diffraction increases to about 14 Å if the solutions are kept in contact with the samples without any change.

In the infrared spectrum of the sample showing a 12.8 Å diffraction, bands appear at 1430, 3240 and 3040 cm^{-1} corresponding to ammonium cations present in the interlamellar spaces (Ahlrichs et al., 1972; Stone and Wild, 1978). The ammonium is produced by the break of the C-N bond of alkylammonium due to their high degree of surface acidity present as a consequence of the pH in the solution used.

When the solution are kept unchanged, the experimental data show the release of Mg^{2+} ions from the vermiculite structure due to the acidity of the medium. This Mg^{2+} displaces the alkylammonium and ammonium from interlamellar space. The ammonium is exchanged completely in the samples treated with aqueous solution, whereas in butanol solution it is partially displaced. The 1430 cm^{-1} absorption band corresponding to NH_4^+ is displaced to 1400 cm^{-1} due to release of structural Mg^{2+} , producing a higher lamellar charge and increasing the interaction between NH_4^+ ion and the surface.

The decomposition of decylammonium cations on the vermiculite surfaces is also produced when the decylammonium vermiculite complex is treated with a solution of an organic compound (N'-(4-chloro-2-methylphenyl)-N,N-dimethyl methanimidamide hydrochloride) in butanol. In this case the C-N bond breaking is due to the high acidity which is produced by dissociation of the scarce water molecules remaining in the interlamellar space.

REFERENCES

- AHLRICH, J.L.; FRASER, A.R. and RUSSELL, J.D. 1972. Interaction of ammonia with vermiculite. *Clay Miner.* 9, 263-273.
- CALVET, et al. 1964. Protons de constitution, protons libres et eau adsorbée. *Bull. Grpe. Fr. Argiles XIV*, 59-104.
- DURAND, D.; PELET, R. and FRIPIAT, J.L. 1972. Alkylammonium decomposition on montmorillonite surfaces in an inert atmosphere. *Clays Clay Miner.* 20, 21-35.
- LAGALY, G. and WEISS, A. 1969. Determination of the layer charge in mica-type layer silicates. *Proc. Int. Clay Conf. 1969, Tokyo, Vol I*, Israel Universities Press, Jerusalem, 234-277.
- STONE, M.H. and WILD, A. 1978. The reaction of ammonia with vermiculite and hydrobiotite. *Clay Miner.* 13, 337-350.

SOME EFFECTS OF DRY GRINDING ON PYROPHYLLITE

J.L. PEREZ RODRIGUEZ, P.J. SANCHEZ SOTO

Instituto de Recursos Naturales y Agrobiología de Sevilla. C.S.I.C.
Avenida Reina Mercedes. Sevilla (Spain).

Pyrophyllite is a relatively rare mineral and has been scarcely studied until quite recently. For that reason it has generally been overlooked in commercial circles. However, its high alumina content and physicochemical properties are useful in many industries, and thus much research is being developed to obtain a better knowledge of its properties. Pyrophyllite is principally used in refractory, ceramic and sundry uses (1).

Fine mineral particles are principally obtained by grinding. This process plays an important role in determining the physicochemical properties of the powdered mineral. The effect of grinding on the pyrophyllite properties has been practically not studied (2,3,4). The aim of this paper is to study the physicochemical properties of pyrophyllite after intensive dry grinding.

The sample used in this study was a natural pyrophyllite from Hillsboro, (USA) and the grinding was carried out in a ball mill.

The grinding process was followed by X-ray diffraction, thermal and nitrogen BET surface area measurements. The differential thermal and thermogravimetric analysis (DTA-TG) of the original and ground pyrophyllite have been carried out at two heating rates (12°C/min and 30°C/min).

The XRD patterns show a higher amorphization of the original sample when the grinding time was increased. It is interesting to note the dramatic change in the X-ray diagrams when the grinding time changed from thirty minutes to longer times.

The BET surface area vs. grinding time plot shows an initial high increase followed by a decrease as amorphization and agglomeration of the particles take place.

The DTA curve for original pyrophyllite has a single broad endothermic peak in the 600-800°C region, with a maximum at 760°C.

For short grinding times this endothermic effect is shifted to lower temperature and becomes sharper and similar to that of kaolinite. After grinding for thirty minutes the peak appears at 540°C.

Grinding for more than thirty minutes does not cause any further changes in the temperature of this endothermic peak, but its intensity decreases until disappearing after long grinding times. For the other hand, the original pyrophyllite shows a small exothermic effect at ~1000°C, probably due to a low proportion of kaolinite present in the sample. This effect increases with grinding time, reaching a maximum after which its intensity becomes constant.

The most significant variation of the exothermic effect agrees with the X-ray diffraction data. This transformation is associated with the progressive destruction of the crystalline structure.

It should be noted the remarkable contrast of the high chemical stability of the mineral against its mechanical instability (5).

The mechanical treatment produces an noticeable proportion of amorphous silica that exsolves in the thermal process, its proportion increasing with the grinding time up to a certain constant value. Mullite and cristobalite phases appear at lower temperatures than in the original material.

REFERENCES

- (1) HARBEN P. W.
I.M. Refractories Survey 125-129 Ed. B.M. Coope&E.M. Dickson London (1981).
- (2) NEMECZ E.
"Clay Minerals" p. 133 Akadémiai Kiadó. Budapest (1981).
- (3) STANCZYK M.H., FELD I.L.
Bureau of Mines Bull. 670, 1-43 (1980).
- (4) KUWAHARA Y.
J. Chem. Eng. Jap. 4, 4, 359-363 (1971).
- (5) PEREZ RODRIGUEZ J.L., MAQUEDA C., JUSTO A.
Clays and Clay Min. 33, 6, 563-566 (1985).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

RETENTION OF TRIPOSITIVE LANTHANIDES (Gd,Ho,Yb,Lu)
BY MONTMORILLONITE.

J.Poyato, M.M.Tobias and J.M^a.Trillo.

Department of Inorganic Chemistry.Institute of Materials
Science.University of Seville-CSIC.Seville.Spain.

If radioactive nuclear waste escape from their canister, they can be expected to be held by surrounding geologic formations. The major barrier for preventing waste movement will be the interaction between radionuclides and the clays surrounding the canister. Geochemical data indicate that montmorillonite will be the major component responsible for ion sorption.

Lanthanide ions simulate to actinide ones, being greater the ease with which the former can be handled. Miller et al. have studied the sorption of Eu(III), Ho(III) and Yb(III) on a Upton, Wyoming, montmorillonite with temperature and pressure as variables (1), (2). On the basis of this study, hydrolysis of hydrated lanthanides ions and migration into octahedral vacant are claimed as likely mechanisms of 4f ions fixation, in excess of the cation-exchange capacity, CEC, of the clay.

The aim of this paper is to determine the extent of Gd(III), Ho(III), Yb(III) and Lu(III) octahedral migration, using a montmorillonite with low Fe(III) content to avoid the difficulties in (1) for infrared spectroscopy data interpretation. At the same time, the 4f ions content has been limited to interlamellar positions, thus avoiding their great excess on the CEC of the clay in (1), which masks the observation of the migration mechanism.

The < 2 μ m fraction of a water suspended Trancos montmorillonite, from Gador (Spain), was collected. After carbonates and organic matter removal, the sample was saturated

with sodium. This Na-montmorillonite, Na-Mt, was used as a starting material for the preparation of montmorillonite saturated with the tripositive 4f cations, Ln-Mt. From the chemical analysis of the starting and reference material, Na-Mt, by X-ray fluorescence, a charge deficit of 0,87(0,36+0,51) per unit cell has been calculated.

Basal spacing, d(001), was examined by X-ray power diffraction using oriented aggregate preparations. The b-dimension was computed from d(060) reflections, with quartz as an internal standard to correct geometrical diffractometer aberrations. Infrared, FT-IR, spectra were recorded in a Fourier Transform Nicolett 5 DXE spectrometer; samples were prepared as oriented aggregated films.

The basal spacings obtained for Ln-Mt samples show a relatively simple behaviour: the interlamellar spacing is almost constant over a wide range of humidities and corresponds to a double-sheet complex. After air heat treatment (300°C, 24 hours) of the Ln-Mt samples, reexpansion with water takes a long period of time before showing peaks narrow enough. However, once that induced period is over, the 001 spacings show that the Ln-Mt samples are still capable of swelling.

The FT-IR spectra in the region 3800-3000 cm^{-1} of the unheated Ln-Mt samples show that the dominant absorption band is due to the AlAlOH group, at 3620 cm^{-1} . It has been observed neither shift in that maximum with the heat treatment at 300°C, nor new absorption bands. Miller et al. (1) have reported the observation of a shoulder at 3700 cm^{-1} for Ln-Mt (Ln=Eu, Ho, Yb) samples which just appears with the heat treatment and is interpreted as due to octahedral migration of the exchangeable cations. The band at 3700 cm^{-1} is here observed in the FT-IR spectra even in the unheated Na-Mt and Ln-Mt samples, without appreciable change in its relative intensity. In addition, no appreciable change has been observed when the angle of incidence of the infrared beam with the oriented sample films was increased from 45° to 90° for each sample. The absorption bands in the 950-750 cm^{-1} region of the FT-IR spectra remain constant with

the heat treatment. Finally, heating does not produce any increase in the b-dimension. All the above mentioned results lead to the conclusion that no migration occurs for 4f ions from exchangeable sites to octahedral ones.

The hydrolysis of exchangeable hydrated cations to poly-hydroxocations has been examined through the generation of hydronium ions, FT-IR absorption band at 1700 cm^{-1} , and the protonation of NH_3 , 1460 cm^{-1} . The hydrolysis occurs even during the preparation of the samples, in an extension which increases from Gd-Mt to Lu-Mt and with heating. As it is excluded an octahedral migration mechanism, the drop in CEC for heated Ln-Mt samples (1), (3), should be ascribed exclusively to the hydrolysis of the hydrated ions of exchange.

On heating the Ln-Mt samples at 300°C the extent of their hydration decreases, as indicated by the intensity of the FT-IR band at 1630 cm^{-1} , except for the Lu-Mt where the initial state is close to the one obtained with the heat treatment. The decrease is ascribed to the one in the water molecules, coordinating in a first sphere to the exchangeable 4f ions. Contrary to the Hofmann-Klemen effect, the remaining hydrated interlamellar 4f ions, after heating, cause the swelling of the montmorillonite.

- (1) Miller, S.E., Heath, G.R. and Gonzalez, R.D. Clays and Clay Minerals. 30, 111-122 (1982).
- (2) Miller, S.E., Heath, G.R. and Gonzalez, R.D. Clays and Clay Minerals. 31, 17-21 (1983).
- (3) Mozas, T., Bruque, S. and Rodriguez, A. Clay Minerals. 15, 421-428 (1980).

GENESIS OF SEPIOLITE IN LACUSTRINE-PALUDINE CARBONATES FROM THE "CUESTA FACIES" (DUERO BASIN, MADRID)

M. POZO and S. LEGUEY.

Department of Agrochemistry, Geology and Geochemistry. Autonoma
University of Madrid. 28049 MADRID (SPAIN).

In the central facies of the Duero basin three sedimentological
stages are observed:

- I) Siliciclastic. ("Detrital facies").
Fluvial-alluvial environments. (bottom).
- II) Transitional. ("Zaratan facies").
Fluvial-lacustrine environments.
- III) Carbonatic. ("Cuesta facies" and "Paramo facies").
Lacustrine environments. (top).

The best development of sepiolite is observed at the "Cuesta fa
cies" where the genesis of the mineral above mentioned is favoured
by the lithological composition with calcite, dolomite, and gypsum
bearing beds.

The study of the mineralogy (X.R.D.) texture (optical microscop
e) and microfabric (S.E.M.) in samples from twelve lithological
sections, let us to establish that sepiolite is associated to minera
logical sequences related with the lacustrine evolution, specially
in regressive stages, where exposed sediments are subject to diage
netic and pedodiagenetic processes. The mineralogical association
observed is: illite-sepiolite-palygorskite (+ dioctahedral smectite +
kaolinite).

Sepiolite is specially abundant in lacustrine environments with
high alkalinity and salinity belonging to a "playa-lake" type.
From a genetic viewpoint sepiolite is related with three main
processes:

- a) Dolomitization (Diagenetic). ($<1 - 2 \mu\text{m}$).

- b) Dedolomitization (Hypergenic). (1 - 2 μ m).
- c) Desiccation by evaporation in ponds. (3 μ m).

In lacustrine environments with lower salinity and alkalinity, sepiolite appears filling secondary porosity or coating desiccation glomerulés, often in relation with pedodiagenetic processes.

A genetic model for sepiolite through silica-magnesium gels, is proposed.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**IR STUDY OF STRUCTURAL OH GROUPS OF KAOLINITE, DICKITE
AND NACRITE BETWEEN 5 AND 600 K**

R. PROST, A. DAMEME, E. HUARD, J.P. LEYDECKER and J. DRIARD
Station de Science du Sol - I.N.R.A. Route de Saint-Cyr,
78000 VERSAILLES, FRANCE

In order to arrive at a better understanding of the structure of kaolin-group minerals, infrared spectra of the structural OH groups of 1 : 1 dioctahedral clays were recorded as a function of temperature between 5 and 600 K. It was shown (PROST et al., 1985) that the low- and high frequency components of the absorption bands of the structural OH groups shifted progressively in opposite directions as the temperature changed from 5 to 300 K and gave different resolution of the spectra.

In order to obtain more precise measurements of band width, position and intensity, the spectra were recorded over a larger range of temperatures (5 - 600 K) and deconvolution calculated. The three parameters were determined using spectra obtained at a temperature where the resolution of the individual band was the best. Then, these parameters were adjusted for spectra obtained at different temperatures. These change continuously with temperature providing a check of the validity of the deconvolution.

The infrared study of structural OH groups of dioctahedral 7 Å minerals as a function of temperature is a new approach which leads to a better knowledge of the individual components. This method improves the accuracy of the assignment of the infrared absorption bands, and thus affords a better understanding of the structure of these minerals.

PROST R., DAMEME A., HUARD E., DRIARD J., 1987. Infrared study of structural OH in kaolinite, dickite and nacrite at 300 to 5 K. Int. Clay Conf. DENVER.

RARE EARTH DISTRIBUTION AND ITS CORRELATION WITH CLAY MINERALOGY IN
THE CLAY-SIZED FRACTION OF CRETACIC AND PLIOCENIC SEDIMENTS (CENTRAL
PORTUGAL)

M.I. PRUDENCIO, M.O. FIGUEIREDO^{*} and J.M.P. CABRAL

Departamento de Quimica, ICEN, LNETI, 2685 Sacavém (Portugal)

* Centro de Cristalografia e Mineral., IICT, 1000 Lisboa (Portugal).

Eight rare earth elements (REE), namely La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, have been determined by instrumental neutron activation analysis in the clay-sized fraction of nineteen sediments of continental facies from the "western border of Portugal" and the Lousã basin. Mineralogical analyses of the same fractions have been done by means of X-ray diffraction. The REE contents were found to vary either in absolute value ($\Sigma \text{REE} = 133 - 520$, only taking into account the elements determined) or in relative value ($\text{La/Lu} = 49 - 629$ and $\text{Eu/Sm} = 0.14 - 0.31$). The main minerals found were kaolinite, illite and smectite. Chlorite was detected only in two samples.

In contrast to what was observed for the Lower Permian Havensville and Eskridge shales¹¹, the REE contents in the clay-sized fraction of the above mentioned sediments seem to vary in response to differing clay mineral proportions. In fact, those contents appear to be correlated positively with kaolinite and negatively with smectite. Kaolinite could account for the higher REE bulk values if one assumes that the REE are retained in the structure of this mineral mainly replacing octahedral Al and, on the other hand, predominantly interlayered in smectites. The smectite group has a high ion exchange capacity with a subsequent easier loss of interlayered elements (REEs included). The REE contents of rock-weathering kaolinites may therefore reflect the original bulk contents of the source rock.

Apparently, the La/Lu ratios is not correlated with the mineralogy of the clay-sized fraction. The differences observed in the REE fractionation may be caused by either chemical weathering processes in the source area or exchange reactions during transportation and/or

deposition. The higher stability of aqueous inorganic and organic complexes of the heavy REE relative to the light REE may contribute to differences in fractionation behaviour under such processes ^{12/}.

As far as the Eu anomaly is concerned, no correlation could be established either with clay mineralogy or with absolute REE contents. It should be noted that such anomaly is usually smaller or even absent in the clay-sized fraction comparatively to the whole sediment or to the fraction $< 38\mu\text{m}$ ^{13/}.

Samples with similar clay mineral composition may present a wide range of REE contents. However, the presence of goethite may account for the higher contents of these elements, as this mineral was clearly identified by X-ray diffraction and the retention capacity of hydroxides is recognized to be high.

Thus, clay mineralogy seems to be responsible for the absolute REE contents in the analyzed sediments but no correlation is apparent with La/Lu and Eu/Sm ratios.

- 1 Cullers, R.L., Chaudhuri, S., Arnold, B., Lee, M. and Wolf, C.N. Jr. (1975), *Geoch. Cosmoch. Acta*, 39, pp. 1691-1703.
- 2 Ronov, A.B., Balashov, J.A. and Miodisov, A.A. (1967), *Geochem. Internat.*, 4, pp. 1-17.
- 3 Prudêncio, M.I. and Cabral, J.M.P. (1986). Communication at the Int. Conference on Methods and Appl. of Radiog. Chem., 1987, USA.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

Chemical and Mineralogical Characterization of a Cretaceous Clay from the Lousã Basin (central Portugal).

Prudêncio, M.I., Waerenborgh, J.C. and Cabral, J.M.P.

Departamento de Química, ICEN, LNETI, 2685 Sacavém, Portugal.

A chemical characterization of clay samples from different deposits in the vicinity of Conimbriga (central Portugal) was previously done in order to identify the source of clay used to manufacture the fine grey pottery recovered at that archaeological site¹. Only one of those deposits, situated near Padrão, was found to be correlated with the ceramics. It consists of clay lenticula incorporated in sand beds (cretaceous period). A detailed study of clay samples from two of these lenticula (P-1 and P-2), consisting of the chemical and mineralogical characterization of the whole sediment as well as of fractions of different particle size (>1mm; 500µm-1mm; 250-500µm; 125-250µm; 75-125µm; 45-75µm; 38-45µm; <38µm; and <2µm), has been carried out. The element contents (Na, K, Sc, Cr, Fe, Co, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U) have been determined by instrumental neutron activation analysis and the mineralogical composition by means of XRD. The minerals identified in both samples were quartz, feldspar (mainly potassic), illite, kaolinite, goethite, hematite, anatase, dolomite and calcite. Mössbauer spectroscopy has also been used in order to give information about the distribution and oxidation state of Fe in the silicate, oxide and hydroxide phases. Up to this stage all spectra have been taken at room temperature.

It was found that the two clay lenticula samples P-1 and P-2 show significant differences in chemical and mineralogical compositions. In fact, the quartz content is higher in P-2 while in P-1 caulinite prevails. Goethite, hematite and dolomite were detected in P-2 but not in P-1. On the other hand, Na, Fe and Co contents in P-2 are about twice the corresponding values obtained for P-1. The REE

contents also reveal some differences particularly as far as the relative contents are concerned (La/Lu=227.2 in P-1 and 109.4 in P-2). However, the Eu anomaly appears to be very similar in both samples (Eu/Sm=0.145 for P-1 and 0.146 for P-2). It should also be noted that the REE contents in these samples deviate significantly from those of European shales (ES)² either in relative value (presenting a larger Eu anomaly; Eu/Sm=0.21 for ES) or in absolute value (ΣREE=323.0 for P-1 and 299.3 for P-2, while ΣREE=176.2 for ES, considering only the elements determined).

Differences in chemical and mineralogical compositions were also observed for the various size fractions of P-1 and P-2. Ferruginous nodules are present in the coarser fractions of both clays though more concentrated in P-1. They are the main constituent of the >1mm and 500µm-1mm fractions of P-1, which therefore have a much higher iron concentration than the others, while in P-2 the iron distribution is more uniform. Feldspars, as well as the alkaline elements, are more abundant in the intermediate fractions. The dominant clay mineral in the clay-size fraction of both samples is kaolinite. It is worth noting that REE, specially the lighter ones, are concentrated in the clay-sized fraction, which can be explained by the low ion exchange capacity of kaolinite.

All Mössbauer spectra showed a central doublet due to ferric iron included in the silicate structure and/or in superparamagnetic oxides. In the spectra of P-2 samples a doublet due to paramagnetic high spin Fe²⁺ was also present. Besides the doublets the spectra also showed a pattern of 6 lines asymmetrically broadened in the way typical for microcrystalline goethite³. The relative intensity of this pattern decreases with the particle size of the sample. A magnetic splitting due to hematite was seen in the coarser fractions of P-1 (>1mm and 500µm-1mm), which are richer in ferruginous nodules, but it could not be detected in P-2 samples.

Further work is in progress. Low temperature spectra are being taken in order to confirm that the pattern attributed to goethite is only due to this mineral, and to establish the fraction of ferric iron present in the clay minerals structure.

Firing the whole sample in air at (1023 K) had no significant effect in its chemical composition. The only changes observed were the transformations of clay minerals and goethite as expected. Accordingly Mössbauer spectra of the calcined samples consisted of a 6 line component due to hematite, and a central doublet due to paramagnetic ferric iron with larger quadrupole splitting and isomer shift than in the case of the untreated sample. The increase in quadrupole splitting is generally attributed to the dehydroxylation process that leaves the clay mineral lattice in a disordered state⁴.

- 1 Prudêncio, M.I., Cabral, J.M.P. and Tavares, A. (1986), submitted for publication the Proceedings of the 1986 International Symposium of Archaeometry.
- 2 Haskin, M.A. and Haskin, L.A. (1966), *Science*, 154, pp. 507-509.
- 3 Morup, S. et al. (1983), *J. Magn. Magn. Mat.* 40, pp. 163-174.
- 4 Kostikas, A., Simopoulos, A. and Gangas, N.H. (1976), in *Applications of Mössbauer spectroscopy Vol. I*, Ed. Richard L. Cohen, Academic Press N.York, pp. 241-261.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

HALLOYSITE FORMATION THROUGH THE "IN SITU" WEATHERING OF VOLCANIC GLASS, FROM TRACHYTIC PUMICES, VICO'S VOLCANO, ITALIA.

Paul QUANTIN ¹, Jacques GAUTHEYROU ¹ and Paolo LORENZONI ²

¹- ORSTOM, 70 route d'Aulnay, 93140, BONDY, FRANCE

²- I.S.S.D.S., Piazza d'Azeglio 30, FIRENZE, ITALIA

INTRODUCTION: This study concerns the weathering of trachytic pumices, which are included in the 4th pyroclastic flow of the Vico's Volcano (Latium, Italia); this flow dates back to about 144.000 BP. Underlying an Andic-Brown Soil (Andic Dystrachrept), the still weakly weathered volcanic flow shows coarse pumices, which are almost completely weathered into a nearly white gel. It is made mainly of 10 Å halloysite. This paper aims at showing the origin, the shape and the composition of this clay.

METHODS: A detailed study was made, in order to compare the strongly weathered pumice and its less 2µm altered product with the slightly weathered one, using the following methods:

- on little fragments: optical and scanning electron microscopy, coupled with micro-probe in situ analysis of major elements;
- on pumice powder: X Ray diffraction and chemical analysis of major elements;
- on <2µm altered fraction: X Ray diffraction, thermo-differential analysis and transmitted electron microscopy.

RESULTS:

1. The grey unweathered pumice: is made of fluidal and vesicular elongated glass, like hair, and of some crystals of sanidine, green augite, biotite, titanomagnetite and few relics of zeolitized leucite. Its composition is similar to alkaline, potassium and aluminium-rich trachyte ($K_2O = 7.1\%$, $Na_2O = 2.6\%$, $Al_2O_3 = 24\%$), but poor in iron, calcium and magnesium. The surface of unaltered glass seems smooth and uniform.
2. The white altered pumice: keeps the initial glass texture and the phenocrystals remain slightly or not altered. But, the glass surface appears granular in scanning electron microscopy (x 1000 enlargement). At a greater enlargement (2000-4000), we can observe: at the glass surface, subangular or round grains; at the edge section, a parallel stacking of prisms, of about 1µm.

The in situ chemical analysis, made at the altered glass surface as well as at one single prism, is quasi-constant. In addition, these results are almost identical to the composition of the whole altered product. The scanning microscopy, coupled with the in situ analysis, shows that the altered products are formed in situ, at the expense of the glass itself. As compared to the initial glass, the chemical composition of altered glass shows a high increase in Al, Fe and Ti, as well as a high decrease in Na, Mg and Ca; but the decrease in K is less and it is rather small in Si. The molar SiO_2/Al_2O_3 and SiO_2/R_2O_3 ratios are respectively ≈ 2.2 and 2.0.

The mineralogy of <2µm fraction shows predominantly a well crystallized 10 Å halloysite, few illites and traces of smectites, zeolites (chabazite, phillipsite) and titanomagnetite. The T.E.M. electron micrographs reveal the abundance of a very fine halloysite, mostly spherical, but barely tubular, and some scarce illite, beidellite and residual glass.

The chemical composition allows to estimate the following mineralogical composition: halloysite \approx 70-72%; illite (+ beidellite and residual glass) \approx 20-18%; zeolites \approx 4%; titanomagnetite (+ non-crystalline FeOOH) \approx 6%. The resulting halloysite is almost pure (mol. $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 2.05$).

CLAY GENESIS: The preceding observations show that the clay minerals were formed in situ, through the glass weathering. In addition, these clays grew under a microporous and water logged conditions, though badly permeable and confined, and slightly alkaline. In the overlying C soil horizon the pH is 7.2. These clays show a high water retention capacity ($\text{H}_2\text{O}^- \approx 65\%$) as well as a high cation exchange capacity (≈ 70 me/100g), which is mostly saturated by Ca^{2+} (≈ 40 me/100g) and by K^+ (≈ 24 me/100g).

CONCLUSIONS: The in situ transformation of an alkaline glass into clay minerals, through the weathering of trachytic pumice, occurs in the case of a poorly permeable material like a pyroclastic flow.

The white clay is made of at least 70% of 10 Å halloysite, of micro-spherical shape (ϕ 10-100nm), and nearly 20% of illite and beidellite and few iron oxides and zeolites. However these minerals seem to be closely mixed in prismatic grain of nearly 1 μ m.

The clay minerals and especially a spherical 10 Å halloysite, are directly formed in the weathered glass; they occur easier under microporous, very hydrated, but confined and slightly alkaline conditions.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MEASUREMENTS OF SOIL SPECIFIC SURFACE AREA BY p-NITROPHENOL ADSORPTION

G.G.RISTORI, E.SPARVOLI, L.LANDI, C.MARTELLONI

Consiglio Nazionale delle Ricerche, Centro di Studio per i Colloidi del Suolo, Piazzale delle Cascine 28, 50144 Firenze (Italy).

p-Nitrophenol (pNP) in aqueous or organic solvents solutions is widely employed for measurement of specific surface area of many organic and inorganic substances.

In a preliminary work (Ristori et al.,1985) the use of this molecule in Xylene solution for the determination of the external and total surface area of smectite minerals has been suggested. It has been shown that the external surface area of these minerals can be calculated from the adsorption isotherms (20°C) of samples saturated with monovalent cations and then heated at 160°C. The total surface area can be obtained from adsorption isotherms (20°C) of samples saturated with divalent cations and equilibrated at about 10% relative humidity (R.H.). The relatively strong polarizing power of divalent exchange cations can account for the penetration of pNP in the interlayer space of these clay minerals also after heating, and for the consequent difficulty in measuring only the external surface area in these samples.

The purpose of this work was to test the possibility of extending the method to natural soil samples.

MATERIALS and METHODS

Eight Italian soils with high clay content have been selected: two Vertisols, three Red Mediterranean soils (Terra Rossa) and three Regosols on Pliocene clays. Only Vertisols resulted to contain swelling clay minerals.

Soil samples, after sieving at 2mm, were Na and Ca saturated by washing with 1M chloride salt solution of the two cations; the excess salt was then removed with distilled water by repeated centrifugation.

Adsorption isotherms were obtained as follows: 10 ml aliquots of different pNP solutions in Xylene (concentration from 2 to 50 mmol/L)

were added to 100 mg. of soil samples, tightly closed in glass tubes and shaken for 24 hrs. at 20°C. The pNP adsorption was then measured after pouring a 0.1-0.5 ml. aliquot of the equilibrium solution in 50-100 ml. volumetric flasks and adjusting to volume with alkaline H₂O; the pNP concentration in the yellow H₂O solution is photometrically determined at 400 nm. Soils samples have been previously conditioned at 160°C or 10% R.H.

RESULTS and DISCUSSION

Na Saturated Samples - The specific surface areas, calculated from the adsorption value at the plateau of L (Langmuir) type isotherms obtained from the samples heated at 160°C, are in very good agreement with the corresponding areas obtained by N₂ sorption at liquid N₂ temperature.

As it concerns the samples equilibrated at 10% R.H., quite similar results are given by the two methods for soils not containing swelling minerals. For Vertisols, the data are not comparable because of the absence of a plateau on the adsorption isotherms, due to the pNP penetration in the interlayers of the swelling fraction of soil clay minerals.

Ca Saturated Samples - Good agreement between N₂ and pNP surface area was found for the six soil samples not containing swelling clay minerals, after heating at 160°C. The same soils equilibrated at 10% R.H. give surface areas lower of about 10% in comparison with N₂ areas, probably because a part of the surface is covered by the cation inner sphere coordination water which is held so strongly to be removed by pNP.

All isotherms of Vertisols equilibrated at 10 % R.H. show plateaux from which a surface area higher than that obtained by N₂ adsorption, can be calculated. As confirmed by X-ray diffraction, a penetration of pNP in the interlayer space of smectite minerals, present in these soils, occurs. The plateau would therefore indicate the complete coverage of the total surface area (internal+external).

The internal fraction of surface area can be easily calculated by subtracting to the total adsorption values: at the plateau the amount of pNP pertaining to the external surface, as obtained by N₂ adsorption. Due to the presence of inner sphere coordination water around the cation, the calculated surface area should be increased of about 10%

As it concerns Vertisols samples heated 160°C, a plateau is not at-

tained within the range of concentration of pNP solution, although X-ray diffraction indicates some penetration of pNP in the interlayer of the smectite minerals.

Considering that total surface area of pure swelling phyllosilicates is about $750 \text{ m}^2/\text{g}$, it seems also possible to calculate approximately the content of these minerals in the soil by the adsorption values at the plateau of Ca saturated samples equilibrated at 10% R.H.

REFERENCES

G.G.RISTORI, E.SPARVOLI, P.FUSI, J.P.QUIRK, C.MARTELLONI, 1985.
Measurements of total and external surface area of homoionic smectites by p-Nitrophenol adsorption. Miner. Petrog. Acta Vol. 29,137-143.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

VARIATION IN MICROORGANIZATION AND PROPERTIES OF SANTA
OLALLA VERMICULITE WITH DECREASING SIZE

M. Robert* , J. Ranger**, P.B. Malla***, D. Tessier*
and J.L. Perez Rodriguez****

* Station de Science du Sol, INRA 78000, Versailles

** Station des Sols Forestiers, INRA 54000, Nancy

*** Department of Soils and Crops Rutgers, University New
Jersey, USA

****Centro Edafologia Sevilla, Spain

Various samples (coarse and fine fractions) of Santa Olalla vermiculite were collected in a Mine near Sevilla (Spain). They were separated according to size and submitted to chemical, mineralogical (XRD, DTA), and microscopic (HRTEM) studies.

The coarse fraction is a pure reference vermiculite and shows all as typical XRD reflection.

Inside the clay fraction two different complexes with ethylene glycol giving 14 and 17 Å can be observed. Using alkylammonium complexes (Lagaly and Weiss, 1969 ; Malla and Douglas, 1986) it is also possible to identify two different 2/1 clay minerals with different charges 0.70 and 0.54 on each side of the vermiculite-smectite border.

The results are compared with those obtained by total chemical analysis and calculation of structural formulae.

By observing ultrathin sections of the clay fraction (coarse and fine) we can characterize the microorganization of natural vermiculite clay which has thick packs of layers of great lateral extension.

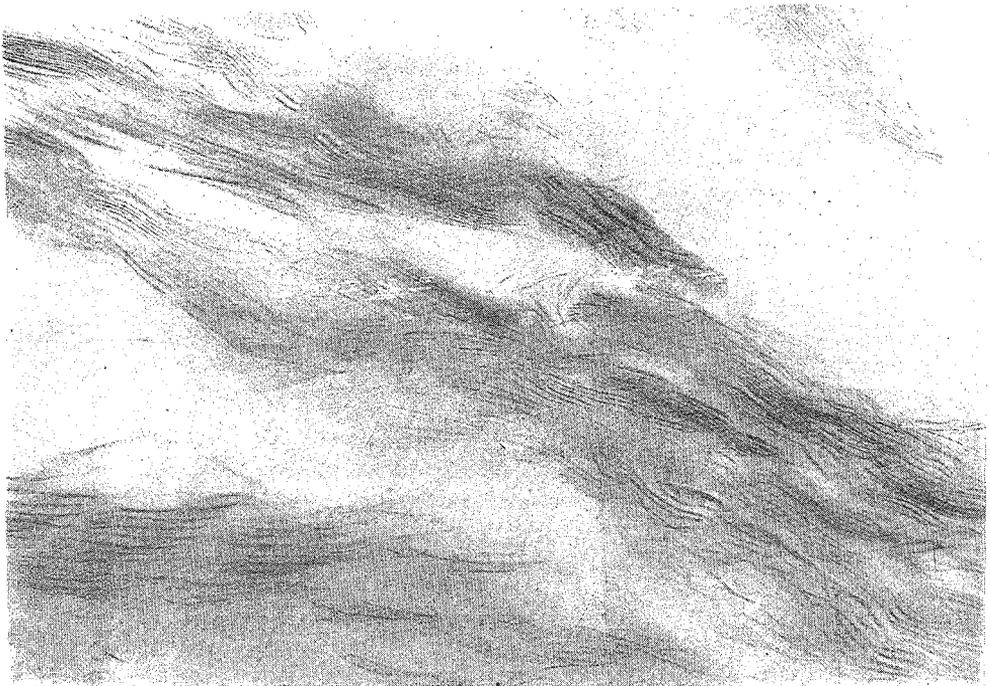
Evolution of this organization with decreasing size and charge is studied and a comparison is done with smectite microorganization (Tessier, 1984).

REFERENCES

Lagaly G. and Weiss A. (1969) - Determination of the layer charge in mica type layer silicates. Proc. Int. Clay Conf. Tokyo. I. Israël Univ. Press, Jerusalem, 61-80

Malla P.B. and Douglas L.A. (1986) - Identification of expanding layer silicates : layer charge expansion properties. Proc. Inter. Clay Conf. Denver, USA, 29-85 (in press)

Tessier D. (1984) - Etude expérimentale de l'organisation des minéraux argileux. Hydratation, gonflement et structuration au cours de la dessiccation et de la réhumectation. Thèse d'Etat, Univ. Paris VII, 361 p.

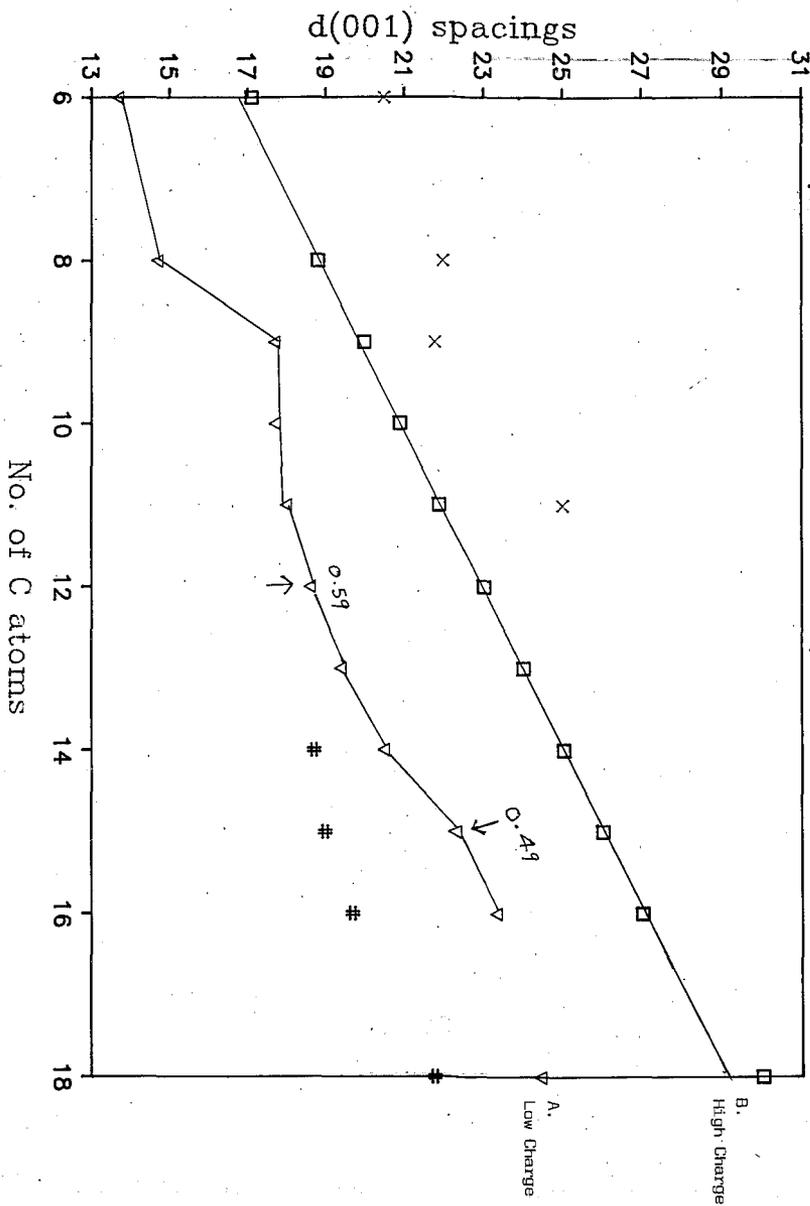


100 nm



HRTEM Aspect of vermiculite clay fraction with alkyl ammonium

Spanish Vermiculite (<2 μ m fraction)



layer charge determination by alkyl ammonium method



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

EVOLUTION OF Fe AND Al POLYCATIONS TO OXIDES OR HYDROXIDES
IN THE PRESENCE OF CLAY MINERALS

M. ROBERT, G. VENEAU, A.M. JAUNET, M. HERVIO

Station de Science du Sol - INRA, Route de St-Cyr -
78000 - Versailles (France)

Iron and aluminium polycations can represent transport forms for these elements and precursors for their different oxides and hydroxides. However, due to their great affinity for negative surfaces, they are adsorbed by clays. This work intends to characterize the conditions of evolution of adsorbed polycations under water percolation.

Fe and Al compounds with different OH /cation ratios ($R = 0$ to 3) are synthesised and fixed on clays kaolinite (Provins) or montmorillonite (Wyoming) (Robert and al., 1979, 1987).

These associations Fe or Al clays are then submitted to distilled water percolation, at 60°C , in a soxhlet apparatus. This system modelises intense hydrolytic weathering conditions giving ferrallitisation process (Pédro, 1964) ; Pédro et Melfi, 1970).

The evolution is followed by XRD, DTA, HRTEM associated with electron diffraction. Evolution of neutral hydrates ($R = 3$) was characterized under similar conditions.

If iron is first considered, the hydrate with $R = 3$ similar to ferrihydrite, rapidly gives both goethite and hematite crystals under percolation.

In the presence of clays, the evolution of Fe compounds is greatly slowed.

With kaolinite after 175 l of percolation, hematite is the only crystalline compounds to be formed. With montmorillonite crystallisation inhibition is higher. Only with $R = 3$ another hematite polymorph is formed.

In all cases, the evolution of adsorbed species on clay gives oxides independent of the surface. Under these conditions there is no epitaxy or epigenesis, but different steps in oxide formation are distinguished.

If aluminium is considered, the precipitated hydrate (R

= 3) was rapidly converted into pseudoboehmite and then into boehmite. The presence of clays inhibit the crystallization for aluminium more than for iron.

In the presence of kaolinite and after 300 l percolation some gibbsite is formed.

In the presence of montmorillonite no evolution can be observed.

Thus the presence of clays can determine the transformation of Fe and Al compounds. In all cases they inhibit more or less temporarily the crystallisation of oxides or hydroxides. This inhibition is higher for aluminum and with montmorillonite. The presence of clay also determines the type of neogenesis ; in our experiments : hematite for iron and gibbsite for aluminium.

REFERENCES

Pédro G., 1964 - Contribution à l'étude expérimentale de l'altération géochimique des roches cristallines. Thèse Fac. Sc. Paris, 334 p.

Pédro G., Melfi A., 1970 - Recherches expérimentales sur le comportement des hydrates ferriques et des constituants silicoferriques amorphes en milieu lessivé. Pédologie, Gand, XX, 1, 5-33

Robert M., Veneau G., Hervio M., 1983 - Influence des polycations du fer et de l'aluminium sur les propriétés des argiles. Science du Sol, 34, 235-251

Robert M., Veneau G., 1987 - Aspects microscopiques des associations argile fer ou aluminium. Cong. Int. de Micromorphologie des sols, Paris 1985, 467-474



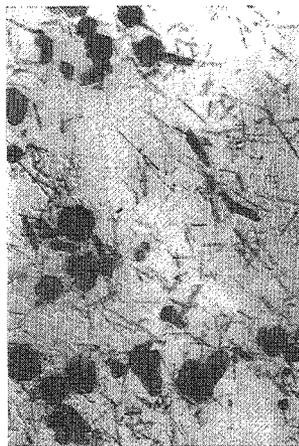
a



b

H R T E M

G - 1. cm = 0,125 μ



c

- a) Evolution of Fe polycation into hematite in the presence of kaolinite
- b) Evolution of Fe polycation into hematite in the presence of montmorillonite
- c) Evolution of ferrihydrite into goethite and hematite



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAY MINERALS EVOLUTION IN LOWER TERTIARY DETRITIC FACIES OF THE SOUTHEASTERN AREA OF THE DUERO BASIN (CENTRAL SPAIN).

M. RODAS(*); F.J. LUQUE(*); R. MAS(*); G. GARZON(*); P. FERNANDEZ GARCIA(*)

(*) Facultad de Ciencias Geológicas. Universidad Complutense de Madrid. 28040 MADRID. SPAIN.

The aim of this work is to establish the genetic relationship between certain clay mineral associations and edafogenetic processes, under specific environmental conditions.

This paper deals with the detritic facies which represent the prearcosic cycle and the lowermost part of the arcotic cycle (Paleogene in age) outcropping in the south-eastern margin of the Duero Basin (Fig. 1).

On the basis of geological mapping and lithological correlation, four informal lithostratigraphic units, which also present different clay mineral associations, have been distinguished:

- Unit 1.- Clays and quartzose sands. The clay mineral association is illite-kaolinite.

- Unit 2.- Quartzose sands with ferruginous paleosoils, with smectite as the main clay mineral.

- Unit 3.- Polimictic conglomerates, arcotic sands and clays, with frequency calcareous profiles. Palygorskite is the most abundant clay mineral.

- Unit 4.- Arcotic sands, with smectite and illite and duricrust levels resembling those of the previous unit.

Throughout the units, clay mineral evolution is as follows:

U.1.- In the stratigraphical series corresponding to this unit, illite is the main phyllosilicate, both in the <20 μ m fraction and in the <2 μ m fraction. This illite is dioctahedral, with a decreasing crystallinity from the bottom to the top of the series. Kaolinite is uniformly distributed along the unit, with percentages up to 20 %. Smectite appears occa-

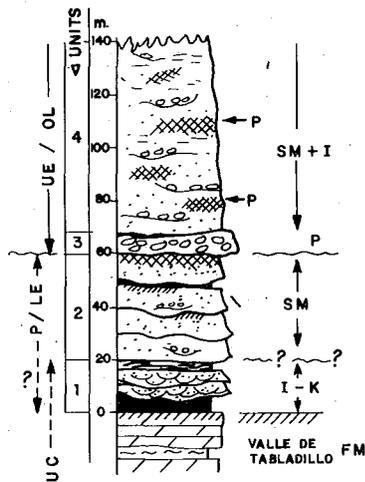
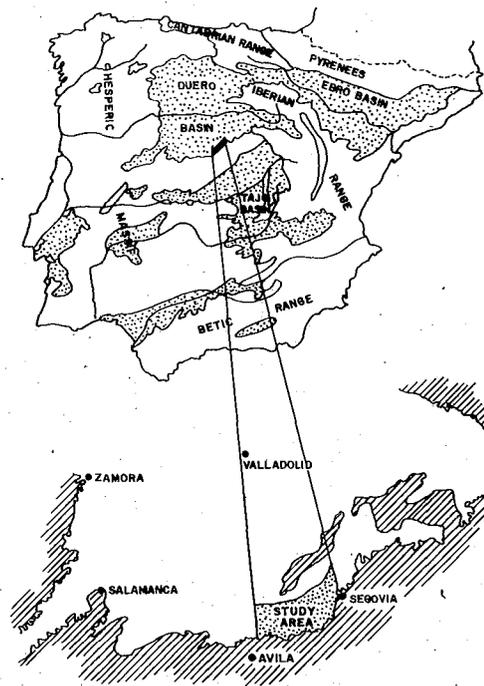
sionally, at the bottom fo the series, with a trioctahedral character and low crystallinity values (Biscaye index).

U.2.- Trioctahedral smectites represent 80-100 % of the total samples studied in this unit, with an increasing Biscaye index towards the bottom of the series, and with a slight reduction in its percentages from the bottom to the top. The presence of kaolinite and illite is related with the alternation of channel facies and flood plain facies.

U.3. Palygorskite represents 70-100 % of the total amount of the samples studies. From the bottom to the top of the series, smectite is observed at the bottom, dissapearing totally in the upper levels. This unit lies in clear unconformity over Unit 2.

U.4.- Trioctahedral smectite is the most abundant clay mineral, with a great crystallinity index, and it is uniformly distributed along the unit. In the duricrust levels, smectite decreases sharply and palygoskite replaces it. Kaolinite is concentrated in the lower levels of the unit and its percentage is always less than 10 %. Dioctahedral illite is distributed uniformly throughout the unit.

From the mineralogical and sedimentological study of the described units, it may be concluded that during the deposit of these materials an important climatic change took place. During sedimentation of Unit 1, climate was warm and wet, with development of braided systems with broad food plains, ferruginous soils in the source area and producing a clay mineral association (illite-kaolinite) typical of well drained areas. Unit 2 corresponds to proximal braides systems and represents a more arid climate with seasonal fluctuations and long dry periods, so smectite is the more prominent clay mineral. Nevertheless, the more drastic climatic change towards arid conditions tood place during the deposit of units 3 and 4, dominated by arid or semiarid alluvial fans. For this reason, this episode presents an important develop. ment of duricrusts, and palygorskite is the characteristic clay mineral, probably related with the edafic processes found in the frequent clacrete levels appearing in these units.



- I - Illite
 K - Kaolinite
 SM - Smectite
 P - Paligorskite
 UC - Upper Cretaceous
 P - Paleocene
 LE - Lower Eocene
 UE - Upper Eocene
 OL - Oligocene
 1, 2, 3, 4 - Lithostratigraphic units

LOCATION MAP AND STRATIGRAPHIC SETTING OF THE STUDY AREA



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CORRENSITE AND ZEOLITE GROWTH IN CARBONATE TURBIDITES AND ASSOCIATED CHERT OF THE GIBRALTAR AREA (SOUTHWEST SPAIN)

P. RODRIGUEZ., M.D. RUIZ CRUZ AND F. CARRASCO

Department of Inorganic Chemistry, Crystallography and Mineralogy. Sciences School. University of Málaga. (Spain).

In this paper is considered the relationship between the process of silicification in turbiditic limestones and the growth of corrensite, as well as the association of fibrous zeolite to silicified limestones. The study of textural and mineralogical characteristics of these materials is done in three sequences of very similar age and litology, which correspond to the Basic series of the Aljibe Unit (Flysch, Campo de Gibraltar).

The mineralogical association found for clays ($<2\mu$ fraction) is:

Illite — Mixed-layers illite-smectite — Corrensite although kaolinite and chlorite may sporadically be found in very low proportion.

The most frequent associations among the nonargillaceous minerals, is:

Calcite — Quartz — (Albite) — (Zeolite)

Albite if found sporadically and zeolite only appear associate to chert.

This mineralogy is thought to be a result of two fundamental factors: a) Type of detrital material, and b) Diagenetic conditions of the environment.

Type of detrital material (in general similar to that found in other calcareous rocks of the Campo de Gibraltar Unit) determine the presence of illite and mixed-layers illite-smectite, limited smectite and scarce kaolinite.

Diagenetic environment is responsible for the corrensite and zeolite growth, and the carbonate silicification. The paragenesis and chemical characteristics studied showed that the environment for the formation of these minerals needs the following conditions: The zeolite

(mordenite) are found to form in most low temperature environment and is demonstrated the relative importance of several chemical parameters: High activity of silica in solutions, alkaly activity (inversely related to that of silica) and the activity of H_2O is important also. This medium is thus favorable for silification process. On the other hand, the chemical medium for corrensite growth in sedimentary rocks requires a high content of iron (divalent) and magnesium, but is not necessarily be in relation with evaporitic deposits and thus alkaline conditions of formations.

In this examples, the silicification process of limestone (Which shows in the chemical analysis a certain proportion of iron and magnesium) is accompanied by iron oxides growth. The release of iron has probably influencied the chemical composition of mordenite. The release of magnesium did not, as it frequently does, cause dolomite growth but, instead, led to the corrensite formation.

Because of the absence of siliceous organisms (radiolarian, sponge-spicules...) in this rocks, the silicification process which has conduced to development of chert nodules probably took place in an early stage of diagenesis, using silica precipitation from the solution. In this case, the volcanic activity cannot be considered as a last source of silica, as there is no evidence of contemporary volcanism with the sedimentation of these materials.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**MINERALOGICAL PROPERTIES OF SOILS ON "RAÑA" FORMATIONS IN
THE PROVINCE OF GUADALAJARA (SPAIN).**

C. RODRIGUEZ-PASCUAL, B. GALVAN, J. GALVAN.

Instituto de Edafología y Biología Vegetal (CSIC).

C. Serrano 115 dpdo. 28006 Madrid, Spain.

In popular usage the word "RAÑA" refers to a certain type of countryside which chiefly consists of flat features with excavated valleys and a detrital cover. Geologically "RAÑAS" are formations at the foot of a mountain. They include quartzite reliefs of fluvial origin, which follow the filled up phase in Tertiary basins and precede the first fluvial terraces.

Soil genesis in "RAÑA" formations results from different geological, geomorphological and climatic factors. Since some important features of the soil depend on the $<2 \mu\text{m}$ fraction, an extensive research on the clay minerals fraction has been carried out for scientific and utility purposes.

The two soil profiles here studied lie in the plain of "Fuentelahiguera de Albatages" (Guadalajara). Their classification and other data are reported elsewhere.

Both profiles are developed on stony Pliocene sandy clay sediments under transitional climatic conditions ranging from semiarid to dry subhumid; their clay content being around 55% in the B horizons.

Profile	Altitude	Drainage	Soil type (FAO)
I	935 m	poorly drained	Gleyc acrisol
II	930 m	moderately drained	Orthic acrisol

These soils have an acid pH, and a low base saturation.

In the 2 mm fraction phyllosilicates are predominant, together with quartz, iron oxides and sometimes feldspars. Quartz and feldspars are found in the upper horizons in unusually small proportions. The feldspars are plagioclases and orthoclase, their content decreasing with depth, and even disappearing completely in the lower horizons. Quartz also decreases with depth in both profiles.

The clay fraction was characterized mineralogically by X-ray diffraction (XRD), infra red (IR) and transmission electron microscopy (TEM). Well crystallized kaolinite predominates, with dioctahedral mica, smectite and chlorite as accompanying minerals. The smectite content increases with depth, to about 30% in the lower horizons, with a parallel decrease of the mica content. Chlorite is only present in the top horizons. The smectite is well ordered beidellite, as indicated by 6 rational 001 reflections, after ethylene glycol treatment. Li-saturation and heating at 300°C overnight results in positive expansion to 1.7 nm after ethylene glycol treatment.

The mineral composition of both the soil and the clay fractions, would indicate intense chemical weathering of the primary minerals under the specific climatic and drainage conditions formerly prevailing. Kaolinite and goethite formation at the expense of feldspars in acid conditions is a well known process in continental mediterranean climates (Paquet, 1970; Dubreuilh, Marchadour et Thiry, 1984).

The presence of chlorite in the top horizons should be related to the existence of amorphous Al-hydroxides, which may precipitate as interlayers within the altering mica. (Van Ranst, Coninck, Embrechts, 1986).

Thin soil sections show a coarse mineral fraction consisting of quartzite fragments, subjected to intense mechanical weathering, associated with altered slate

fragments. The micromass has reddish-brown areas together with greyish yellow ones, which indicates pseudogleyization, and it shows a striated fabric of birefringence.

As hydromorphism prevents oxidation of Fe^{2+} , which would be required for vermiculite formation (Douglas, 1977) the conditions favour beidellite formation from the weathering of detrital dioctahedral mica. (St. Arnaud and Mortland, 1963; Komarneni and Breval, 1985).

Douglas, L.A. (1977). Vermiculites, 259-292. In J.D. Dixon and S.B. Weed (Ed.). Minerals in Soil Environments. Soil Sci. Soc. U.S.A., Madison, W1.

Dubreuilh, J. Marchadour, P. et Thiry, M. Cadre géologique et minéralogie des argiles des Charentes, France. Clay Miner. 19, 29-41.

Komarneni, S. and Breval, E. (1986). Characterization of smectites synthesised from zeolites and mechanism of smectite synthesis. Clay Miner. 20, 181-188.

Paquet, H. (1970). "Evolution géochimique des minéraux argileux dans les altérations et les sols des climats méditerranéens et tropicaux à saisons contrastées". Thèse. Université de Strasbourg et Mém. Serv. Carte Géol. Alsace Lorraine, 30, pp. 210.

St. Arnaud, R.J., and M.M. Mortland. 1963. Characteristics of the clay fractions in a Chernozemic to Podzol sequence of soil profiles in Saskatchewan. Can. J. Soil Sci. 43:336-349.

Van Ranst, E., De Coninck, F., Embrechts, J. (1986): "Trioctahedral and dioctahedral chlorite in soils". XIII Congr. Int. Soc. Soil Sci. (Hamburg) IV, 1488-1489.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

STUDY AND CHARACTERIZATION OF A CHLORITE-SMECTITE INTERSTRATIFIED MINERAL BY SORPTION OF ORGANIC COMPOUNDS

A. RUIZ AMIL, E. VILA AND F. ARAGON DE LA CRUZ

Instituto de Química Inorgánica "Elhuyar". C.S.I.C. Serrano 113. 28006 Madrid (Spain).

The aim of this paper is the study and characterization of a chlorite-smectite interstratified mineral contained in a pottery stone, from Niwatorizawa mine, Izushi-cho, Hyogo Prefecture, Japan (Geological Survey of Japan), by means of sorption of different organic compounds, as well as the study of the behaviour of these organic compounds. (De Miguel et al., 1981), (Doval et al., 1985)

The interstratification of the components of this material is investigated, treating the oriented aggregates of the samples with ethylene glycol, glycerol, aliphatic amines, diamines, pyridine, etc.

From X-ray diffraction data on oriented aggregates, the distribution function of interlayer distances ("direct Fourier method", used for a preliminary study) and "diffraction intensity function" (MacEwan et al. 1961) are calculated with the aid of a "computer program for analysing interstratified structures by Fourier transform based methods" (named INTER program). (Vila and Ruiz Amil, 1987).

The experimental X-ray diffraction intensities are compared with theoretical data, given in the calculated "diffraction intensity function", stating the presence of the interstratification and their characterization after the treatment with organic compounds.

The study of the sample by sorption of glycerol is shown.

Fig. 1 represents the "distribution function of interlayer distances" (calculated from spacings $d(A)$ and intensities I_{est} of Table 1) and shows these interlayer distances: $A=14 \text{ \AA}$ (chlorite); $B=17.8 \text{ \AA}$ (smectite + glycerol); $AA=28 \text{ \AA}$; $AB, BA=31.8 \text{ \AA}$; $BB=35.6 \text{ \AA}$; $AAA=42 \text{ \AA}$; $AAB=45.8 \text{ \AA}$; $ABB=49.6 \text{ \AA}$.

TABLE 1

$d(\text{\AA})$	I _{est}
33.90	20
16.10	100
8.01	30
6.26	10
5.3	15
4.56	30
3.53	40
2.90	20

Fig. 2 represents the results obtained for a binary interstratification of 14 Å (chlorite) and 17.8 Å (smectite + glycerol) for $p_A=0.5$ and $p_{AA}=0.1$. Curve (a) is the F^2 function for the mixed layers; (b) is Lorentz-polarization function, Θ , for $\text{CuK}\alpha$ radiation; (c) is the mixing function, Ψ ; and (d) represents the resultant X-ray diffraction intensity function, I . In (e) the values of spacings and relative intensities are plotted and they corresponds to an X-ray diffraction diagram of glycerol treated chlorite-smectite sample (Table 1).

An almost alternating regular chlorite-smectite interstratification appears, because $p_A=p_B=0.5$, $p_{AA}=0.1$ and $p_{AB}=0.9$.

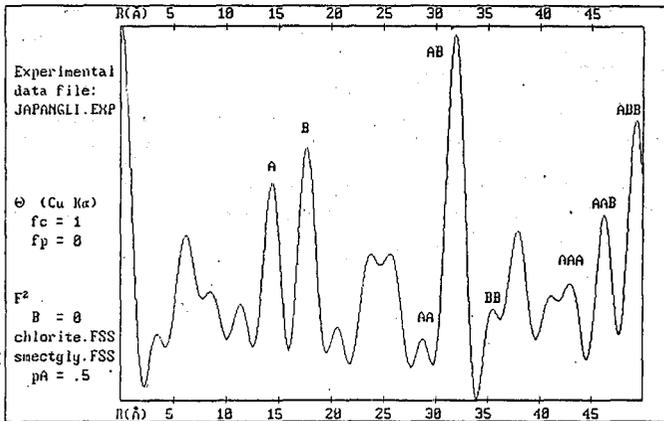


Figure 1

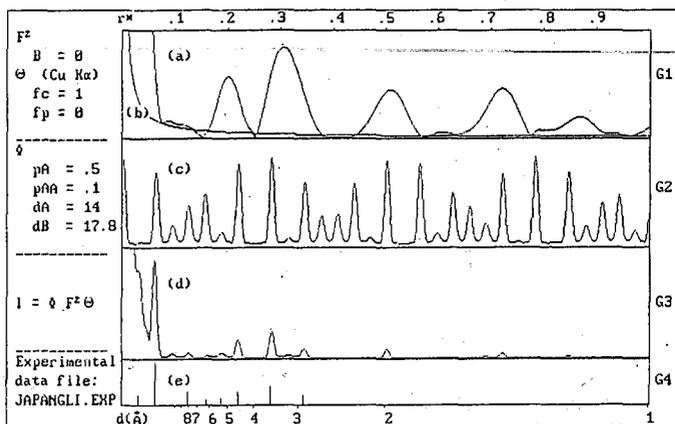


Figure 2

REFERENCES

- De Miguel Rodríguez R., Ruiz Amil A and Aragón de la Cruz F. 1981. - "Sorción interlaminar de aminas alifáticas en minerales mica-montmorillonita II". Anal. Edaf. Agrob. XL, 2163-2175.
- Doval M., Rodas M., Ruiz Amil A. and Aragón de la Cruz F. 1985. "Identificación de un mineral interestratificado clorita-esmectita por sorción de aminas. Facies verdes de la Cuenca del Tajo III". Anal. Edaf. Agrob. XLIV, 1335-1339.
- Mac Ewan D.M.C., Ruiz Amil A. and Brown G. 1961. "Interstratified clay minerals in: The X-ray identification and crystal structures of clay minerals" (G. Brown editor). Mineralogical Society, London.
- Vila E. and Ruiz Amil A. 1987. "Computer program for analysing interstratified structures by Fourier transform based methods". Powder Diff. (enviado para su publicación).

DIRECT METHOD

The distribution function $W(R)$ of interlayer distances, R , is obtained from the observed diffraction intensities, I_s , and the basal spacing, d_s , by means of a Fourier transform:

$$W(R) = a/\pi \sum_s (I_s/\theta_s^2 F_s^2) \cos 2\pi R/d_s$$

where θ_s and F_s^2 are the values of the θ and F^2 function at the position d_s .

The INTER program calculates the $W(R)$ function from d_s and I_s values.

In this program, the direct method is used, principally, in a preliminary survey of X-ray diffraction diagrams and gives a very valuable information about the possible values of p_A , p_{AA} , p_B and d_B . They can be used as starting inputs to calculate the X-ray diffraction intensity function.

REFERENCES

- .International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
- .MacEwan, D.M.C. and Ruiz-Amil, A (1959). Ko11-Z5 162, 93-100.
- .MacEwan, D.M.C. and Ruiz-Amil, A (1975). Soil Components, Vol. 2, edited by J. Gieseking, pp. 265-334. New York: Springer Verlag.
- .MacEwan, D.M.C., Ruiz Amil, A. and Brown, G. (1961). X-ray identification and Crystal Structures of Clay minerals, edited by G. Brown, pp. 393-445. London: Mineralogical Society.
- .Reynolds, R.D. (1980). Crystal Structures of Clay minerals and their X-ray identification, edited by G.W. Brindley and G. Brown, pp. 249-302. London: Mineralogical Society.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

STUDIES OF STACKING DEFECTS NATURE IN THE STRUCTURE OF
 Fe^{3+} -CONTAINING MINERALS WITH X-RAY ANALYSIS

B.A.Sakharov*, G.Besson**, M.Yu.Kameneva***, B.B.Smolyar*,
K.Tchoubar**, V.A.Drits*

*Geological Institute of the USSR Academy of Science,
Moscow, USSR

**Laboratoire de Crystallographie, Universite d'Orleans,
France

***Institute of Geology and Geophysics, Siberian Branch
of the USSR Academy of Science, Novosibirsk, USSR

Fine-dispersed mica minerals with low concentrations of swelling layers often include structures of polytype modification 1M-1MD. Reflections in diffraction patterns of these minerals vary from sharp and strong to wide and weak. It points to defects in their structure's packing.

One of methods to study disperse systems with defect layered structures which has found a practical application was developed in works by Plancon, Tchoubar, 1977a,b; Sakharov et al., 1982a,b, 1983. The essence of the method is simulation of defect structures and calculation of corresponding diffraction patterns which can be directly compared with the experimental ones.

To define the nature of structural distortions in mica minerals, crystal-chemically possible models of defect structures have been considered. It is known that in micas, relation $b = a / 3$ between unit cell parameters may be sometimes violated both for individual layers and for the whole of the structure. Let us write $b/a = 1/q$, where $q = 3$ or $q \neq 3$.

Models with $q = 3$. The most probable types of defects in packing may be due to:

- layer rotation to $n120^\circ$ (n is an integer);
- layer rotation either only to $+120^\circ$ or only to -120° .

- layer rotation to $n60^\circ$.

In the first two models all interlayer K cations have the same anionic environment, whereas the 3rd model leads to their prismatic coordination in some interlayers.

Models with $q \neq 3$. In this case, crystal layers must be characterised with identical in the shape and size unit cells and a common two-dimensional lattice for the crystal in general. Stacking defects may be connected with alternation of enantiomorphic layers and their rotation to 180° relative to c^* . Depending on the coordination environment of K cations, two types of models can be differentiated: K coordination is octahedral in all interlayers. In such crystal, only two enantiomorphic layers can alternate; - K coordination can be either octahedral or trigonal-prismatic, depending on the azimuthal orientation of 2:1 layers. Four types of layers alternate in the crystals that are connected with each other either by two perpendicular slide planes, or rotation to 180° around c^* .

In all above models, a consecutive change in the proportion of different types layers is possible, as well as in their distribution in the crystal volume. The latter ranges from total disorder via all transitional stages to the segregation in blocks of layers with identical azimuthal orientations.

The fitting parameters are: the size of coherent domains in the crystals; unit cell parameters; value of interlayer shift; the mode of cationic distribution over trans- and cis-octahedral sites of 2:1 layers, etc. Mixed-layering and the variations in heights of layers and interlayer shifts were taken into account too.

The chemical composition and the unit cell parameters were used to simulate atomic coordinates of micaceous layers.

The analysis of the simulated diffraction patterns has allowed to set forth diffractive criteria to be used while defining specific types of defects in mica minerals.

Two mica samples have been used with different Fe content: B.Patom, $K_{0.74}Na_{0.01}Ca_{0.06}(si_{3.46}Al_{0.54})(Al_{1.11}Fe^{3+}_{0.41}$

$\text{Fe}_{0.13}^{2+}\text{Mg}_{0.42})\text{O}_{10}(\text{OH})_2$ and Babino, $\text{K}_{0.75}\text{Na}_{0.05}\text{Ga}_{0.03}(\text{Si}_{3.58}\text{Al}_{0.42})(\text{Al}_{0.53}\text{Fe}_{0.94}^{3+}\text{Fe}_{0.13}^{2+}\text{Mg}_{0.43})\text{O}_{10}(\text{OH})_2$. The samples were free of impurities and had a low swelling layers content (<10 %). The samples had not been crushed to preserve the globular shape of the aggregates. Diffraction experiment was performed on CGR diffractometer with a linear detector and $\text{MoK}\alpha_1$ -radiation. All necessary corrections of experimental profiles have been done.

Comparison of experimental diffraction curves with the simulated ones for various models of defective structures has shown that their best agreement is:

- for sample B.Patom, with $q = 3$, $b = 9.038 \text{ \AA}$, $\gamma = 90^\circ$ in the model of layer rotation to $n60^\circ$. All six types of layers occur in equal proportions with $w_i = 0.167$, while their segregation throughout the volume of the crystals is described, with coefficient $P_{ii} = 0.55$ and $P_{ij} = 0.09$ ($i, j = 1, 2, \dots, 6$).

for sample Babino, with $q = 2.97$, $b = 9.100 \text{ \AA}$, $\gamma = 89.5^\circ$ in the 4-layers segregational model with $w_i = 0.25$, $P_{ii} = 0.5$, $P_{ij} = 0.167$ ($i, j = 1, 2, 3, 4$).

Thus, we may conclude that:

- stacking defects concentration in the mica minerals under study is rather high;
- their distribution in the crystal volume is not random;
- K cation coordination is heterogeneous.

Plancon A., Tchoubar C. (1977a) Clays and Clay Minerals, 25, 430-435

Plancon A., Tchoubar (1977b) Clays and Clay Minerals, 25, 435-450

Sakharov B.A., Naumov A.S., Drits V.A. (1982a) Dokl. Akad. Nauk USSR, 265, 339-343

Sakharov B.A., Naumov A.S., Drits V.A. (1982b) Dokl. Akad. Nauk USSR, 265, 871-874

Sakharov B.A., Naumov A.S., Drits V.A. (1983) Kristallografiya, 28, 951-958



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

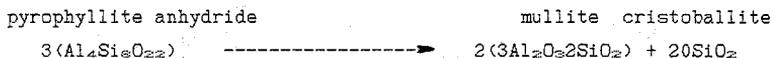
THERMAL TRANSFORMATION OF PYROPHYLLITE BY ELECTRON OPTICAL METHODS*

CECILIA SALVADORI AND HELENÁ DE SOUZA SANTOS

Laboratório de Microscopia Eletrônica-Instituto de Física da Universidade de São Paulo. São Paulo, SP, Brazil

A Brazilian pyrophyllite from Diamantina, MG, Brazil, was progressively heated at temperatures from 600°C to 1300°C and studied by transmission electron microscopy associated to selected area electron diffraction.

The phase transformation studied were represented by the equation:



Up to 900°C it was not possible to characterize structurally the anhydrous phase of pyrophyllite; however morphologically it could be observed a crescent number of Moiré patterns in relation to the pyrophyllite without treatment; this fact is justifiable by the superposition of plates of the original and anhydrous pyrophyllite, since the last has a basal spacement slightly larger, after the liberation of water vapour during the dehydration and dehydroxylation.

It was possible to follow from 950°C up (morphologically and crystallographically) the progressive growth of mullite crystals, beginning with the nucleations stages and presenting complete development at 1200°C.

* Grant from FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo)

THE DIATOMITIC DEPOSITS OF SORBAS BASIN (ALMERIA, SE SPAIN)

SANCHEZ, C. (1,2); RODRIGUEZ FERNANDEZ, J. (1,2) & ORTEGA HUERTAS, M. (2,3)

- (1). Dpto. Estratigrafía y Paleontología. Universidad de Granada (Spain)
- (2). Instituto Andaluz de Geología Mediterránea. C.S.I.C.-Universidad de Granada (Spain).
- (3). Dpto. Mineralogía y Petrología. Universidad de Granada (Spain).

INTRODUCTION

The area under study is shown in Fig. 1.

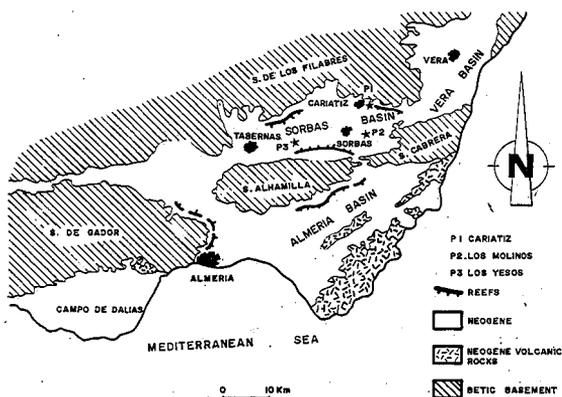


Fig. 1. Location of sequences

ENVIRONMENTAL CONSIDERATIONS

A microscopic study of the samples provides, among others, the results set out in Table I.

Diatoms account for 85% of the total siliceous phase (centric diatoms 55% and pennate forms 30%), while the remaining 15% is made up of silicoflagellates (10%) together with sponge spicules and fragments of radiolaria (5%). The deposits have been assigned to the Messinian-upper-Messinian on the basis of the presence of *Thalassiosira* Miocenica (Schrader, 1974) zone 15 of the T.I.D. zone established by this author, which coincides with the *Thalassiosira* Convexa zone of the E.P.D. zone (Burckle, 1972).

These materials foretell the desiccation of the basin, corresponding to the widespread salinity crisis of the Mediterranean as a whole, as they were laid down immediately before the thick beds of selenitic gypsum. A palaeo-ecological analysis was carried out, taking into account such chemico-physical parameters as the salinity of the basin, the sedimentary environment and the possible temperature-fauna relationship that may have existed. The following conclusions can be drawn:

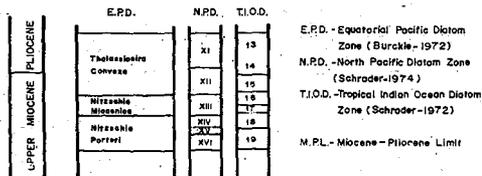
- 1) All the species are marine, as the mean salinity values are above 25‰ according to Kudal's classification (1971);
- 2) It is clearly a coastal

environment despite the fact that species may appear that do not belong to such an environment. These were, in fact, probably transported to the area. The fauna in general are to be found as isolated individuals, in colonies, in association with individuals of the same species and as epifites living in association with different species.

As far as depth is concerned the dominant fauna are benthonic although mesoplanktonic, holoplanktonic and ticoplanktonic organisms also exist. The temperature varies greatly, between 5°C and 30°C.

Table I. Distribution of diatoms.

	E.P.D.		N.P.D. Z.						T.I.O.D. Z.						LOS ANGELES	LOS ANGELES	
	13	14	x	xii	xiii	xiv	xv	xvi	13	14	15	16	17	18			19
CENTRIC DIATOMS																	
<i>Actinocyclus Miocenicus</i>																	•
<i>Actinocyclus Oppenoorthi</i>																	•
<i>Biddulphia Subjuncta</i>																	•
<i>Biddulphia Tridens</i>																	•
<i>Coscinodiscus Vetustissimus</i>																	•
<i>Esporas</i>																	•
<i>Rhizosolenia Matuyamai</i>																	•
<i>Thalassiosira Miocenica</i>																	•
PENNATE DIATOMS																	
<i>Dimerogramma Fulvum</i>																	•
<i>Diploneis Bombus</i>																	•
<i>Grammatophora Oceanica</i>																	•
<i>Navicula Hennedyi</i>																	•
<i>Rhabdonema Adriaticum</i>																	•
<i>Rhaphoneis Nitida</i>																	•
<i>Rhopalodia Gibberula</i>																	•
<i>Thalassiotrix Lanceolata</i>																	•
<i>Trachyneis Aspera</i>																	•



MINERALOGICAL AND DIAGENETIC CONSIDERATIONS.

Apart from opal-A and/or opal-CT, the following minerals are to be found: calcite (24%), dolomite (26%), quartz (8-10%), feldspars (5%) and clay minerals (58-65%). The clay minerals, which occur in very variable proportions, are: illite (5-60%), paragonite (5%), kaolinite (5%) and smectite (35-96%).

The main interest of this study is the analysis of the kinds of silica present in association with certain clay minerals, pointing to significant diagenetic conditions.

When the association of minerals found in these sediments is fitted to Aoyagi and Kazama's diagram (1980) several different groups of samples are identifiable:

1) Opal-A in very variable proportions and very significant quantities of smectites (96%) (samples M-1-1, CZ-1-2 and CZ-1-3). These correspond to an early-diagenetic zone, as the abundance of smectites suggests, according to the schemes of Burst(1959) and of Hower et al. (1976), among others. Even when the opal-A is relatively abundant it can still be maintained that these sediments have not been subjected to diagenetic conditions exceeding those of 920 m depth and 45°C.

2) Opal-A to opal-CT transformation and lesser quantities of smectites (50%) (samples Y-1-2, M-1-2, CZ-1-1 and CZ-2-1). These correspond to sediments that have been subjected to intermediate diagenetic conditions of slightly more than 920 m depth and 45°C temperature.

3) Opal-CT lepispheres+clinoptilolite+quartz (sample M-1-2-Bs). This mineral association represents the most advanced stage of diagenesis in the samples studied and points to the following conditions: an upper limit of 1.260 m in depth and 50°C and a lower limit of somewhat more than 1.660 m in depth and 70°C, as the presence of quartz indicates a late diagenesis zone.

According to the hypotheses of Wise and Weaver(1974), Kastner et al. (1977) and Riech and Von Rad(1979), the transformation of opal-A into opal-CT takes place in early diagenesis, either through the dissolution of the siliceous organism and the subsequent precipitation of opal-CT or by "in situ" reemplazamiento with no previous dissolution. The transformation of opal-CT to quartz may occur by means of a subsolidus reaction (Ernst and Calvert, 1969), which is then followed by processes of recrystallisation and a consequent modification of textures. It is finally worth pointing out that these diagenetic transformations are controlled not only by pressure and temperature but also by such factors as the chemical composition of the interstitial water, the availability of Al, Fe, Mg and Mn hydroxides and the nature and permeability of the sediment (Kastner et al., 1977).

REFERENCES

- Aoyagi, K. and Kazama, T. (1980). *Sedimentology*, 27, 179-188.
Burckle, L.H. (1972). *Nova Hed.* 39, 217-246.
Burst, J.F. (1959). *Clays Clay Miner.* 2, 154-187.
Ernst, W.G. and Calvert, S.E. (1969). *Amer. J. Sci.*, 267-A, 114-133.
Hower, J.; Eslinger, E.V.; Hower, M.E. and Perry, E.A. (1976). *Bull. geol. Soc. Am.* 87, 725-737.
Kastner, M.; Keene, J.B. and Gieskes, J.M. (1977). *Geochim. Cosmochim. Acta.* 41, 1041-1059.
Riech, V. and Von Rad, U. (1979). In: *Deep Drilling results in the Atlantic Ocean: continental margins and paleoenvironment*. Talwani, Hay and Ryan, (eds.).
Schrader, H.O. (1974). *Init. Rep. D.S.D.P.*, XXIV, 887-967.
Wise, S.W. and Weaver, F.M. (1974). *Geol. Soc. Amer. Progr. Abst.*, 4, 116 pp.

(This work forms part of the "Análisis sedimentológico, mineralógico y evolución tectono-sedimentaria de las Depresiones Béticas Orientales" project. C.S.I.C.-C.A.I.C.Y.T.)



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

OCCURRENCE OF PYROPHYLLITE IN SOILS FROM SIERRA DE SAN PEDRO (CACERES, SPAIN)

M. SANCHEZ-CAMAZANO, J. FORTEZA AND L.F. LORENZO

Centro de Edafología y Biología Aplicada de Salamanca (Spain)

The frequency with which the aluminó-phyllósílicates, kaolinite and pyrophyllite appear in soils and sediments varies considerably. Kaolinite is a common mineral in soils and sediments, whereas pyrophyllite is rarely found in these environments. The presence of pyrophyllite has been reported in sedimentary rocks and in most cases is considered to be of detrital origin. Neither is this mineral frequent in rocks of low diagenetic or metamorphic grade. This mineral has been found in hydrothermally altered shales and as a product of high-grade metamorphism through the kaolinite+quartz reaction. Recent data concerning the stability of pyrophyllite from this reaction have established the lowest limit at 270°C at 1-2 kbars (Hemley et al, 1980). In the Al_2O_3 - SiO_2 - H_2O system, the limits of stability of this mineral extend from 345 to 380°C at 2 kbars (Haas and Holdaway, 1973). To a certain extent, these data account for the limited geological presence of the mineral.

The presence of pyrophyllite in soils has been very seldom described (Dixon and Weed, 1977; Maqueda et al., 1986). According to the conditions of synthesis of this mineral it is not possible that its formation can occur during pedogenesis; it will always be inherited from the parent material.

Recently, the presence of pyrophyllite has been detected in several soil profiles of the Sierra de San Pedro (Cáceres, Spain). This mountain range, belonging to what is known as the "Montes de Toledo", forms a narrow vertical crest of some 75 km in length and constitutes the limit between the provinces of Cáceres and Badajoz. It has a maximum height of 703 m. Its basement is composed of Cambrian shales, followed by Silurian quartzites and shales with a strong metamorphism due to contact with hypogenic rocks. Mallada (1972) has reported the existence of talc (this must correspond to the pyrophyllite described in the present work) and mica in the Cambrian and Silurian shales.

In the present work a study was made of the presence of pyrophyllite in a representative profile of the area; it is an orthic Acrisol (Palixerult) with A, Bt, Bt/Cl, Cl and C horizons, acid at the sur-

face and strongly acid in deeper horizons; such acidity is partly due to the original rock, to the climate and also to the vegetation covering, which provides a medium content in organic matter and a high C/N ratio. The mineralogical composition of the clay (<2 μm), silt (2-20 μm), fine (20-200 μm) and coarse (> 200 μm) sand fractions taken from the different horizons of the profile was determined. The study used the X-ray diffraction, thermogravimetric and differential thermal analysis techniques. Semiquantitative estimation of the minerals was performed using characteristic reflections and their relative intensities according to Schultz (1964) and Galan and Martín Valdi (1973).

In general, the X-ray diffraction diagrams show reflections of pyrophyllite (9.20, 4.60, 3.06, 2.57, 2.41, 2.30, 1.84 \AA), of illite (9.98, 4.48, 4.43, 3.32, 2.56, 2.00 \AA), and of kaolinite (7.14, 4.43, 3.55, 2.56, 2.29 \AA) and also of quartz, rutile, goethite and feldspaths. The X-ray diagram of pyrophyllite separated from the rest of the minerals (Pérez Rodríguez et al 1985) shows that it is of the 2 M type with a small proportion of the 1 Tc type (Brindley and Wardle, 1970).

The metamorphic shale over which the profile was developed contains 45 % pyrophyllite, 45 % illite and 10 % kaolinite, together with small amounts of quartz, rutile, goethite and feldspaths. The illite is mainly trioctahedral (reflection (060) at 1.53 \AA).

In the deeper horizons, C and Cl, the pyrophyllite is concentrated in the silt, fine sand and coarse sand fractions, representing approximately 50 % of these fractions. In the Bt horizon the content in pyrophyllite decreases markedly in the fine and coarse sand and moderately so in the silt fraction. In the A horizon the content in this mineral is very low in the fine and coarse sand and medium in the silt.

In the clay fraction the content in pyrophyllite increases from 10 % in the C and Cl horizons up to 25 % in the A horizon. This increase, coinciding with the decrease in the proportion of the mineral in the other fractions, is due to a process of microdivision, caused by the high degree of weathering of the profile; in turn, the resistance of this mineral to acid chemical alteration is also patent.

The strong weathering gave rise to an increase in the content of kaolinite in the clay fraction of the upper horizons, parallel to the increase in pyrophyllite. In the other fractions the content of this mineral remains low but constant.

The content in illite is greater in the clay fraction than in the other fractions and always decreases with the height of the profile. In the rock and coarser fractions it is partly dioctahedral and partly trioctahedral ((060) reflections at 1.50 and 1.53 \AA), whereas in the clay fraction it is totally dioctahedral. This distribution in the horizons and fractions is in accordance with the greater ease observed in the destruction of the trioctahedral micas by organic acids, abundant in this profile in view of the characteristics of the organic matter.

- BRINDLEY, G.W. and WARDLE, R. 1970. Am. Miner., 55, 1259-1272.
- DIXON, J.B. and WEED, S.B. 1977. Minerals in Soil Environments. Soil Science Society of America. Madison (USA).
- GALAN, E. and MARTIN VIVALDI, J.L. 1973. Bol. Soc. Esp. Ceram. Vidr., 12, 79-89.
- HAAS, H. and HOLDAWAY, M.J. 1973. Am. J. Sci., 273, 449-464.
- HEMLEY, J.J., MONTEYA, J.W., MARINENKO, J.W. and LUCE, R.W. 1980. Econ. Geol., 75, 210-228.
- MALLADA, L. 1927. Explicación del Mapa Geológico de España. II. Sistemas cambriano y siluriano. Comisión del Mapa Geológico de España. Madrid (España).
- MAQUEDA, C., PEREZ RODRIGUEZ, J.L. y JUSTO, A. VIII Reunión Sociedad Española de Arcillas. Zaragoza, Junio 1986. Resúmenes, 108.
- PEREZ RODRIGUEZ, J.L., MAQUEDA, C. y JUSTO, A. 1985. Clays Clay Miner., 33, 563-566.
- SCHULTZ, L.G. 1964. U.S. Geol. Surv. Prof. Pap. 391-C, 1-31.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THERMO-ANALYTICAL STUDY OF MONTMORILLONITE-PIRIMICARB COMPLEXES

M. J. SANCHEZ-MARTIN AND M. SANCHEZ-CAMAZANO

Centro de Edafología y Biología Aplicada. C. S. I. C. Salamanca.
Spain.

The carbamate insecticide Pirimicarb (2-dimethylamino-5,6, di-methyl pyrimidin 4-yl dimethyl carbamate) forms regular interlayer complexes with homoionic samples of Tidinit Montmorillonite with d_{001} spacings ranging between 16.98 Å and 18.55 Å, in agreement with the nature of the interlayer cation. The mechanism of interaction is mainly ion-dipole and takes place between the oxygen atom of the C=O group of the organic molecule and the interlayer cations of the silicate (Sánchez-Camazano and Sánchez-Martín, 1986).

With a view to determining the thermal stability of these adsorption complexes a thermoanalytical study was carried out of free pirimicarb (diluted in calcined Al_2O_3), of the complexes of Cu, Cd, Mg, Ca and Ba montmorillonite with pirimicarb and of artificial mixtures of the same montmorillonites with pirimicarb. The techniques employed were thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The curves were obtained in a dynamic atmosphere of nitrogen (45 ml min^{-1}). Decomposition of the organic compound was followed by X-ray diffraction and I.R. spectroscopy.

The TG curves of the pure compound show a weight loss in the 140-275°C temperature range, representing a 100 % loss of the compound. The curves corresponding to the montmorillonite-pirimicarb complexes showed, apart from the weight losses due to dehydration and dehydroxylation of the clay, a further two losses in the 170-300°C and 440-600°C range. The X-ray diffraction diagrams of the samples removed from the oven after each of the losses show that after the first loss destruction of the compound must take place, with the observation of d_{001} basal spacings ranging between 12.27 Å and 12.62 Å, according to the case. The I.R. spectra point to the disappearance of the stretching band corresponding to the carbonyl group of pirimicarb (1710 cm^{-1}) whereas those corresponding to the pyrimidine ring persist ($1525, 1450, 1380$ and 1335 cm^{-1}). After the second loss, the diagrams of the samples all show the same spacing, 11.97 Å, and the I.R. spectra do not show any absorption band of the organic compound.

In the curve corresponding to the Cu-montmorillonite complex, the first weight loss takes place in two steps in the 170-235°C and 235-320°C temperature range which must correspond to the decomposition of pirimicarb molecules more or less energetically adsorbed by montmorillonite by ion-dipole or coordination mechanisms.

The TG curves of the artificial samples are practically identical to those of the complexes. According to the results of the X-ray diffraction study it was observed that after melting the organic compound (105°C) the formation of the interlayer complex in the melted phase takes place, the later decomposition phase being similar to that of the complexes.

According to these results the molecules of free and adsorbed pirimicarb or pirimicarb mixed with the clay are broken at 170-300°C, giving rise to volatile products. These are given off during the heating of free pirimicarb, whereas they are partially retained by the clay in the case of the complexes or mixtures.

In the DTA and DSC curves of the pure compound it is possible to observe two endothermal effects, one relating to melting (105°C) and the other corresponding to pyrolysis of the compound. The curves of the complexes and the artificial mixtures show two endothermal effects corresponding to the weight losses recorded in the TG curves. With the DSC technique it was possible to determine the enthalpies of the pyrolysis process, taking into account the pirimicarb content in each of the complexes as calculated from the TG curves. The highest enthalpy value was observed for pirimicarb in the free state.

The enthalpy values show that the bonding energy of the molecules in crystalline state is greater than when the molecules are adsorbed by the clay. It may also be observed that a certain relationship exists between the enthalpy values and the polarizing power of the interlayer cation of the silicate.

SANCHEZ-CAMAZANO, M. and SANCHEZ-MARTIN, M.J. 1986. Aspects of the adsorption of pirimicarb by smectites and soils. Z. Pflanzennaehr. Bodenkd. (In press).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

TIME-DEPENDENT RHEOLOGICAL BEHAVIOUR OF SEPIOLITE
SUSPENSIONS¹

J. SANTAREN, R. PEREZ-CASTELLS and A. ALVAREZ

Research and Development Department, Tolsa S.A.
P.O. Box 38.017, 28080 Madrid (SPAIN).

The rheological behaviour of aqueous suspensions of three sepiolite-based products obtained by different milling processes has been studied. The products studied were a dry ground sepiolite (DG sepiolite), a wet ground sepiolite (WG sepiolite) and a wet micronized sepiolite (WM sepiolite) whose particle size obtained by wet screening are: $D(80\%)=37 \mu\text{m}$, $D(90\%)=44 \mu\text{m}$ and $D(90\%)=5 \mu\text{m}$.

The viscosity measurements were carried out in a Brookfield RVT viscometer and a Haake Rotovisco RV-100.

The aqueous suspensions were prepared in a Silverson mixer at 4000 rpm for 10 minutes.

Because of the different viscosities that can be obtained with these products, different concentrations in water were used. WM-sepiolite suspensions were prepared at 6% of solid concentration meanwhile the WG-sepiolite and DG-sepiolite suspensions were prepared at 9% and 17% respectively. Once prepared, the suspensions were allowed to stand overnight before measuring the time-dependent rheological behaviour. This behaviour was determined using a Brookfield RVT Viscometer, taking readings at regular intervals for 1 hour while the spindle of the viscometer is rotating at 5 rpm. The plot of shear stress vs. time in a Haake Rotovisco RV-100 was also recorded at two different shear rates: 45.1 and 360.8 s^{-1} .

The results show that the time dependent rheological behaviour of sepiolite suspensions depends on the previous processing of the sepiolite as well as the shear rate at which the behaviour is studied. Thus, the suspensions of WM-sepiolite are thixotropic in the measuring conditions of the Brookfield and Haake RV-100 viscometer (see Table I and II).

The flow behaviour of the WM-sepiolite suspensions is different depending on the shear rate. When it is measured in the Brookfield viscometer at 5 rpm the behaviour is thixotropic, however when it is measured in the Haake the suspension shows a time independent behaviour at 45.1 s^{-1} and a rheopectic behaviour at 360.8 s^{-1} .

DG-sepiolite suspensions are thixotropic when measured in Brookfield viscometer at 5 rpm and Haake RV-100 at 44 s^{-1} , though in this case the viscosity is slightly recovered after shearing for 20 minutes. When this suspensions is sheared at 110 s^{-1} the viscosity decreases initially but after 4 minutes the behaviour becomes rheopectic.

The different rheological behaviours can be explained as the result of the equilibrium between the effect of the breakdown and building of structure produced by the shear rate. If the breakdown effect prevails the suspension is thixotropic and if the building effect dominate the suspension is rheopectic.

The needle-like particles of the sepiolite clay mineral occur as agglomerates forming large bundles of fibres. The production process of WM-sepiolite produces an extensive disentanglement of the needle-like particles initially forming bundles giving rise to a large number of fibers that can form a randomly intermeshed network

when WM-sepiolite is dispersed in water. When this suspension is sheared the structure is broken down, the fibers are oriented in the sense of flow and the viscosity decreases.

On the contrary during the production of WG-sepiolite by grinding with a small amount of water, the particles are less disentangled than in the case of WM-sepiolite giving rise to suspensions with less viscosity. When these suspensions are subjected to shear the behaviour depends on the shear rate. At low shear rate the behaviour is thixotropic because the breakdown effect prevails, however when the shear increases it is possible to disentangle particles that are forming the bundles increasing the number of individual particles that can be incorporated to the structure as well as the viscosity and the behaviour becoming rheopectic.

In the case of DG-sepiolite, produced by grinding in dry conditions that breaks the bundles into smaller bundles, there is a similar effect. However since this product has not been subjected to any special process of disentanglement of the needle-like particles, it is necessary to supply more energy by increasing the shear rate or the time of shearing in order to disperse the fibers. Thus, at 44 s^{-1} there is a thixotropic behaviour initially but after 20 minutes an increase in viscosity is observed which can be attributed to the dispersion of the fiber after the initial breakdown of the structure.

When the shear rate increases the thixotropic effect decreases and the rheopectic behaviour appears after only 4 minutes. That is the dispersion of the bundles is more effective and the building up of structure produced by the new individual particles balance the breakdown of structure and overcome it, as a rheopectic behaviour

appears.

PRODUCT	BROOKFIELD VISCOSITY AT 5 rpm (poise) after						
	0.5min	1min	5min	15min	30min	45min	60min
WM sepiolite ⁽¹⁾	284	272	218	178	158	154	150
WG sepiolite ⁽²⁾	312	292	216	184	168	160	156
DG sepiolite ⁽³⁾	750	690	450	420	495	520	500

TABLE I. Brookfield viscosity of sepiolite suspensions as a function of time under a constant rate of 5 rpm.

PRODUCT	SHEAR RATE (s ⁻¹)	VISCOSITY (mPaS) after						
		0.5min	1min	5min	15min	30min	45min	60min
WM sepiolite ⁽¹⁾	45.1	1165	1140	1090	1014	952	927	902
	360.8	250	243	227	213	205	200	197
WG sepiolite ⁽²⁾	45.1	1127	1127	1127	1127	1127	1127	1127
	360.8	178	179	183	193	200	203	203
DG sepiolite ⁽³⁾	44.0	2963	2704	2186	1852	1852	1889	1926
	110	1274	1185	1111	1141	1208	1267	1319

TABLE II. Viscosity measured in a Rotovisco RV-100 of sepiolite suspensions as a function of time under constant shear rate.

- (1) Suspension at 6% in water
- (2) Suspension at 9% in water
- (3) Suspension at 17% in water



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

NOTES ON THE CRYSTALLINITY OF KAOLINITES OF CAMBRO-ORDOVICIAN TONSTEINS IN THE CANTABRIAN MTS. (NW SPAIN).

A. SANZ, M.J. GARCIA AGRAMUNT, J. BASTIDA, C. ARAMBURU*,
& J.M. AMIGO.

U. Cristalografía y Mineralogía; Dep. Geología. Universidad de Valencia (España).

* U. Estratigrafía; Dep. Geología. Universidad de Oviedo (España).

Kaolins from two cambro-ordovician tonsteins in the Barrios Fm. - Armorican Quartzite of the Cantabrian Mountains (Asturias-León, NW Spain) are studied in the present work. Tonsteins are assumed to constitute "in situ" diagenetically-altered volcanic ash fall tuffs (ARAMBURU & GARCIA RAMOS, 1983; GARCIA RAMOS et al., 1984).

The kaolins have been studied under the microscope and by S.E.M. Two varieties have been recognized: "coarse grained" and "fine grained" kaolin.

Quartz and kaolinite contents have been obtained by the CHUNG (1974) method.

X-ray diffraction patterns with high goniometer speed ($1^\circ 2\theta/\text{mn}$) recording the 001 and 002 reflections and the 0211 bidimensional band have been performed. The 001 and 002 reflections have also been studied in X-ray diffraction patterns of oriented powder aggregates with low goniometer speed ($1/10^\circ 2\theta/\text{mn}$).

A first estimation of the crystallinity has been obtained by comparing the high speed patterns with classifications given in the bibliography. The low speed X-ray patterns have been used to calculate the crystallite size by the WILLIAMSON & HALL (1953) method. The results obtained by this way have been compared with those of the program SIZE (suministrated by SIEMENS with the DIFRAC 310 equipment).

Likewise, the extent of hydrazine intercalation between the kaolinite layers has been compared by the TCHOUBAR et al. (1982) index.

A good correlation between the WILLIAMSON & HALL (1953) treatment and the program SIZE, and between crystallinity as it is observed in the powder pattern, crystallite size in the 001 direction and the extent of the hydrazine intercalation reaction has been observed.

Usually, fine grained facies show lower quartz content and lower half maximum breadth of the 001 X-ray reflection of the kaolinite, which is related to high crystallinity gradation, than the coarse grained facies.

BIBLIOGRAPHY

ARAMBURU, C. and GARCIA RAMOS, J.C. (1984). 5th European Regional Meeting of Sedimentol., I.A.S., Abs., 30-31, Marseille, 1984.

GARCIA RAMOS, J.C.; ARAMBURU, C. and BRIME, C. (1984). Tra bajos de Geología, 14, 27-33.

WILLIAMSON, G.K. and HALL, W.H. (1953). Acta Metallurgica, 2, 245-251.

CHUNG, F. (1974). J. App. Cryst. 7, 519-525.

TCHOUBAR, C. et al. (1982). Bull. Minéral. 105, 477-491.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GOETHITE AND HEMATITE FORMATION IN THE PRESENCE OF CLAY
MINERALS AT 25° C

U. SCHWERTMANN

Lehrstuhl für Bodenkunde, Technische Universität München, 8050 Freising-Weihenstephan, F.R.G.

In soils and sediments iron oxides usually form in the immediate vicinity of clay and other minerals. The minerals may have an effect on the rate of formation, the type of Fe oxide minerals, their crystallinity and their Al-for-Fe substitution. Possible modes of interactions are epitaxial crystal growth and supply of Si and Al into the soil solution from which the oxides form, thereby inhibiting or retarding crystal growth, lowering crystal order or inducing Al substitution.

To simulate natural conditions as much as possible a long-term experiment was conducted. A freshly precipitated ferrihydrite ($\text{Fe}(\text{NO}_3)_3 + \text{NH}_3$) was stored at pH 5.0 and 25°C in the presence of 200 mg clay mineral per 10 mmole of Fe. The following clay minerals were used: smectite < 0.2 μm (Houston clay, Black Belt Experiment Station, Mississippi); illite < 0.2 μm (Fithian); kaolinite (400 mg) < 2 μm (Rosenthal, Germany); smectitic soil clay < 0.2 μm (soil from a tuffaceous basalt, Daun, Eifel, Germany); allophane (crude sample, New Zealand); and a synthetic gibbsite. Two more samples, one without

any addition (control), and one with an amount of soluble Al equivalent to 200 mg Al(OH)₃ coprecipitated from Al(NO₃)₃ with ferrihydrite, were used for comparison.

After 8.4 years at 25°C under water, ferrihydrite was almost completely converted into a mixture of goethite and hematite. In contrast, the presence of various clay minerals retarded the transformation (kaolinite, illite, smectite, gibbsite) or even blocked it (soil smectite, allophane, soluble Al). The transformation rate was inversely related to the Si concentration in solution. The clay minerals served as source of Al incorporated into the goethite and hematite structure. Further effects of clay minerals were lower mean crystallite dimensions of both oxides and a higher hematite to goethite ratio. Similar effects were observed for coexisting goethite and hematite in soils.

THE EVOLUTION AND DISTRIBUTION OF THE CLAY MINERALS IN THE N.E. SECTOR OF THE BAZA BASIN. (BETIC CORDILLERA, GRANADA, S. SPAIN).

E.M. SEBASTIAN^(1,2) AND F.J. SORIA⁽³⁾.

(1,2) Dpto. de Mineralogía y Petrología. Universidad. Instituto Andaluz de Geología Mediterránea C.S.I.C. Granada. Spain.

(3) Dpto. de Estratigrafía y Paleontología, Universidad de Granada. Spain.

INTRODUCTION AND STRATIGRAPHIC DATA.

The Guadix-Baza depression constitutes the best example of a mountainous-zone basin in the central sector of the Betic Cordillera. The basin is situated at the convergence of the so-called Internal and External Zones of this Cordillera and the materials which fill it are Neogene-Quaternary.

In the NE sector of the depression (the Orce Sector) the outcrops are of detrital material from the Guadix Formation (von Drasche, 1879), together with evaporitic-rich marls and limestones from the Baza Formation (Vera, 1970), these latter materials predominating (cf. Fig. 1)

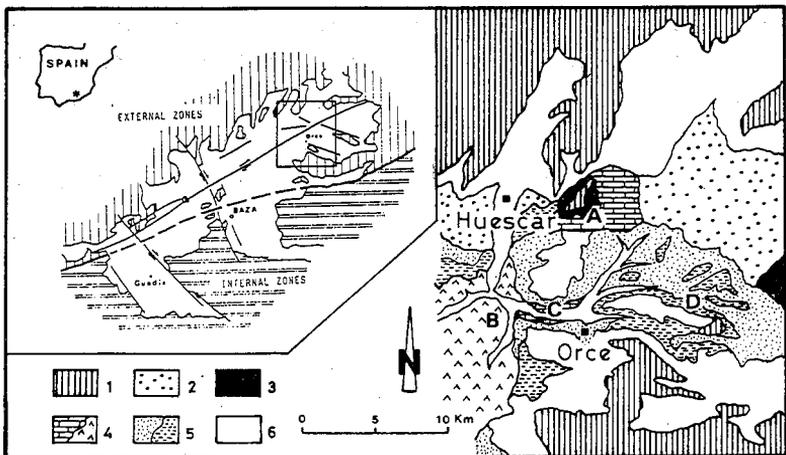


Figure 1. Distribution of the stratigraphic units within the sector studied and the location of the sequences sampled: A. Huescar sequence; B. Galera sequence; C. Cortijo Vista Alegre sequence; and D. Venta Micena sequence. (1. Calcareous sustratum; 2. Guadix Formation; 3. Lower Unit; 4. Second Unit; 5. Third Unit; 6. Recent Terrains).

A general stratigraphic column of the Orce Sector shows a succession of 4 units lying unconformably upon each other.

The bottom unit is made up of tenuously-cemented, alluvial-fan conglomerates and sands. The second unit (Pliocene) consists of marls with lignite and micrites containing gastropods, which, towards the centre of the basin, change laterally to marls and dolomites with a high gypsum content. These materials would appear to have been deposited, within the broad context of the basin as a whole, in a swamp-to-lacustrine environment. The third unit (lower-mid-Pleistocene) begins with sandy and red-limestone fluvial deposits, changing gradually upwards to calcilutites, marls and palustrine limestones with frequent emergent episodes, where numerous vertebrate deposits are to be found. The top unit, or expansive terminal unit, (upper-Pleistocene), lies unconformably on an erosion surface and is characteristic of a progradation, imposing fluvial and coastal terms on top of the lacustrine ones.

The presence of detrital metamorphic rocks within the conglomerates of this unit, deriving from an area considerably to the South, is especially significant.

MINERALOGY

The materials sampled contain quartz, calcite, dolomite, gypsum and clay minerals in varying proportions from one unit to the next, although calcite is almost always abundant. The dolomite and gypsum are always closely related, gypsum being the second most important mineral wherever dolomite is the predominate carbonate.

The clay minerals present are: illite, smectite, chlorite, kaolinite, paragonite, palygorskite and sepiolite. The appearance of this last clay mineral is especially interesting as it is the first time it has been recorded in the Guadix-Baza basin. The vertical distribution of the clay minerals shows a repetition of the mineralogical and geochemical sequence of the type proposed by Huertas et al. (1970) for sedimentary endorreical basin. Thus, in the upper Miocene, bottom unit the sequence begins with detrital depositions of illite, chlorite, kaolinite and very scarce quantities of smectite. Moving upwards the smectites become the predominant phyllosilicate, followed by the palygorskite and finally the sepiolite.

This same sequence is then repeated from the mid-pliocene to the mid-Pleistocene materials at the top of the fourth unit.

This mineralogical distribution leads to certain conclusions concerning the palaeoclimates involved in the sedimentation processes. Both cycles appear to have begun in a relatively wet, cool regime which gradually became warmer, although high rainfall persisted.

The average temperatures continued to rise and the precipitation levels diminished until the final stages of sedimentation occurred in isolated, alkaline basins. Sepiolite was formed and stabilised under $\text{pH} \sim 8$ and low-to-absent Al^{3+} conditions. There appears to have been no appreciable tectonic activity at this time.

The paragonite is found only in the Pleistocene samples and would seem to have been transported to this area from the emerged metamorphic relief of the Internal Zone to the South (cf. Fig.1). The presence of this mineral in Huescar and Venta Micena still poses some problems, however, as these two sites are a considerable distance from the source rocks and also very close to reliefs made

up entirely of sedimentary materials, which, in the case of Venta Micena at least, would have acted ~~as a barrier against~~ detritus coming from the southern massifs (cf. Fig. 1). Furthermore, the fluvial systems running from the North and East would have to have been very weak, or absent altogether, if they were not to impede the force of the currents arriving from the South and thus to allow the paragonite to be transported all the way to Huescar and Venta Micena within the lacustrine system. It may well be that this redistribution of paragonite was related to tectonic pulsations that periodically rejuvenated the southern metamorphic relief. This hypothesis would also explain the absence of paragonite in the lower two units, although it might also be argued that this is due to the existence of several lakes in the basin rather than a single, interconnected lacustrine system, as the presence of paragonite in sediments of this age has been recorded somewhat further to the South around Baza and Benamaurel (Sebastian et al., 1980).

REFERENCES

- Huertas, F.; Linares, J. and Martín Vivaldi, J.L. (1970). R. Hispano Belga Min. Arcilla. Madrid, 211-214.
- Sebastián, E.M.; Rodríguez Gallego, M. and López Aguayo, F. (1980). Est. Geol., 36, 289-299.
- Vera, J.A. (1970). Bol. I.G.M.E., T:LXXXI-V, 429-462.
- Von Drasche, R. (1879). Bol. Com. Mapa Geol. España, VI, 353-388.

(This research forms part of the "Análisis sedimentológico, mineralógico y evolución tecto-sedimentaria de las Depresiones Béticas Orientales" projet. C.S.I.C.-C.A.I.C.Y.T.).



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF SWEDISH KAOLINS

N.A. SHAIKH

Geological Survey of Sweden, Box 670, S-751 28 Uppsala (Sweden)

In Sweden the products of the kaolinite weathering crust are wide spread in the province of Scania, south Sweden. The residual kaolins as well as their redeposition products have been and still are of considerable economic interest. Economic utilization of kaolin in Sweden started around 1860. Since then, kaolin has been used for different purposes. Latest exploited deposit is Näsåm near Bromölla, where kaolin was extracted for refractory products. Prospecting for high quality kaolin and systematic sampling started by the Geological Survey of Sweden in 1976 and from 1978 financed by the State Mining Property Commission, has revealed a number of new deposits in Scania. These investigations have provided extensive geological and mineralogical data, which together with that from Finland, will significantly advance our knowledge regarding "formation of the weathering crust" in the Baltic Shield area.

PARENT ROCKS

Various Precambrian rocks of the crystalline complexes of the Shield were subjected to kaolinization and the mineral composition of the kaolins reflects often the composition and structure of the parent rock. The kaolinized parent rocks of major deposits in Scania are: various kinds of gneisses, granite-gneisses and metavolcanites. Gneisses are by far the most important kaolin parent rock. In unweathered conditions, these rocks vary in colour from grey to reddish grey, are rather inhomogeneous and generally fine - medium-grained in texture. Main mineral constituents are: plagioclase 23-43%, quartz 20-27%, K-feldspar 21-53%, hornblende 8%, biotite 4% and some opaques. Depending upon varying conditions, the weathering profiles have different thicknesses and maturity. The kaolin deposits in the north-

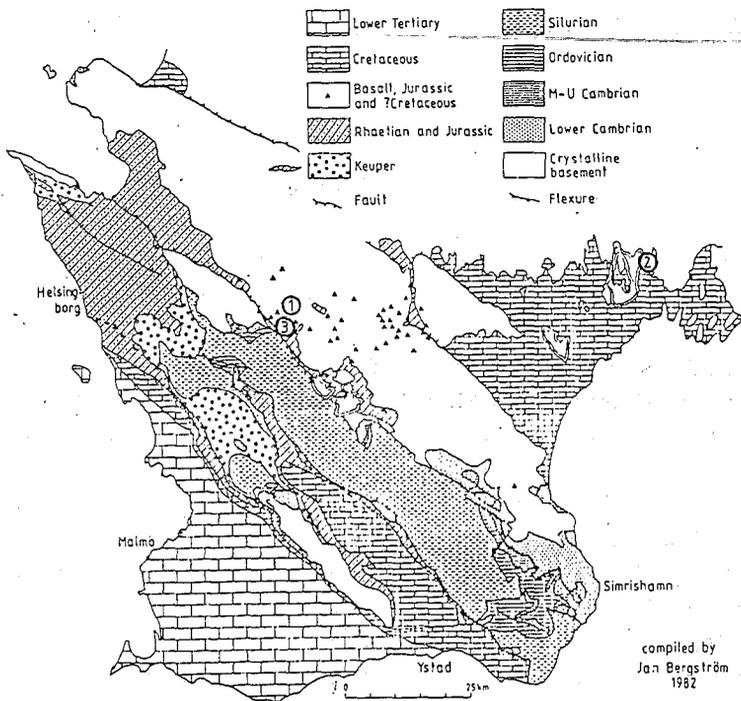


Fig. 1. Simplified bedrock map of Scania with location of the described kaolin deposit. ① Annarp (veined gneiss); ② Klagstorp (metavolcanite); ③ Billinge (granite-gneiss).

eastern part of Scania are often overlain by upper Cretaceous sediments; those in central Scania by sandstones of Lower Jurassic age. A systematic investigation of the various occurrences is far from complete however, the best type being derived from granite-gneiss with little or no biotite. The Billinge deposit is an example of the general kaolinization of such type of granite-gneiss. It has the following modal composition: quartz 30%, K-feldspar 45, plagioclase 15, biotite, chlorite 2-5%, hornblende 1-2%, and small amounts of epidote, apatite, sphene, zircon, garnet and opaques. The granite-gneiss at Billinge is rather homogeneous, foliated and generally fine-grained in texture.

The deposits of kaolinized metavolcanites occur in the northeastern part of Scania. These rocks are acid to intermediate in their composition and are often fine-grained. Main mineral constituents are: plagioclase 23-31%, K-feldspar 25-31%, quartz 20-28%, biotite 6-20%, muscovite 5% and opaques 1%.

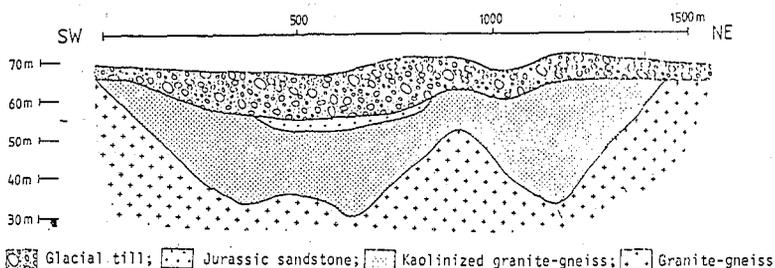


Fig. 2. Cross-section through the Billinge deposit (Shaikh, Wik 1987).

Kaolin deposits are explored by geophysical measurements and core-drillings. Investigations on drill-cores show regular vertical zoning — decreasing intensity of kaolinization downwards. Many deposits are of large extent.

The sequence of the weathering crust composed of kaolin has a thickness up to about 50 m. Generally, its thickness fluctuates within the limit of 10-30 m.

MINERAL AND CHEMICAL COMPOSITION

Mineralogy of the altered rocks is very variable in dependence on the composition of the original rocks and of local genetic conditions. Depending on the degree of alternation, the content of kaolinite as well as other minerals in the rock vary in wide range. Kaolinite content varies from below 10% in poorly kaolinized rock, to 65% in strongly kaolinized rock. Kaolinite is generally not well crystallized.

Table 1. Chemical composition of parent rocks and washed kaolins (<0.025 mm).

	Veined gneiss	Washed kaolin	Meta- volcanite	Washed kaolin	Granite- gneiss	Washed kaolin
SiO ₂	75.8	46.3	75.9	48.5	78.2	47.5
TiO ₂	0.31	1.40	0.25	0.07	0.12	0.47
Al ₂ O ₃	13.3	34.7	13.7	34.7	12.0	36.3
Fe ₂ O ₃	1.3	2.3	1.49	1.0	0.67	0.90
MnO	0.02	0.20	0.08	0.01	0.05	0.03
CaO	0.2	0.3	0.1	0.3	1.2	0.11
MgO	0.15	0.37	0.47	0.47	0.06	0.21
Na ₂ O	3.1	< 0.1	0.26	< 0.1	3.3	< 0.2
K ₂ O	6.1	1.1	7.1	1.6	4.8	1.66
H ₂ O ⁺	0.60	11.7	1.3	10.9	0.40	11.8
H ₂ O ⁻	0.30	0.9	0.40	2.4	0.20	0.5
CO ₂	0.10	0.3	0.10	< 0.1	-	0.2
BaO	0.11	0.02	< 0.01	0.01	-	< 0.02
Total	101.39	99.59	101.15	99.96	101.00	99.68

Modal composition (%)

Kaolinite	79	69	81
Illite	10	10	10
Berthierine	3	-	-
Smectite	-	15	-
Quartz	2	2	1
K-feldspar	2	3	6
Carbonate	0.7	-	0.5
Anatase	1.4	0.1	0.5
Others	2	1	1

CONCLUSIONS

The characteristics of the primary kaolins of Sweden are illustrated by description of three typical occurrences. Different Precambrian rocks of the crystalline complexes of the Baltic Shield have given rise to these kaolin deposits in the province of Scania, south Sweden. Earlier it was thought that only insignificant relics of kaolinic profiles are left after denudation. Recent investigations show that vast deposits have been preserved. The best known are those from central Scania. It is generally assumed that surface weathering played the dominant role in the genesis of these kaolins. The results can be summarized as follows:

Various rock types of Precambrian age are kaolinized.

The kaolinization probably took a continual course.

Large extent of deposits with considerable depth.

Regular vertical zoning - decreasing intensity of kaolinization downwards.

The weathered rocks show clearly the original structure of the parent rock.

Kaolins in central Scania are often overlain by the lower Jurassic sandstone and those in the northeastern part by the upper Cretaceous sediments.

Kaolinite is the dominant mineral in washed kaolins - generally not well crystallized.

Titanium in kaolin is fixed in the structure of anatase.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE ADSORPTION OF AMINES BY SEPIOLITE AND Palygorskite

U. SHUALI*, M. STEINBERG*, S. YARIV*, M. MULLER-VONMOOS**, G. KAHR**
AND A. RUB**

*Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.

**Institute of Foundation Engineering and Soil Mechanics, Federal Institute of Technology, Zurich, Switzerland.

Sepiolite and palygorskite are closely related clay minerals. They both have acidic sites and defined porous structures, which are essential properties for controlling constitution and distribution of products in acid catalyzed reactions. The adsorption and acidic properties of these two clay minerals were studied by exposing them to the amines n-butylamine, pyridine and 2,4,6-trimethylpyridine, representing bases with different pK_a values. The three molecules have different effective diameters and shapes, properties which may be used for the study of steric properties on the adsorption capacity of the minerals. The following amounts of butylamine, pyridine and trimethylpyridine respectively, were adsorbed from the gaseous phase: 115, 98 and 64 m mole amine per 100 g sepiolite, and 62, 42 and 29 m mole amine per 100 g palygorskite.

The organo-clay adducts were studied by IR spectroscopy, both subsequent to adsorption and after thermal treatments of the samples at various temperatures. Simultaneous DTA and TG on the solids with mass spectrometry of the evolved gases were carried out. Based on the characteristic exothermic peaks and the mass spectrometry thermal curves it is proposed that the three amines were adsorbed into the tunnels of both minerals.

The present results showed that the adsorption of the amines is affected by their basic strengths. Butylamine, the strongest of the three bases, gives the most stable clay complexes. Tri-methyl pyridine is a stronger base as compared to Pyridine, however due to its higher affective diameter its adsorption is smaller.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

"MONTMORILLONITE AS A CATALYST IN BIOCHEMICAL REACTIONS"

B. SIFFERT AND A. NAIDJA

Centre de Recherches sur la Physico-Chimie des Surfaces
Solides, 24, Avenue du Président Kennedy - 68200 MULHOUSE
FRANCE.

In order to study and to elucidate the catalytic activity of clays in biochemical reactions, we examined two reactions occurring during the Krebs' cycle (Weil, 1975).

- Decarboxylation of oxaloacetic acid into pyruvic acid and carbon dioxide in the presence of montmorillonite saturated with different cations (Na^+ , Cu^{2+} , Mn^{2+}) and in the presence of the same cations but in their free state (non incorporated). The catalytic effect depends on the nature of the exchangeable cation, i.e., its easiness to form chelate complexes with oxaloacetic acid. The clay mineral structure plays an important role in the formation and/or the decomposition of these complexes. Apparently, it contributes to the decomposition of $\text{Me}(\text{C}_4\text{H}_5\text{O}_5)$ by an electron transfer. In that way, the clay acts as a metalloenzyme. Activation energy computations for the different systems illustrate the influence of the clay structure in this catalytic process. The contribution to the activation energy is maximum with Na^+ -montmorillonite for which not any complex can be formed and is minimum with Cu^{2+} -montmorillonite. In the presence of montmorillonite, the reaction yield was high up to 60°C . At 60°C the activity of the specific enzyme (decarboxylase) is zero since the enzyme is practically destroyed.

- Deamination of l-glutamic acid into α -cetoglutaric acid in the presence of the l-glutamate deshydrogenase enzyme and Nicotinamide Adenine Dinucleotide (NAD) co-enzyme on the one hand, and in the presence of montmorillonite saturated with different cations and NAD, on the other hand. At room temperature, the rate of NH_3 formation was considerably reduced when replacing the enzyme with the clay. The same result was observed for the reaction yield. The best results were obtained with montmorillonite saturated with manganese cation which presents the highest complexation constant with glutamic acid. The role of the NAD co-enzyme, in the presence of clay, is so far only poorly understood. It seems to exhibit no effect on the deamination reaction in the presence of Na^+ and Mn^{2+} -montmorillonite. However, it activates the reaction in the presence of Cu^{2+} -montmorillonite. When Na^+ , Cu^{2+} and Mn^{2+} were present as dissolved salts, the reaction did not proceed in the absence of the NAD co-enzyme. When associated with NAD, their activity remained however very low, confirming the hypothesis of a co-enzyme protection by the clay structure. In that case, the aluminosilicate structure could work as an apo-enzyme and could play the role of the proteic part of the normal enzyme.

REFERENCE :

WEIL J.H. (1975) Biochimie Générale, Ed. Masson and Co.,
2e édition, PARIS.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS AND MINERALOGY OF THE RIO CALLEJON KAOLIN DEPOSIT
/CUBA/

J. ŠINDELÁŘ

Geoindustria, U průhonu 32, Prague 7 /Czechoslovakia/

The largest kaolin deposit of Cuba occurs in the northern part of the Isla de la Juventud island. This island in the Caribbean sea is separated from the southern coast of the province Pinar del Río by the 55 km broad strait and it is world famous for its production of marbles and grapefruits.

Geologically the island is formed by the oldest formation of Cuba called basal complex, which is probably of Jurassic age. Clayey and carbonate sediments were metamorphosed during the huge tectonic movements, which took place in the Upper Cretaceous and Lower Tertiary /Laramic phase/, into mica schists, disthene gneisses or other metamorphites with different stage of metamorphism. The age of these rocks is about 190 millions years /according to the argon method/. Acidic granites in the form of small massifs with numerous apophyses and veins intruded to this metamorphosed mantle. The age of granite rocks was determined on 70 millions years /Upper Cretaceous/.

The upper parts of metamorphites and granites were more or less kaolinized. The processes of kaolinization have been developed from the Paleogene to the recent time in the condition of underground water. It is not possible to observe any zonality of weathering crust. The contents of kaolin fraction /under 20 μm / in the whole 5-20 m thickness of kaolin horizons usually varies irregularly and depend from the amounts of feldspars in the mother rocks. The boundary between the both kaolinized and underlying fresh rock is always sharp.

The kaolins of Río Callejón deposit originated by a progressive alteration and leaching of sericite schists rich of alkali feldspars and dark to black coloured due to the dispersed graphite. The graphite substance has changed in first stages of weathering processes into isotropic or weakly anisotropic particles of a mataantracite type. Four coloured varieties of kaolin inside of open-pit mine may be distinguished according to the presence of mentioned organic matter and ferruginous minerals : 1. white, 2. light-grey, 3. dark-grey, 4. variegated. These varieties differ one from another also in their mineral composition. The percentages of kaolinite, quartz, mica minerals, Fe- and Ti-minerals in four natural kaolins is given in the following table :

	kaolinite	mica	quartz	Fe-min.	Ti-min.	others
1	66	13	18	0.3	1.6	1.1
2	52	17	28	0.2	1.3	1.5
3	26	12	58	0.06	0.6	3.3
4	42	17	37	1.0	1.2	1.8

The size of kaolinite crystals oscillates in the rank of 0.05 to 3.0 μm . The kaolinite aggregates of both white and light-grey kaolins exhibit well ordered triclinic structure /according to the absorption bands due to the vibration at 3 700 cm^{-1} and 3 650 cm^{-1} in infrared spectra and according to the X-ray data as well/ meanwhile the dark kaolins contain badly ordered pseudomonoclinic kaolinite. The original sericite degraded in all kaolin varieties into dioctaedric hydrosericite to illite. The average size of irregular, subangular forms of quartz is 0.1 mm. The only mineral of titanium is represented by anatase. The principal mineral of white kaolins is pyrite, in rosaceous varieties prevail limonitic metacoloids. Goethite was determined in dark-grey kaolins. The X-ray data of some dark

coloured kaolins reveal the peaks of palygorskite and gorceixite.

All above mentioned mineralogical research served as basis to solve the problem how to decrease titanium and iron contents in studied kaolins by using electromagnetic separation and other methods.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

HORMITE DEPOSITS OF BRAZIL

PÉRSIO DE SOUZA SANTOS

Departamento de Engenharia Química - Escola Politécnica da
Universidade de São Paulo - São Paulo - SP - Brazil

Until recently, hormite clays were found in Brazil only in small occurrences without commercial value. The sediments from the Caatinga Formation and the Bauru Group, in the State of São Paulo, contain only 2-3% of palygorskite. Veins and pockets of palygorskite were found in the vesicular basalts of the State of São Paulo. Palygorskite and sepiolite were found in pockets in the bentonite deposits in Ponte Alta, State of Minas Gerais. Sepiolite in pockets was found the magnesite deposits in the State of Bahia and in the nickeliferous clays in Niquelândia, State of Goiás. Palygorskite is found in pockets or mixed with the white smectite associated to the green smectite deposits of Boa Vista, State of Paraíba.

Significant deposit of palygorskite was recently found in evaporites of the Motuca Formation in the Counties of Basa; Carolina and Riachão in the State of Maranhão.

Large deposits of palygorskite were found recently in the region of Nova Guadalupe, Piauí Formation, in the State of Piauí.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SURFACE PROPERTIES OF AN ACTIVATED BENTONITE*

E. SRASRA, F. BERGAYA and H. VAN DAMME

C.R.S.O.C.I., C.N.R.S., 1B, rue de la Férellerie, 45071 ORLEANS
CEDEX 02, FRANCE.

Clay materials are widely used to decolorize oils. The materials generally used may be crude clay (Fuller's earth) or clay which has been modified by chemical and physical treatment. Acid activation frequently enhances the decolorizing power of some smectites (montmorillonites). It is known that not all montmorillonites can be activated (1).

A tunisian bentonite (Haïdoudi-Gabès) which is a mixed-layer Na smectite (80%) and illite (20%) is activated by H_2SO_4 (2N) with increasing duration of treatment. This activated bentonite shows a high decolorizing power for vegetable oils (namely rape seed oil). Adsorption of a coloring model molecule (carotene in CCl_4) on the activated tunisian bentonite shows that a treatment of two hours is sufficient to increase the adsorption capacity by a factor of 5. Further prolonged treatment does not bring a marked improvement. We try to connect the adsorption mechanism to the surface properties of the activated clay.

- Acid activation increases the nitrogen BET surface area from 80 to 250 m^2/g after two hours.

- The total pore volume, V_p , measured by the Conway Pearce method increases also threefold after 10 h, but only twofold after two hours.

- The surface polarity is measured by the fluorescence of pyrene adsorbed on the activated bentonite ($\lambda_{exc.} = 330$ nm). The relative intensity of the vibronic components of the emission spectrum shows that the environment is highly polar, comparable to that of amorphous silica.

- Infrared spectra show that the band at 1030 cm^{-1} assigned to Si-O-Si decreases whereas the band at 1100 cm^{-1} assigned to Si-O increases.

- The CEC values (Cu-Ethylene Diamine Titration) for activated clays are dramatically reduced from 60 meq/100 g to 35, after 30 mm and to 15 meq/100 g after 15 h.

- The fractal dimension at the molecular scale of the N_2 -accessible external surfaces was estimated from the shape of the adsorption isotherms, using the theory of multilayer adsorption on fractal surfaces (2). The fractal surface dimension, D_s is close to 2.8 for the starting material ; it decreases progressively towards $D_s = 2$ after fifteen hours of activation.

All these results confirm that the activation process resulted in :

- a textural effect, related to increase of the surface and the porosity, decrease of the fractal surface dimension.
- a physico-chemical modification of the surface groups with the formation of highly acidic sites capable of linking with the carotene.

Obviously both the above consequences of the activation process are important in increasing the total quantity of the coloring matter which can be removed from the oil.

* This work is a part of the thesis of E.SRASRA (University of Tunis, 1987).

- (1) R.GRIM - Applied Clay Mineralogy, McGraw-Hill Company, Inc. New York (1962).
- (2) J.J.FRIPIAT, L.GATINEAU and H.VAN DAMME - Multilayer Physical Adsorption on Fractal Surfaces. Langmuir, 2, 562-567 (1986).



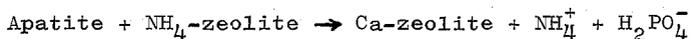
Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SMECTITIC CLAYS AS COMPONENTS OF ION-EXCHANGE FERTILIZER

J. ŚRODOK

Institute of Geological Sciences, Polish Academy of
Sciences, Senacka 3, 31-002 Kraków, /Poland/.

A slow-release phosphorus fertilizer, composed of a phosphate rock and a natural exchanger, was proposed by Lai and Eberl /1986/ as an ecologically sound alternative to highly soluble fertilizers and was successfully tested by these authors with NH_4 -zeolite clinoptilolite in the role of the exchanger. This new fertilizing system is based on the principle that exchangers can sequester ions released by the dissolution of a sparingly soluble mineral thereby leading to further dissolution of this mineral, eg:



The system must be free of more soluble Ca-minerals, such as calcite and gypsum. Most of Polish soils fulfill this condition. Zeolite is a natural first choice as an exchanger for its very high CEC. The lack of zeolite deposits in Poland forced us to test the performance of smectitic clays.

Four calcite-free clay deposits were selected for the preliminary study / a bentonite, a weathering crust on basalts, a fresh-water lake sediment, a deep sea sediment/. These rocks contained 50-80% of swelling clay / smectite or randomly interstratified illite/smectite / and their CECs were between 30 and 90 meq/100 g. Phosphate rocks from Tunisia, Poland, and Florida were used.

The release of phosphorus was tested in closed system in laboratory by shaking phosphate rock + NH_4 -exchanger + water mixtures for 48 h at 25°C, followed by colorimetric determination of P in solution. Big differences in

P release rates were observed among the phosphate rocks tested in blank experiments / without the exchangers /. NH_4 -clays, added to a phosphate rock in proportion 5:1, increased the yield of P from 3 to 6 times. The yield is positively correlated with CEC of the clay. The correlation is different for clays and for zeolites. Our best clay released more P than NH_4 -clinoptilolite under the same experimental conditions, though the CEC of the clay was about 1/2 of that of the zeolite. The increase in clay:phosphate rock ratio from 5:1 to 15:1 results in proportional increase in P yield.

The effect of alternate wetting and drying, characteristic for the topsoil, was checked in laboratory by submitting the fertilizer mixtures to 20 wetting and drying cycles at 60°C. No effect of wetting and drying was observed for phosphate rock + NH_4 -zeolite mixtures, but runs with NH_4 -clays yielded up to 3 times more P than the control runs /without drying/.

20 pot experiments were made with growing rye grass on sandy soil fertilized with mixtures of phosphate rock / 50 kg/ha / and NH_4 -zeolite or NH_4 -clay / 0-500 kg/ha /. Fertilizing with the phosphate rock without the exchanger did not affect the yield of crop. The presence of the exchangers gave up to 70% increase in the yield of crop, correlated with the dose of the exchanger. Differences in yield between the zeolite and the clay system were small: below 350 kg/ha the zeolite performed better, above this value the clay yielded higher crops.

REFERENCE

Lai T-M. and Eberl D. D. /1986/ Controlled and renewable release of phosphorus in soils from mixtures of phosphate rock and NH_4 -exchanged clinoptilolite. Zeolites 6, 129-132



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PROBLEM OF PARTICLE THICKNESS IN SOIL MECHANICS

EWA T. STEPKOVSKA

Instytut Budownictwa Wodnego PAN, 80-953 Gdansk, POLAND

Results of mechanical processes in the clay-water system are measured in Soil Mechanics in macroscale, i.e. in m or cm. These values are resultants of minute deformations, occurring between particles or structural elements and being of the order of nm or μm . These minute deformations depend on arrangement of structural elements (particles, clusters, aggregates or flocs) and on forces between them, which are known functions of crystal structure, of their size and of distances between them, $2d$. Long range forces, expressed as pressures are: P_R - diffuse layer repulsion and P_A - van der Waals attraction, and they may be calculated from known formulae.

Also physical properties of clays are dependent on their crystal structure and are interrelated: CEC, water sorption, WS, content of fraction less than $2 \mu\text{m}$ are proportional to particle specific surface, S . Physico-mechanical properties of clays, such as Atterberg limits, angle of internal friction, angle of shearing resistance, cohesion component, swelling depend as well on S and on particle thickness, δ , which is inversely proportional to S .

Particle collapse, i.e. increase in particle thickness, may occur in a clay during drying. This process is reversible and in water vapour particle delaminate again, possibly to the δ -value before drying. The decrease in δ during water sorption may be interpreted in terms of action of water molecules in gaseous state (where action, H , is energy multiplied by time) and this delamination is dependent on temperature, thus on kinetic energy, on time t and on pressure, p , which is a space density of energy, E , at constant entropy S : $p = -(dE/dv)_S$. Also $E = dH/dt$.

Particles delaminate at a high water content (clay suspensions, clay pastes) after a prolonged storage. Change in particle thickness was also observed in certain mechanical processes. If such a change occurs at constant water content, distances between structural

elements change as well and so do interactions P_R and P_A and also strength of the system: water is evenly distributed between parallel faces of clay particles, $W_d = d S \rho$. Here $\rho = 1 \text{ g/cm}^3$ is the density of water and the remaining values may be estimated from WS test.

If a clay of low water content may attract water from the environment, a pronounced increase in volume may occur (clay swelling) which may have following reasons: (1) diffuse layer repulsion which action is analogous to osmotic pressure, (2) particle delamination which results in increased swelling, proportional to the increase in specific surface, (3) reorientation in rebound of rigid clay particles (kaolinite) due to attraction between positive particle edges and negative particle faces.

Shear strength, i.e. maximum shear stress, τ_r , at the given normal stress, δ_n , is in cohesive soils (clays) usually described by Coulomb equation as a sum of cohesion component, c , and friction component which is proportional to δ_n :

$$\tau_r = c + \delta_n \operatorname{tg} \theta = c' + (\delta_n - u) \operatorname{tg} \theta' = c' + \delta_n' \operatorname{tg} \theta'$$

Here $\operatorname{tg} \theta = \mu$ is coefficient of internal friction, θ is the angle of internal friction, δ is total stress, δ' is effective stress and u is the pore water pressure.

At a high water content exceeding plastic limit, W_p , thus at high interparticle distances ($d > \text{ca. } 3 \text{ nm}$) when repulsion prevails, its value is equal to the cohesion component and it is responsible for shear strength (compression).

At a low water content ($d < \text{ca. } 3 \text{ nm}$) repulsion may equal attraction between clusters and the measured strength may be equal to calculated p_A (tension).

This is explained by the first law of thermodynamics: The internal energy when decreasing (repulsion energy in tension, $dd > 0$, or attraction energy in compression, $dd < 0$) dissipates either as heat or transforms into any other kind of energy, e.g. energy necessary for particle delamination, (or particle collapse), which contributes to the frictional component.

Increase in specific surface thus particle delamination was measured along with the increase in shear strength (shear stress) at higher δ_n , i.e. at higher frictional component. $\Delta \tau_r$ accompanying the

delamination of an average clay particle by one unit layer (u.l.) depends on the clay mineral present (τ_0) and on the initial particle thickness. In Grimmen clay this value was 25 kPa if $\delta >$ ca. 17 u.l. and it was 110 kPa if $\delta <$ ca. 17 u.l. In Kuzmice bentonite the average estimated value was 132 kPa for $\delta = 8-11$ u.l. $\Delta \tau$ is thus a measure of activation energy of delamination process which indicates the probability of this process.

Particle delamination depends as well on particle arrangement (microstructure) in parallel, cluster, aggregate or floc structure. δ as measured by WS was different in powder sample and in oriented sample (dispersed by NaOH addition and dried on a glass slide). Also particle delamination in compression process was dependent on orientation of particle edges to the pressure applied.

This indicates the great importance of microstructure and of particle thickness in interpretation of mechanical phenomena in clays.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

DIAGENETIC KAOLINITE IN SANDSTONES, ITS FORMATION,
PROPERTIES AND INDUSTRIAL APPLICATION

L. STOCH, Z. STOCH*

Academy of Mining and Metallurgy, 30-059 Cracow (Poland)

*Institute of Glass and Ceramics, 30-702 Cracow (Poland)

In sandy sediments the pores and interstitial spaces filled with water solutions represent a particular environment favouring the neoformation of minerals e.a. kaolinites. They are formed mainly in fresh-water deposits infiltrated by atmospheric or underground water in the early stages of the diagenesis (eogenesis). As a result of postsedimentary kaolinization of arkoses deposits of kaolins of commercial value were formed. Both kaolinite and dickite were formed also in marine sediments buried at the stage of mesogenesis. The formation of authigenic minerals under these conditions has been the subject of several studies.

The subject of the present paper is the formation of kaolinite in the sandy fresh-water sediments during diagenesis and their comparison with kaolinite formed in the surficial weathering of granite and gneiss, the same rocks which constituted the original material for the formation of the sandy deposits. The data have been supplied by the investigations of clay minerals of the matrix of the Cretaceous sandstones and clays filling the old sedimentation basin (Bolesławiec Trough) of the North Sudetic Depression in Lower Silesia (Poland). They are formed by the brackish sediments of the type of sandstones interstratified with thin layers of kaolinite clays with coal sheets (Santon). Underneath there occur continental sandstones of the Coniacian. The sediments are covered with a thin layer of continental sediments of the Tertiary and Quaternary.

The examination of the mineral assemblage of the matrix of sandstones enabled to distinguish a number of repeating sedimentation cycles. Each cycle begins with a matrix made up of fine-grained poorly crystallized kaolinite and illite. They are replaced next by better and better crystallized coarse-grained kaolinite and muscovite. Here are reflected the changing fluvial rate and the type of the transported material during sedimentation. The sandstones of the Coniacian contain perfectly crystallized kaolinite with only trace quantities of muscovite. Feldspar does not occur in the sediments or occurs only in very small quantities.

Sandstones the cements of which compose of perfectly crystallized kaolinite with coarse muscovite admixtures are typical for the examined sediments. Kaolinite is developed in the form of plates of almost ideal hexagonal shape. Aggregates of plates are rare. The study of the morphology of kaolinite indicates that it crystallized from pore solutions. The components were supplied by the dissolving feldspar and fine poorly crystallized kaolinite from layers of sediments situated below. A part of kaolinite exhibiting perfect hexagonal shape of plates, formed inside the flakes of muscovite through rearrangement of its structure (intra-crystal process).

Kaolinite originated from detritical mica usually forms aggregates of a fan or vermicular shape. They are formed as a result of incongruent dissolution of mica. In the examined sediments kaolinite, which developed from mica has elevated dehydroxylation temperature corresponding to kaolinite known from Keokuk.

Simultaneous occurrence of different modifications of kaolinite has been frequently recorded and has not been explained so far. The investigations suggest that the cause were the different crystallization conditions. Fast crystallization from locally supersaturated solutions leads to the development of modification of low degree of structure order and metastable thermodynamically. Slow crystallization under stable conditions, from dilute solutions, produces

more stable varieties. The empirical Oswald's rule of degrees becomes thus realized in nature.

The cements of the Coniacian contains perfectly crystallized kaolinite plates, but no kaolinite of elevated dehydroxylation temperature has been found in it. The detritic material out of which it developed was made up of feldspar; the proportion of muscovite was small. This is confirmed by the small amounts of anatase (about 0.1 wt % of TiO_2) in the cement, against 0.5 - 0.8 wt % of TiO_2 in the cement of Santon sandstones. Muscovite is the main source of titanium in sediments. Here the effect of the primary material becomes evident.

Kaolinite forming processes proceed in permeable, porous sandstones at the diagenesis stage in a different way than in the weathering crust. This results from free displacement of substance and near equilibrium composition of interstitial solutions. A macroscopic manifestation of this difference is the lack of zonality which is typical of the weathering crust. Kaolinite has a specific crystal habit and grain size. It contains less Fe^{3+} in structure (0.2 wt % of Fe_2O_3) as compared with residual weathering kaolin (about 1 wt % of Fe_2O_3).

The richer in feldspar is the original sediment, the smaller are the differences between the residual weathering kaolins and kaolins of diagenetic origin, formed in the particular area.

Washed kaolin obtained from sandstones described here is a good filler of rubber, plastics and paper. It can be bleached by chemical methods. Kaolins from the weathering of this region are successfully applied in the ceramic industry and the production of refractory materials. The technology of their processing differs also. The sandstones of the Coniacian are also used as glass making sand of high purity.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MAGNETIC PROPERTIES OF KAOLINITE

M. STÖRR¹, D. STÖSSER², R. ROSSBERG¹

¹Department of Geological Sciences, University of Greifswald (G.D.R.), Jahnstr. 17a, Greifswald, 2200, G.D.R.

²Department of Chemical Sciences, Humboldt-University Berlin (G.D.R.), Bunsenstr. 1, Berlin, 1040, G.D.R.

Magnetic susceptibility data of kaolinite are essential, especially for the effective use of high-gradient magnetic separation, by which magnetic and coloured components are removed from industrial kaolins. But so far such data have not been available for pure kaolinite.

In our investigation magnetic susceptibility of almost pure kaolinite, dickite and halloysite was measured at room temperature and at various field strengths using a magnetic balance after GOUY. Moreover, EPR measurements were made to obtain data on the type of bonding of iron or on paramagnetic centres in the samples.

Investigated were natural as well as synthetic kaolinites, moreover natural halloysite and dickite. In order to reduce the content of free iron compounds, the samples were treated with 1 n HCl at 350 K for 1 h. The hydrothermal synthesis of almost pure kaolinites was carried out at 475 - 580 K from SiO₂-gel and Al-hydroxide (ratio 2:1) in autoclaves lined with Pt or Teflon. The reaction times varied from 2 to 16 days.

The magnetic susceptibility values we measured were as follows:

kaolinite, synthetic	-0.39·10 ⁻⁵ to -0.45·10 ⁻⁵ SI
kaolinite, natural	-0.26·10 ⁻⁵ to -0.43·10 ⁻⁵ SI
dickite	-0.21·10 ⁻⁵ to -0.42·10 ⁻⁵ SI
halloysite	-0.35·10 ⁻⁵ to -0.39·10 ⁻⁵ SI

Thus, all kaolinite minerals are weakly diamagnetic. The Fe_2O_3 -content of samples with susceptibilities $\chi < 0.3 \cdot 10^{-5}$ SI was < 0.1 %. For higher Fe_2O_3 -contents the susceptibility increases linearly, furthermore the field strength dependence of the susceptibility values increases, which is indicative of free iron compounds. These results correspond with our investigation of the magnetic properties of synthetic kaolinite (STÖRR et. al., 1986).

EPR-examinations of samples with minimal susceptibility revealed only very small quantities of free Fe- or Mn-compounds but showed a small amount of Fe^{3+} -ions in the lattice of the kaolinite, which usually displays rhombohedral distortion.

References:

SRÖRR, M., GÜNTHER, A., LORENZ, R. and ROSSBERG, R.: Zur Ermittlung der magnetischen Suszeptibilität von Kaolinit. Abstract, 10th Convergence on Clay Mineralogy and Petrology, Ostrava, Czechoslovakia, August 26 - 29, 1986



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FIRST STEPS OF GROWTH PROCESS IN ALUMINUM AND IRON HYDROXIDE SOLUTIONS

D. TCHOUBAR*, J.Y. BOTTERO**, M.A.V. AXELOS*** AND P. QUIENNE*

*Laboratoire de Cristallographie, U.A. 810, B.P. 6759, Rue de Chartres, U.F.R.- Faculté des Sciences, 45067 ORLEANS Cédex, FRANCE

**Centre de recherche sur la Valorisation des Minerais de l'E.N.S.G., L.A. 235, B.P. 40, 54501 VANDOEUVRE Cédex, FRANCE

***Laboratoire de Physico-Chimie des Macromolécules, Centre de Recherche INRA, Rue de la Géraudière, 44072 NANTES Cédex, FRANCE

The Al and Fe hydroxide particles which are formed in far from equilibrium conditions are highly reactive with the surrounding medium. This property can be explained by their very devided state (high specific surface area and charge) (1). We have investigated the chemistry and structure of such particles in partially neutralized Al chloride and Fe nitrate aqueous diluted solutions. (0,1 M of Al or Fe). The kinetics of the growth process first steps were studied using ^{27}Al N.M.A. in both liquid and solid states and using Small Angle X Ray Scattering (S.A.X.S.).

SAMPLES

We have essentially considered two parameters:

- i. the neutralization ratio:

$$R = \frac{[N^*OH]}{[Al \text{ or } Fe]} \text{ with } \begin{cases} 0 < R < 3 \text{ for Al} \\ 0 < R < 1.5 \text{ for Fe} \end{cases}$$

- ii. The ageing time T of resulting solutions with:

$$100 \text{ sec} < T < 24 \text{ hours.}$$

RESULTS

Aluminium Solutions

The ^{27}Al NMR in liquid showed that $\text{Al}_{1.5}$ polycations are formed during hydrolysis. At $R=2.0$, 80 to 100% of Al atoms are condensed in the $\text{Al}_{1.5}$ structure. From $R>2.2$ the $\text{Al}_{1.5}$ cluster concentration decreases and colloid particles are formed $R=2.6$ is the colloid particle flocculation threshold. The ^{27}Al NMR in solid state showed

that colloid species result from Al_3 cluster aggregation. For T lower than 1 hour the aggregates contain only these species whatever R value within the range: 2.2 - 2.8 (2). Beyond this last value bayerite is precipitated.

S.A.X.S. investigations have shown that the structure of colloid species depends on value of R and T. The data analysis were performed by fitting experimental spectra with simulated ones from mass fractal structure models (3).

Figures 1 and 2 display the experimental curves which are characteristic of such fractal structure in log-log plots for solutions corresponding respectively to $R=2.5$ and $R=2.6$. $I(s)$ is the scattering intensity and $s=2\sin\beta/\lambda$ where β is the half angle scattering and λ the X ray wave length.

Fitting with simulated curves show that:

for $R=2.5$ and $T \leq 500$ sec the colloid particles results from aggregation by diffusion and tip to tip sticking type of Al_3 clusters (3,4). The average number of aggregation per particle is about 65 and the aggregate fractal dimensions is $D_f=1.45$. For $R=2.6$ and $T \leq 1$ hour the particles are built by cluster-cluster type aggregation (3,4). The average number of aggregation per particle is about 500 and the fractal dimensions D_f is equal to 1.86. This last type of structure keeps on the same whatever the $pH \leq 9$.

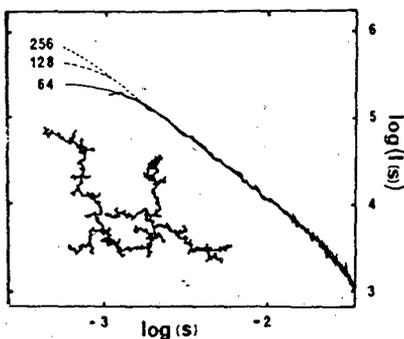


Fig.1. $R=2.5$

Fitting S.A.X.S. with simulated curves for three particle sizes in tip to tip cluster aggregation process. Shape of resulting aggregate

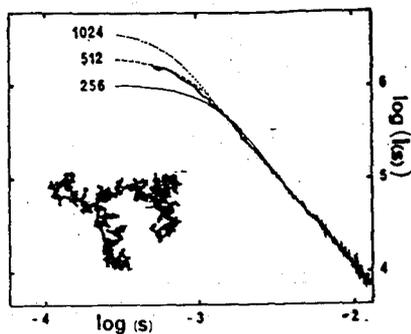


Fig.2. $R=2.6$

Fitting of S.A.X.S. experiment with simulated curves for three particle sizes in cluster-cluster aggregation process. Shape of resulting aggregate.

Fe solutions

The Fe solutions give spectra which are quite different from the previous ones which were obtained for Al solutions. In the figure 3 relative to $R=0.75$ the shape of curve could be characteristic of linearly connected units as chains. The branch of curve which shows the highest slope could traduce an interconnection of these chains. The figure 4 which is relative to $R=1.5$ displays a linear log-log plot which is similar to the curves previously obtained with Al solution and characteristic to fractal aggregation. In that last case the fractal dimension D_f is equal to 1.67 meaning that the structure of Fe hydroxide aggregates is intermediate in compactness between the two models of figures 1 and 2.

Fig.3
S.A.X.S experiment for
Fe solution $R= 0.75$

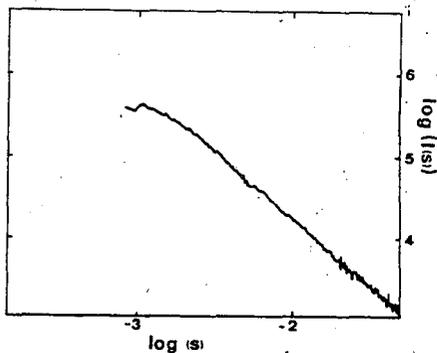
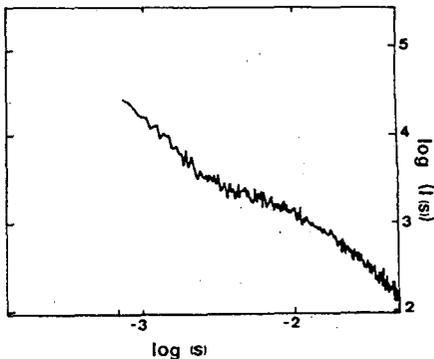


Fig. 4
S.A.X.S. experiment for
Fe solution $R=1.5$

The fitting of experimental curves with simulated ones is in progress which will permit to precise the sizes of units which are in connection in these structures. The number of Fe atoms which are condensed in the unit clusters will be deduced from comparison of S.A.X.S. data and others experiments such E.X.A.F.S. which are planned.

CONCLUSION

*The first steps of Al hydroxide growth follow an aggregation process of small Al₃ clusters. The fractal aggregates evolve from a loose structure ($D_f=1.43$) to a more dense one ($D_f=1.73$) with aging time T or $R=(OH)/(Al)$.

*The first steps of Fe "hydroxide" growth follow a more complicated process not yet completely understood. Further chemical investigations (EXAFS...) are in progress to precise the subunit structure.

REFERENCES

- (1) E. RAKOTONARIVO, J.Y. BOTTERO, J.M. CASES, F. FIESSINGER (1984). Colloids and Surface, 9 pp. 273-292.
- (2) J.Y. BOTTERO, M.A.V. AXELOS, D. TCHOUBAR, J.M. CASES, J.J. FRIPIAT and F. FIESSINGER (1987). Journal of Colloids and Interface Science (to appear in May).
- (3) R. JULLIEN and R. BOTTET (1987). Aggregation and Fractal aggregates World Scientific Publishing CO PTE LTD.
- (4) M.A.V. AXELOS, D. TCHOUBAR and R. JULLIEN (1986). J. Physique, 47, pp 1843-1847.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

EFFECT OF TEMPERATURE AND EXCHANGEABLE CATION ON
WATER DIFFUSION IN MONTMORILLONITE

M. TECILAZIĆ-STEVANOVIĆ, L.J. PAVLOVIĆ-TERZIĆ, D. IZVONAR, AND
J. HAVRDA[‡]

Faculty of Technology and Metallurgy, University of Belgrade,
4 Karnegijeva St., 11000 Belgrade, Yugoslavia

[‡]Institute of Chemical Technology, 16628 Prague, Czechoslovakia

OBJECTIVES

Water transfer phenomena in the interlayer space of montmorillonite structure is a complex and not yet completely solved scientific problem.

The main objective of this paper was to determine the coefficients of water molecular diffusion dependence on the exchangeable cation of montmorillonite and the temperature of the system.

By using the diffusion couple method in isothermic conditions, at five different temperatures, viz.: 303, 308, 313, 318 and 323 K, the coefficients of molecular diffusion of water were determined. The water transfer was studied in the diffusion couple with saturated boundary between two samples of different water content, ranging from 34 to 50 percent.

To calculate the molecular diffusion coefficient of water, the simplified Wagner's equation for the incompressible system was used. The results are interpreted in terms of standard diffusion theory based on Flick's laws.

EXPERIMENTAL

The starting material, homoionic Na and Ca - montmorillonite, particle size $< 2 \mu\text{m}$, was obtained from the Yugoslav bentonite "Jelenkovac". The cation exchange capacity was determined by the ammonia-acetate method and the

CEC value was $94 \text{ meq} \cdot 100^{-1} \text{ g}$.

The homoionic Na and Ca forms were obtained by treating the montmorillonite with a 1M NaCl solution and a 1M CaCl_2 solution, added in excess.

In experiments was used the diffusion couple method. The saturated diffusion couple consisted of two parts of different water contents, W_2 and W_1 , in which the air was absent. The sample layers, for the determination of the water content profile after diffusion, were obtained by means of a mechanical cutter. The water content was expressed in non-dimensional moisture, the relative water concentration, Y , according to the formula:

$$Y = \frac{C - C_1}{C_2 - C_1}$$

where C is the water content for the x -values given, x being the distance in the direction of the diffusion. C_1 and C_2 are the water content in volume fractions ($\text{m}^3 \cdot \text{m}^{-3}$) in the two parts of the diffusion couple, with $C_2 > C_1$. On the ground of the calculated values of the x coordinates and Y value, the function $Y=f(x)$ was given graphically for the value interval Y from 0.1 to 1.

CALCULATION AND RESULTS

Wagner's (1969) equation (1) for the incompressible system, derived from Sauer and Freise's (1962) research, was used in calculating the coefficients of the molecular water diffusion from the experimentally obtained data:

$$D = (2 \tau \partial_x Y)^{-1} \left[(1-Y) \int_0^x Y dx + Y \int_x^u (1-Y) dx \right] \quad (1)$$

The partial derivative values of $\partial_x Y$ in all points is calculated as well as that of the integrals:

$$I_1 = \int_0^x Y dx \quad I_2 = \int_x^u (1-Y) dx$$

where u is the coordinate x for which the function Y reaches its limiting value of 1; τ - diffusion time.

Both the partial derivative $\frac{\partial Y}{\partial x}$ and numerical values of the integral I_1 and I_2 were determined graphically for each point from 0.1 to 0.9. By introducing into Wagner's equation (1) these partial derivatives and numerical integral values, the following is obtained:

$$D = (2\tau \frac{\partial Y}{\partial x})^{-1} [(1-Y)I_1 + YI_2] \quad (2)$$

Using equation (2), the determined coefficients of molecular water diffusion in montmorillonite at various temperatures are presented in Table 1.

TABLE 1. Water Molecular Diffusion Coefficient in Montmorillonite

Temperature, K	Diffusion coefficient, $D \cdot 10^9, m^2 s^{-1}$	
	Ca - form	Na-form
303	2,14	1,10
308	3,13	1,22
313	4,00	1,56
318	4,5	1,80
323	5,24	2,10

The molecular water diffusion coefficient dependence on temperature was determined for the 303-323 K interval and was presented by the following expression for the Ca and Na cationic forms of montmorillonite:

$$D_{Ca} = 6.9 \times 10^{-6} \exp(-2316.7/T)$$

$$D_{Na} = 9.2 \times 10^{-5} \exp(-3441.0/T)$$



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**PHYSICO-CHEMICAL STUDY AND MATHEMATICAL MODELING OF
BENTONITE ALKALI ACTIVATION PROCESS IN THE PRESENCE
OF INSOLUBLE MAGNESIUM SALTS**

M. TECILAZIĆ-STEVANOVIĆ, T. JANAČKOVIĆ, Z. RADOJEVIĆ
AND J. JANAČKOVIĆ

Faculty of Technology and Metallurgy, University of
Belgrade, 4 Karnegijeva St., 11001 Belgrade, Yugoslavia

OBJECTIVES

The study of the alkali activation mechanism and behaviour of bentonite in a system containing sodium carbonate magnesium basic carbonate as activation agents was performed. Two approaches were used in this study: multifactor experiments and physicochemical analysis of bentonite samples before and after activation (x-ray, IR, chemical analysis). By using a multifactor experiment the effect of simultaneous action of the two activation agents on the quantity of exchangeable Na^+ cations and the viscosity of the 6% suspension of the activated bentonite was determined. The results of the physicochemical methods gave reasons to believe that some structural changes of montmorillonite occurred.

EXPERIMENTAL

The starting material used was the Yugoslav bentonite "Jelenkovac", CEC = $86 \text{ meq} \cdot 100^{-1}$. The cation exchange capacity was determined by the ammonium acetate method. The main exchangeable cations were Ca^{2+} and Mg^{2+} , 70% and 20% of total CEC respectively. For the physicochemical investigation, particles of less than $2 \mu\text{m}$ grain size were separated from bentonite using the multigrade sedimentation. The activation processing consisted in adding Na_2CO_3 and $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2$ (MBC) in different concentrations to the raw materials (1-4% and 1-3% mas. respectively). The processing temperature was 25°C . The paste was allowed to stay for 20 hrs. After that the system was dried at 70°C up to

10% water content. The activated bentonite was used for the determination of the rheological properties. The viscosity of the 6% bentonite suspension in water was determined by using the Stormer viscosimeter. The exchangeable sodium cation of the activated samples of bentonite was determined by the standard laboratory procedure.

MATHEMATICAL MODELING

Using the Box-Wilson's orthogonal plans of the full multifactor experiment, type 2^2 , two mathematical models were established:

1. The dependence of exchangeable sodium cation, y_1 , of activated bentonite on the concentrations of Na_2CO_3 and MBC, x_1 and x_2 respectively;

2. The viscosity dependence, y_2 , of the activated bentonite 6% suspension, on the Na_2CO_3 and MBC concentrations, x_1 and x_2 respectively.

The mathematical model obtained in the first case may be described by the following equation:

$$y_1 = 55,16 + 20,0 x_1 - 4,25 x_2 \quad (1)$$

By using the Fischer criterion and experimental test, it was proved that this linear method, given by eq. (1) was quite adequate. The values of the regression coefficients show that the quantity of Na_2CO_3 added is the controlling factor for the value of the exchangeable Na^+ ion. The model makes it possible to predict:

- the values of exchangeable Na^+ cations for any content of activation agents used, and
- an optimal addition of activation agents for the process.

The linear mathematical model of the first order for the dependence of the viscosity on the activation agent concentration proved, through an experimental test, to be inadequate. It was therefore necessary to increase the number of experiments and to approximate the relationship by means of a non-linear equation of the second order:

$$J_2 = 17.17 + 2.42x_1 + 5.25x_2 - 5.25(x_1^2 - \phi) - 3.25(x_2^2 - \phi) \quad (2)$$

where ϕ has the value of $2/3$, 0.6667 for the orthogonal plan 2^2 . The experimental results confirmed the validity of the proposed model, given by eq.(2).

The model presented by eq.(2) shows that the quantity of MBC added is more significant in getting higher viscosities than the addition of Na_2CO_3 . The experimental results have shown that the increase in exchangeable Na^+ ions is not followed by the rise of viscosity. This points out that in the mechanism of this activation process, the exchange phenomena of the exchangeable cation present in raw bentonite are not the only controlling factor and that a more complex mechanism is being dealt with.

PHYSICOCHEMICAL STUDY

The results of the x-ray and infrared study and of chemical analysis of the montmorillonite before and after activation have shown that the structure of montmorillonite was changed to a certain degree. A unit cell dimension changed in the direction of the c-axis, i.e. an increase of the c-axis spacing, d , took place. This change was permanent even after heating of activated montmorillonite up to 450°C .

It can be assumed that $\text{Mg}(\text{OH})_2$ precipitation occurred in the interlayer space of montmorillonite structure. This phenomenon will be the object of further investigations.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ALTERNATIVE RAW MATERIALS FOR THE CERAMIC INDUSTRY: ALTERATION PRODUCTS OF BASIC ROCKS FROM TUSCANY (ITALY)

A. TENAGLIA, A. POZZUOLI* and A. SALOMONI

Centro Ceramico, Via Martelli 26, 40138 Bologna (Italy)

* Department of Geophysics and Volcanology, University of Naples, Largo S. Marcellino 10, 80138 Napoli (Italy).

This work constitutes part of a research program on Italian raw materials for the production of ceramic floor and wall tiles. Samples from operating quarries of blocks used as foundations or paving materials were chosen and characterized with the aim of finding new and cheap raw materials which can be used as substitutes for some of the traditional materials in the production of ceramic tile.

The following samples were examined (the number in brackets indicates the sheet of the geological map of Italy showing the sample location):

- RC/050/2 (sheet 112): the material comes from a little quarry of semilithoid serpentine-like material, green-gray in colour with blackish veins located along the road Chianni-Castellina; it is reported on the geological map as "diabase- δ ".

- RC/050/3 (sheet 112): this material is similar to the previous sample (diabase- δ) and comes from a larger quarry near Pomaia.

- RC/050/4 (sheet 112): this sample was collected from a large quarry located along the road from S.S. 206 to Rosignano Marittimo. It is similar to the previous samples, but contains a certain amount of soil.

- RC/050/5 (sheet 112): this material comes from a quarry of a serpentine-like material (diabase- δ) located on the right side of a little valley to the west of Riparbella.

- RC/050/6 (sheets 113 and 107): the sample was collected from a small quarry of "varicoloured schists", mainly red and green; belonging to the VR formation and located near Villa Radda in Chianti.

- RC/050/7 (sheet 113): the quarry from which this material was taken is rather large and is located near Badiaccia Montemuro. The materials in the quarry are rather heterogeneous (SP formation).

- RC/050/8 (sheet 113) : this is a serpentine, similar to diabase- δ found in a small quarry near Rencine.

- RC/050/9 (sheet 106): this sample comes from a large quarry of serpentine-like material northwest of Figline.

The following analytical methods were used to characterize the samples: chemical analysis, DTA+TG analysis, dilatometric analysis and X-ray powder diffraction analysis.

The firing behaviour of the materials was studied using dry pressed samples of the powders (moisture content: 6.5%; specific forming pressure: 250 kg/cm²), in the form of 40-mm diameter disks and firing in an electrical gradient kiln. The maximum firing temperature generally used was 1200 - 1210 °C. Samples RC/050/4 and RC/050/8 (with lower melting point) were fired at a maximum temperature of 1130 °C. The most refractory materials were also fired at 1250 °C. The fired samples were characterized by linear shrinkage measurements; water absorption determinations were carried out only for samples showing a sufficiently high degree of sintering. A technical data sheet containing all the laboratory results was compiled for each sample, useful both for an overall evaluation of the characteristics of the raw materials and to make the proper comparisons with analogous raw materials in use on industrial scale.

The results may be summarized as follows:

1 - Based on X-ray powder diffraction and thermal analysis data, samples RC/050/2, 3, 5, 8 and 9 are serpentine rocks. There is no evidence of free quartz or other crystalline minerals except for some kaolinite found in sample RC/050/3. The chemical compositions are within the following ranges:

LOI	11.10 - 12.77 %
SiO ₂	34.53 - 37.69 %
Al ₂ O ₃	4.97 - 8.92 %
TiO ₂	0.00 - 0.07 %
Fe ₂ O ₃	6.68 - 10.67 %
CaO	0.14 - 0.53 %
MgO	32.67 - 37.25 %
K ₂ O	0.00 - 0.01 %
Na ₂ O	0.45 - 0.84 %

Commercial deposits of serpentine may run from 37% to over 40% of MgO. These samples, then, are rather pure. Although these samples all had a high shrinkage, their water absorption also was high, indicating poor sintering. This means that these raw materials may behave as "inert" or non-plastic materials in a ceramic body, also at higher temperatures. In contrast, the marked shrinkage

indicates that these materials may not be suitable for such a use because of dimensional instability arising inside the body during firing.

2 - In addition to serpentine, sample RC/050/4 also contains feldspars and traces of other clay minerals (mainly chlorite). Its chemical analysis is as follows:

LOI	4.23 %
SiO ₂	49.85 %
Al ₂ O ₃	16.52 %
TiO ₂	0.70 %
Fe ₂ O ₃	8.55 %
CaO	5.97 %
MgO	9.99 %
K ₂ O	0.30 %
Na ₂ O	3.57 %

This sample has an interesting firing behaviour. The shrinkage is reasonable up to 1130 °C and above this temperature it begins to fuse quickly. This is indication of its suitability for use as an inert material for bodies to be fired at low temperatures and as a fluxing agent for use with thermal cycles at higher temperatures.

3 - Samples RC/050/6 and 7 both contain quartz, feldspars and, to a lesser extent, clay minerals (in particular disordered kaolinite). Their chemical analyses are as follows:

	RC/050/6	RC/050/7
LOI	4.64 %	5.66 %
SiO ₂	65.50 %	65.75 %
Al ₂ O ₃	16.68 %	15.19 %
TiO ₂	0.32 %	0.22 %
Fe ₂ O ₃	6.74 %	7.77 %
CaO	0.64 %	0.63 %
MgO	2.13 %	2.25 %
K ₂ O	2.32 %	1.58 %
Na ₂ O	0.67 %	0.55 %

The shrinkage during firing is rather low, especially for sample 6. Both samples fuse at temperatures above 1200 °C. Like sample RC/050/4, these materials too may be used as "inerts" at low

temperatures (up to around 1150 °C), assuring good dimensional stability to the fired products.

The results of these studies show the possibility of using, in the ceramic floor and wall tile industry, new inexpensive raw materials obtained as byproducts from the mining industry of materials to be employed for other purposes. Limitations in the use of serpentine-like materials in the ceramic floor and wall tile industry also are discussed.

Work is now being directed towards studying the various possibilities for using these materials by formulating and testing suitable mixtures.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SERPENTINE-LIKE, KAOLINITIC, HIGH DENSITY ALTERATION PRODUCTS OF VOLCANIC ALKALINE ROCKS IN CENTRAL KALIMANTAN (BORNEO), INDONESIA .

S. TJOJUDO* and G. SIEFFERMANN**

* Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Sekip Unit IV Yogyakarta Indonesia

** ORSTOM - Gadjah Mada University programme of cooperation Sekip K 3, Yogyakarta, Indonesia.

A B S T R A C T

This study concerns thick layers of wax like, isovolumetric transformation products developed from miocene Trachyandesit with nepheline content, in the uplands of Central Kalimantan Province (Borneo).

After a short presentation of the present ecological environment the study of this rare alteration material is carried on by means of chemical and thermal analysis, of X-ray diffraction and of electron microscopy.

The wax like isovolumetric alteration material shows a density close to 2,4 and a very low porosity ranging from 10 to 18%. There are no more remains of minerals of the original rock, all are changed in clay material, but the initial volume of the rock seems to be perfectly preserved.

The clay material of these alterations is mainly composed of minerals from the kaolin family (80 to 90%) mixed with a small amount of three sheet clay minerals.

The interpretation of the formation of this material is difficult and raises a lot of problems :

The isovolumetric calculation shows that the alteration material contains 40 to 60% more Al_2O_3 than the same volume of initial rock. This increase in Al_2O_3 go on a par with a similar increase in Fe_2O_3 (60 to 70%) and TiO_2 (40 to 100%).

If we try to understand the formation mechanism of the excess kaolinite and Fe, Ti oxydes, we can only imagine an input of Al, Fe and Ti under soluble ionic form during the hydrolysis process of the primary rock. The question is which type of solution has brought simultaneously Al, Fe and Ti, in ionic form to the weathering front to give excess kaolinite and iron and titanium oxydes : hydrothermal or meteorological?

We have no evidence of a hydrothermal mechanism, and a meteorological process cannot be, a priori, excluded in this case. Several studies suggest that complex organic acids such as fulvic acids and humic acids play an important role in the mobility of the aluminium. The formation of the excess kaolinite can possibly be explained by the coming of Al in chelated form from the upper horizons.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SOURCE AND DISPERSAL OF CLAY MINERALS FROM PRESENT AND LATE QUATERNARY
SEDIMENTS OF SOUTHERN ADRIATIC SEA

L. TOMADIN AND M. BORGHINI

Institute of Mineralogy and Petrography, University of Urbino (Italy)

Bottom samples collected in the southern Adriatic basin have been investigated in order to ascertain the present-day provenance of the clays, and to evidentiate the influence of different dynamic agents on their distribution in the basin. For comparison with the clay sedimentation during the Late Pleistocene 4 cores (IN68-10, 9, 5 and 2) from different physiographic environments of the basin have been also studied.

The clay sediments of the southern Adriatic basin are composed of clay minerals supplied from different sources:

- a - from the Central Adriatic Sea: sediments mainly constituted (70-80%) by poorly organized illite and well crystalline smectite; chlorite content higher than kaolinite content.
- b - from Albanian rivers (chiefly the Drin R. from the N and the Vjosa R. from the S): sediments composed (60-70%) by well organized illite and smectite, associated with an important (15-20%) chlorite content.
- c - from Apulian rivers (mainly the Ofanto R.): sediments characterized by abundant kaolinite (20-30%), low crystalline smectite and poorly organized illite.
- d - from eolian dusts: large amounts of clay minerals are present among the atmospheric particles, as chlorite mainly wind-blown from E-SE (Albanian source) and highly degraded illite and kaolinite from S-AW (Saharan source).

Many evidences show that the clay minerals of the southern Adriatic

basin are affected by different dynamic agents, able to transport and distribute them. The most important features are:

- 1 - the longitudinal descendant current of the main Adriatic circulation, locally associated with a current transversal to the axis of the basin. The combined action of these currents generates an area of low energy level (the Manfredonia Gulf) favourable to the sedimentation of small-sized smectite particles. More southerly the tractive longitudinal current favours the dispersion of clay materials along the southernmost Apulian shelf.
- 2 - countercurrents moving counterclockwise are very active on the inner shelf of the Manfredonia Gulf. Here the clay material transported by the Apulian rivers is reworked and distributed in curved belts along the coast.
- 3 - turbidity currents transport abundant clays from the continental shelf to the plain, through the canyons eroding the slope between Bari and Brindisi. Evidences of a clay transport transversal to the basin are given from the distribution maps of illite and smectite in the surficial sediments.
- 4 - eolian currents mostly from the S-SW direction in connection with Sirocco wind episodes.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MICROSTRUCTURE OF Mg CLAY MATERIALS AT SATURATED WATER CONTENT

O. TOURAY, CH.H. PONS*, D. TESSIER** AND Y. TARDY

CNRS Centre de Sédimentologie et de Géochimie, 1, Rue Blessig,
67084 Strasbourg Cédex (FRANCE)

* Université d'Orléans, Laboratoire de Cristallographie (UA 810)
45067 Orléans Cédex (FRANCE)

** Station de Science du sol, INRA, 78000 Versailles (FRANCE)

Small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to determine the structure, microstructure and pore distribution of Mg clay materials at saturation water content.

Materials and Methods

The studies were carried out with different clay materials which physicochemical properties have proven to be significantly different from the properties of pure clay minerals. Five clay materials saturated by Mg were studied at saturation water content : an hectorite from hector California, a montmorillonite from wyoming, USA and from Camp-Berteaux, Morocco, a nontronite from Pennsylvania, USA and a vermiculite from Santa-Olalla, Spain.

The clay mineral is packed in a glass tube which has a porous bottom . The bottom of the glâce tube was placed in a beaker containing water so that the water would be imbibed by the clay. The glass tube is regularly weighed (Turky, 1983), the equilibrium and the total water content are obtained after five months.

Starting from this equilibrium, the sample are investigated by SAXS and TEM. TEM was carried out on ultrathin sections of about 500 Å thickness (Tessier, 1984). SAXS experiments were carried out with the X-rays ($Cu\ k\ \alpha\ 1$) emitted by a 12 kw generator . The diagrams can be directly compared with theoretical SAXS curves . Computation models were used which assumed the particles to be stacks of M parallel silicate layers. The internal structure of

	M	\bar{d}	$\bar{\delta}^2/\bar{d}^2$	1	2	3
Hec Mg	4	22.96	0.058	24%	48%	28%
Wyo Mg	19	21.39	0.062	32%	42%	26%
C.B Mg	10	21.73	0.074	58%	20%	22%
Nont. Mg	7	21.51	0.081	51%	24%	25%
Verm. Mg	30	15.78	0.082	68%	13%	19%

Table

- 1 → Water content between aggregates in % of total water
 2 → Water content between particules in % of total water
 3 → Water content within particules in % of total water

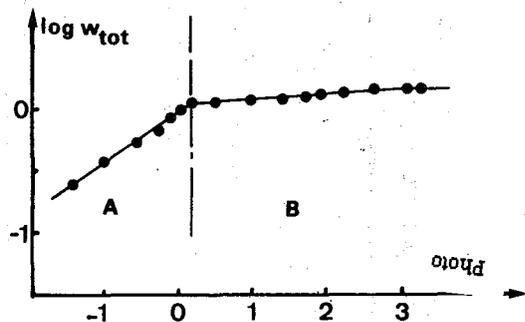


Figure 1



1 cm = 1000 Å

- A → particles
- B → aggregates
- C → pores between aggregates

such a particle is given by the following parameters (1) the average distance \bar{d} characterizing the average interlayer spacing (2) the ratio $\delta^2 / (\bar{d})^2$ where δ^2 is the variance of the interlayer distance distribution (the higher this ratio, the more disordered the system (see table) (Pons et al., 1982).

Results.

Actually TEM and SAXS data give a more complete picture of water clay systems by providing a link between internal particle structure or aggregate structure and system geometry. For example, for a Mg-nontronite, TEM and SAXS data showed the structure to be made up of particule aggregates separated by large pore size (see photo). Within the aggregates, internal small size pores delimited by small particules ($M < 10$) were observed.

From SAXS and imbibed water data*, the water status was thus established by distinguishing the water within the interlayer spacing (i.e. within particles) from the water within the small pores between particles (i.e. within aggregates) and from the water within the large pores (i.e. between aggregates).

* Remark. For example the results for Mg saturated nontronite summarized in figure 1 show that the curve $\log W_{tot}$ versus $\log(t)$ present two parts (A and B). From the two slopes of the curve, it is possible to calculate the amount of water between and within the aggregates (Turky, 1983).

References.

Pons, C.H., Tessier, D., Ben Rhaïem H. and Tchouber D. (1982)
Clay. Conf. Bologna, Pavia.

Tessier, D. (1984)
Thesis univ. Paris, INRA, Versailles Publ. 360 pp.

Turky, F. (1983)
Thèse de 3ème Cycle Université de Strasbourg (France).



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

BEHAVIOUR, MICROSTRUCTURE AND STABILITY OF SOILS DEVELOPED ON ARANGUREN
(SPAIN) TERTIARY MARLS

M.E. TREBOL¹, C. CHENU² AND D. TESSIER²

¹Centro de Edafología y Biología Aplicada de Salamanca.C.S.I.C. Spain

²Station de Science du Sol. INRA. 78000 Versailles. France

Soils which are developed on tertiary marls from Aranguren in the northern area of Spain are very unstable and particularly susceptible to erosion. This work was carried out in order to understand better and predict the behaviour of these soils.

MATERIALS AND METHOD

Soil pastes were prepared from a B horizon by means of mechanical stirring in water. Fraction $< 2 \mu\text{m}$ was separated from bulk samples using a 10^{-3} M NaCl solution. Drying and wetting curves were drawn from the data obtained after subjecting the samples under increasing and decreasing suction pressures (≤ 10 bar), or leaving the samples at different vapour pressures for stresses > 10 bar. Water content was measured by weighing the sample heated to 150°C and porosity by recording the pressure exerted by the sample on kerosene. Preparation methods for transmission and scanning electron microscopy observations were conducted in such way that the microstructure at any given state of water was preserved (Tessier, 1984).

HYDRATION PROPERTIES AND VOLUME CHANGES

Fig.1 shows that paste preparation from a natural material leads to an increase in both the porosity and water content in the whole range of stress under study. The samples are saturated with water for stresses ≤ 0.32 bar. At a strong dehydration (i.e. 1000 bar - R.H. = 50 %), the porosity of the soil paste is roughly twice that of the undisturbed one. Results obtained on the soil paste as well as on the $< 2 \mu\text{m}$ fraction showed that the presence of calcite prevented the compaction of the system.

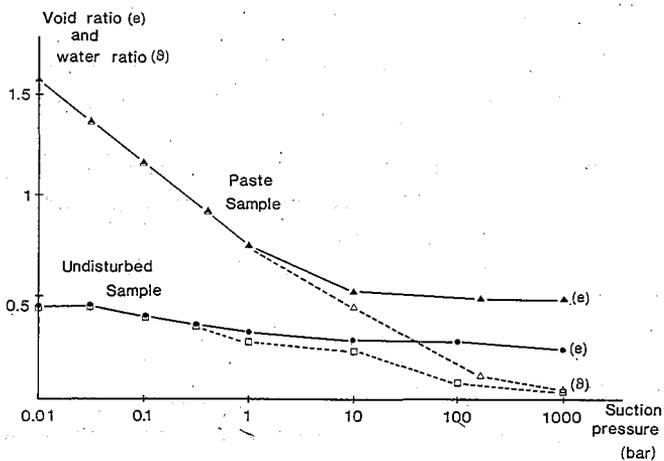


Fig. 1 - Aranguren drying curves (a) undisturbed natural sample ; (b) soil paste sample. Results expressed in void ratio ($e = V_v/V_s$) and water ratio ($\theta = V_w/V_s$)

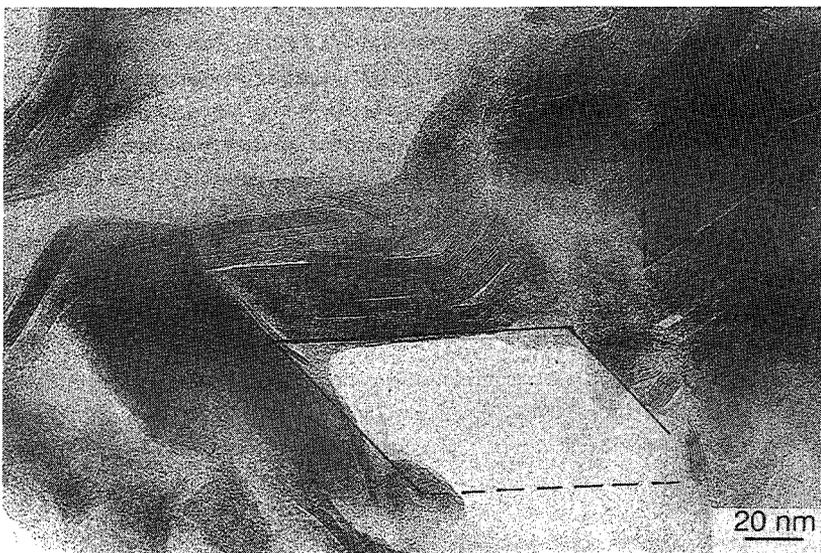


Fig. 2 - General organization of the material after calcite dissolution showing the arrangement of illite-smectite crystals

MICROSTRUCTURE

S.E.M. observations showed that calcite crystals are mainly $< 2 \mu\text{m}$ in size and that clay matrix occupies the space between the rhombohedral calcite crystals. In the soil paste containing calcite, a very loose particle arrangement was identified. As shown on Fig.2 after calcite dissolution the initial arrangement of clay particle is partly preserved. This is confirmed by the arrangement of the clay crystals with angles similar to those of the calcite crystallization rhombohedrons.

DISCUSSION - CONCLUSION

This work demonstrates that crystallization conditions of calcite during parental material genesis and in particular, stresses developed during calcite crystal growth, are responsible for the creation of a specific clay particle arrangement.

Thus, the properties of a soil developed over this type of marl are a function of the genetic factors of the later. After calcite dissolution there is an incomplete destruction of the initial clay particle arrangement which explains the loss of structural stability of the soil.

In conclusion both mechanical disturbance and/or calcite dissolution modify all physical properties and enhance the susceptibility to erosion.

REFERENCE

Tessier D. (1984) - Etude expérimentale de l'organisation des matériaux argileux. INRA Versailles, pub. 361 p.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

EFFECT OF POTASSIUM REMOVAL BY CROP ON TRANSFORMATION OF
ILLITIC CLAY MINERALS

H. TRIBUTH*, E.v. BOGUSLAWSKI, A.v. LIERES**, D. STEFFENS
AND K. MENGEL***

- * Institut für Bodenkunde und Bodenerhaltung, Justus-Liebig-Universität Gießen (Germany)
- ** Institut für Pflanzenbau, Justus-Liebig-Universität Gießen (Germany)
- *** Institut für Pflanzenernährung, Justus-Liebig-Universität Gießen (Germany)

INTRODUCTION

It is well known that weathering of K^+ bearing minerals results in a transformation of 2:1 clay minerals (RICH 1968). According to SCHROEDER (1976) the sequence of transformation is as follows: micas \rightarrow hydromicas \rightarrow illite \rightarrow transition minerals \rightarrow vermiculite or smectite. TRIBUTH (1981), however, holds the view that there is not a general transformation sequence valid for all soils, since clay mineral transformation depends on soil conditions, especially on base saturation of clay. In this transformation process, plants may also be involved since plant roots may excrete H^+ which can attack clay minerals. (MENGEL and STEFFENS 1982). Beside H^+ excretion, H^+ uptake of plant roots may decrease the K^+ concentration of the soil solution at the root surface as has been shown by BARBER (1962) and recently by KUCHENBUCH and JUNGK (1984). Low K^+ concentrations favour the net release of nonexchangeable K^+ which is mainly interlayer K^+ of clay minerals (MARTIN and SPARKS 1983). It is thus feasible that exploitation of K^+ by plants may contribute to the transformation of clay minerals.

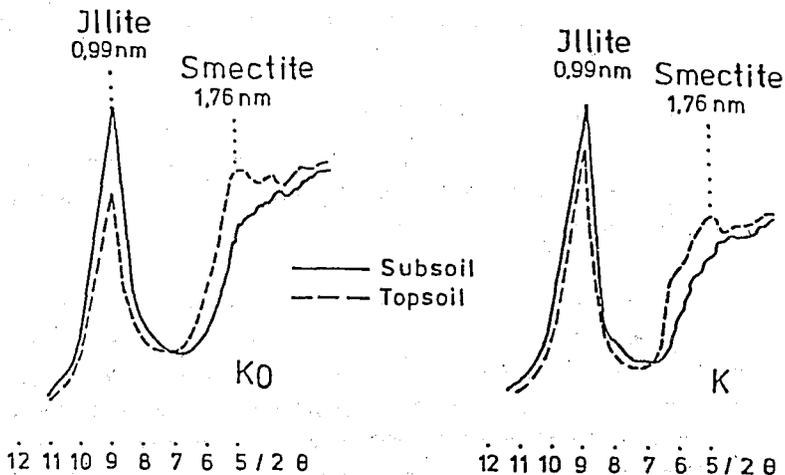
RESULTS

The effect of K^+ fertilizer application or non-application on the transformation of clay minerals was studied in soils from long term field experiments and exhaustive cropping pot experiments. Soils used were alluvium, gray brown and brown soils with illite as the principal clay mineral. X-ray diffraction analysis of soil samples revealed that cropping without K^+ fertilizer application had led to a substantial decrease in illite content and to an increase of smectite and interstratified illite/smectite minerals. In the alluvium soil containing carbonate, stable smectite was formed probably because of the high soil pH, whereas in the other soils with lower pH, degradation of illite resulted in the formation of labile minerals which expand to more than 2.0 nm. Illite degradation was especially intensive in the $<0.06 \mu\text{m}$ and $<0.2 \mu\text{m}$ particle size fraction.

It is suggested that the removal of K^+ by plants resulted in a depletion of interlayer K^+ in illite followed by the degradation of the clay mineral. Pot experiments with clover and rye-grass showed that the K^+ uptake of the crop from the nonexchangeable fraction (interlayer K^+) was quantitatively related to the increase in the dry K^+ fixation capacity of the soil.

The most important arable soil type in Central and Western Europe is the gray brown soil (typic Hapludalf) derived from loess. These soils can release large amounts of K^+ when intensively cropped, as has been shown by numerous field experiments (v. BOGUSLAWSKI and v. LIERES 1981).

The difference between K-fertilized and K_0 -samples was extremely great in the soil from "Rauischholzhausen", because after 26 years of cultivation under field conditions this soil was additionally and in a very intensive way cropped in Mitscherlich-pots.



• Fig. 1: X-ray diffraction diagrams of the effect of K^+ fertilizer application (Rauischholzhausen).

In Fig. 1 it is furthermore shown that the illite content of the K_0 -sample has decreased to a far greater extent in the topsoil than in the subsoil. This fact especially emphasizes the influence of the plants, which promote the transformation of illite by K -removal especially from the topsoil.

CONCLUSION

Permanent removal of K^+ from illite containing soils leads to the degradation of illite and formation of smectite and interstratified minerals. On natural habitats such K^+ removal from the top soil layer may be brought about by leaching. In cultivated soils large amounts of K^+ are removed from the soil by crops. If the resulting K^+ deficit in the soil is not balanced by K^+ fertilizer application a transformation of clay minerals, especially illite, will more quickly proceed. Therefore in cropped soils with illite as the main clay mineral, K^+ fertilizer application is not only a question of plant nutrition but also of clay conservation.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

HEATING-INDUCED EFFECTS ON THE ANIONIC CLAY MINERAL $[\text{Al}_2\text{Li}(\text{OH})_6]$ (Picrate),
 $n \text{H}_2\text{O}$

M.A. ULIBARRI, J.M. LUQUE and J. CORNEJO

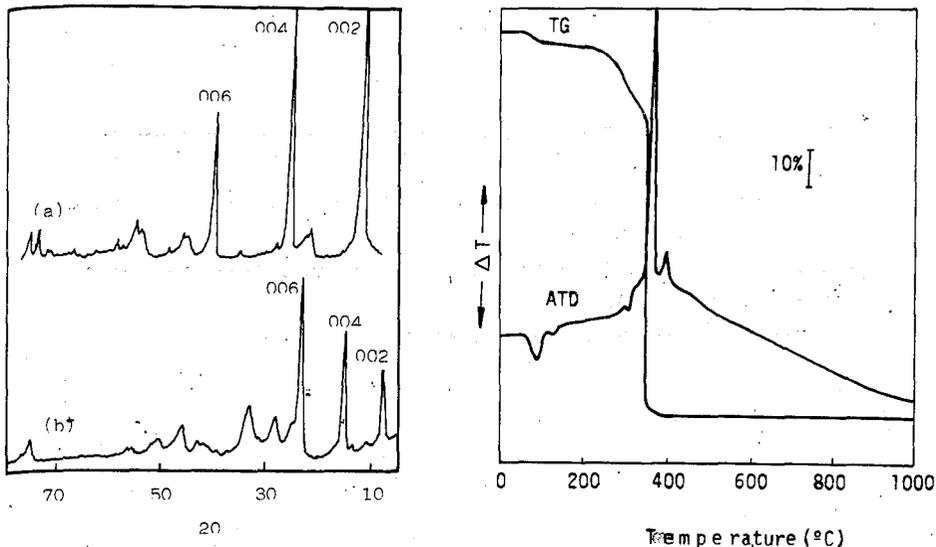
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Córdoba (Spain) e Instituto de Recursos Naturales y Agrobiología, CSIC, Aptdo.1052 E.P., 41080 Sevilla (Spain)

Structures with negatively charged layers and intercalated exchangeable cations are well known. In contrast, compounds having positively charged layers and exchangeable anions in the interlayer space are far less common; they form in terms of charges, the mirror image of clays. Many of these are based on metal double hydroxide compounds with hydro-talcite-like structure, which consist of positively charged brucite-like layers, $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+}$ with intercalate and exchange anions (1,2). The synthesis and characterization of hydro-talcite-like compound $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ extend the class of inorganic anion exchangers from $\text{M}^{2+} \text{M}^{3+}$ to $\text{M}^{3+}\text{M}^{2+}$ compounds (3), (M=cation).

The present study is part of a wider one on the anionic exchange capacity of the Al,Li-hydroxycarbonate and the properties of their exchanged forms (4,5). For this study the picrate form was obtained and studied after different thermal treatments by X-ray powder diffraction (XRD) scanning electron microscopy (SEM), thermal analysis (DTA-TG) and N_2 adsorption isotherms techniques.

The synthesis of Al,Li-hydroxycarbonate was conducted as previously described (3) and the anionic exchange reaction with picrate was carried out by placing it in a 0.1 M picric acid solution prepared from CO_2 -free distilled water and 48 h continuously stirred. The resulting gel was filtered, washed and dried at 60°C .

For comparison purposes the XRD patterns of $[\text{Al}_2\text{Li}(\text{OH})_6]_2\text{CO}_3$ and $[\text{Al}_2\text{Li}(\text{OH})_6]$ (Picrate) are shown in Fig.1a and 1b, respectively. It is suggested that these compounds have a layered structure (pronounced basal reflections) with the layer distance following closely the size of the intercalate anion.



The DTA and TG diagrams of the Al,Li-picrate are shown in Fig.2. A 3% of weight loss, corresponding to elimination of molecular water from the interlayer sheet is observed under 200°C. No changes were observed on the XRD patterns of samples heated at 300, 400 and 500°C indicate that poorly crystalline solids are formed. Different Al_2O_3 phases and the spinel LiAl_5O_8 formed by the interaction of oxides produced during the thermal decomposition of the original sample have been detected at 300-400°C. Those phases were also found by thermal decomposition at 300°C of Al,Li-nitrate (6). However, the thermal decomposition pathway of the Al,Li-picrate seems to be different than that of Al,Li-carbonate because of in this compound $\gamma\text{-Al}_2\text{O}_3$ was only found at 500°C. No significant changes in specific surface area (S_{BET}) of samples treated under 300°C was observed (43-45 m^2/g). A similar behaviour was found by SEM micrographs. However, an important destruction of the crystals occurs at 300-400°C and the corresponding S_{BET} values increases (75 m^2/g). At higher temperatures ($\geq 500^\circ\text{C}$) the S_{BET} values decreased because of sintering.

The above results show that the new hydroxalcite-like compound synthesized (Al,Li-picrate) behaves in a different way than hydroxalcite under similar heat treatment.

BIBLIOGRAPHY

- (1) M.C. Gastuche, G. Brown and M.M. Mortland, *Clay Miner.* 7, 177 (1967)
- (2) S. Miyata, *Clays and Clay Minerals*, 23, 369 (1975)

- (3) C.J. Serna, J.L. Rendón and J.E. Iglesias, *Clays and Clay Minerals* 30,180 (1982)
- (4) M.J. Hernandez, M.A. Ulibarri, J.L. Rendón and C.J. Serna, *Phys.Chem. Minerals* 12, 34 (1985).
- (5) M.A. Ulibarri, M.J. Hernandez, J. Cornejo and C.J. Serna, *Mat.Chem. Phys.* 14, 569 (1986).
- (6) G. Mascolo, *Thermochim. Acta* 102, 67 (1986)



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

QUARTZ GRAIN SIZE DISTRIBUTION IN THE ILLITE - KAOLINITE
- QUARTZ MINERAL TRIANGLE AND CERAMIC PROPERTIES OF
BRICK PRODUCTS

H. Urban and U. Wedemeyer

Institute for Nonmetallic Materials, Technical University
Clausthal, Federal Republic of Germany

ABSTRACT

Investigations of ceramic properties and phase transformations in illite-kaolinite-quartz mineral triangles with quartz of different grain size as corner components show up to 1200 °C relations between the mineral content of the raw mixtures and the properties of the fired ceramic bodies as well as the influence of different quartz grain size distribution.

INTRODUCTION

The illite - kaolinite - quartz mineral triangle is the basic triangle for many raw materials for brick products. If optimal ceramic properties are to be reached by varying the raw material composition it is necessary to know the course of ceramic properties all over the triangle at the usual firing temperatures of 1000-1100 °C.

The first systematic investigation of this triangle up to 1200 °C with respect to ceramic properties and phase transformations was published by Babczinski and Urban (1983), and the main results including the influence of different illite chemistry were presented at 5th EUROCLAY by Urban, Babczinski and Wedemeyer (1983).

For these investigations a pretty coarse quartz was used as corner component of the triangle in order to get most of the triangle points into the fields suitable for bricks according to Winkler's diagram (Winkler 1954).

The influence of different quartz grain size therefore remained open.

During the last years the whole mineral triangle was reinvestigated using a much finer quartz as corner component. The following chapters compare both triangles with respect to ceramic properties and phase transformations.

EXPERIMENTS

The experimental program was the same for both triangles, in each of the triangles a net of 20 points was investigated.

All samples were fired up to 1200 °C in a simulated tunnel kiln program. The bending strength was measured in samples according to DIN 51030. Water adsorption (open porosity) and total shrinkage were measured in samples according to DIN 51056. Transformations of mineral phases were determined by X-ray diffraction and microscopy.

RESULTS

THE TRIANGLE WITH COARSE QUARTZ

The following corner components were used in the experiments:

Illite	Eisenberg clay	I (90) K (6) Q (4)
Kaolinite	Schnaittenbach kaolin	K (93) I (5) Q (2)
Quartz	Grasleben quartz	Q (100)

Grain size distribution of quartz		
equivalent diameter (µm)		%
< 2		1,7
2 - 6,3		2,5
6,3 - 20		9,7
20 - 63		27,1
63 - 200		54,3
> 200		4,7

The triangle may be divided into two parts, separated by a line corresponding to 60% illite in the raw mixtures.

In the range of industrial firing temperatures for brick products (1000-1100 °C) the field below 60% illite is characterised by a steady and equal directed course of the ceramic properties. Increasing content of illite in the raw mixtures is accompanied by increasing strength and shrinkage and by decreasing open porosity.

The maximum of strength is found around the points I (60) K (40) and I (60) K (20) Q (20), the minimum of water adsorption between the points I (80) K (20) - I (80) Q (20) - I (60) K (20) Q (20) - I (60) K (40).

The increase of strength with increasing illite content following the kaolinite - illite - side of the triangle is more significant than the same effect along the opposite quartz - illite - side. The new formed mullite from kaolinite and melt causes higher values for bending strength than the remaining quartz not dissolved in the melt at the opposite side of the triangle.

The field above 60% illite shows anomalies especially at and above 1100 °C. Secondary porosity and dilatation (blowing) caused by degasification of the melt arising from illite destruction is found as well as break down of strength.

THE TRIANGLE WITH FINE QUARTZ

Corner components:

Illite	Eisenberg clay	I (90) K (6) Q (4)
Kaolinite	Schnaittenbach kaolin	K (93) I (5) Q (2)
Quartz	Frechen quartz	Q (100)

Grain size distribution of quartz		
equivalent diameter (μm)		%
< 2		21
2 - 6,3		8
6,3 - 20		27
20 - 63		24
63 - 200		20
> 200		0

In this triangle the anomal field is reduced to illite contents above 80% in the raw mixtures.

The whole triangle below 80% illite is characterised by the same steady and equal directed course of ceramic properties which was found in the triangle with coarse quartz as corner component.

Fine quartz generally causes higher values of bending strength with a maximum around the points I (80) Q (20) and I (60) K (20) Q (20). The reason is the higher solubility of fine quartz in the melt with the consequence of increasing viscosity of the melt and smaller quartz grains remaining and offering less weak points at the grain boundaries. Higher viscosity of the melt further leads to less mullite forming from kaolinite and melt. Therefore mullite plays a less important role in this triangle.

The minimum of water adsorption is found in the field between the points I (60) K (40) - I (40) K (40) Q (20) - I (60) K (40) - I (100).

Blowing effects seem to be blocked by higher viscosity of the melt enriched with SiO_2 in the field between 60 and 80% illite in the raw mixtures.

It further should be mentioned, that comparative experiments with ultrafine quartz along the line quartz - illite resulted in lower values of bending strength. This only happens if quartz goes into solution almost totally and the ceramic body consists almost completely of inhomogenous glass.

REFERENCES

- BABCZINSKI, L., URBAN, H. (1983): Das Mineraldreieck Illit-Kaolinit-Quarz. (Keramische Eigenschaften und Phasenumwandlungen bis 1200 °C). - Keram. Z., 35, 506-510.
- URBAN, H., BABCZINSKI, L., WEDEMEYER, U. (1985): Illite chemistry and ceramic properties of bricks. - 5th meeting of the European clay groups, Prague, 1983, 529-533.
- WINKLER, H.G.F. (1954): Bedeutung der Korngrößenverteilung und des Mineralbestandes für die Herstellung grobkeramischer Erzeugnisse. - Ber. DKG, 31, 337-343.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

FORMATION OF REGULAR INTERSTRATIFICATION IN POTASSIUM DEPLETED TRIOCTAHEDRAL MICA - VERMICULITES

U. UTERMANN AND H. GRAF V. REICHENBACH

Institut für Bodenkunde und Sonderforschungsbereich 173,
Universität Hannover, FRG

The formation of regular 1 : 1 mica - vermiculite interstratification as exhibited by "hydrobiotite" is generally attributed to the interaction between the orientation of lattice hydroxyl groups and bonding conditions of interlayer cations. However, the mechanism of the generation of order by cation exchange in a multilayer system is still unexplained.

Our experiments are concerned with the consequences of oxidation of structural ferrous iron for the formation of interstratification.

The 6 - 20 μm fraction of a biotite from Miask, Ural, was transformed to vermiculite by exchanging interlayer potassium with either magnesium or barium in a repeated batch type exchange procedure. Only traces of regular interstratification could be observed in the X-ray diffraction patterns of samples taken during the biotite-vermiculite transformation. However, by adding K - Mg mixed solutions in a suitable proportion to the K-depleted Mg-saturated vermiculite, a pure 1 : 1 interstratification was produced, showing only the integral series of 1.0 + 1.4 = 2.4 nm diffraction peaks in the X-ray diagram. The total iron content of the Mg-vermiculite was 20.5 % by weight with 58 % of it being in the divalent form.

In order to investigate the influence of the degree of oxidation upon mixed layer formation, the structural ferrous iron in minerals was oxidized by hydrogen peroxide added in different proportions.

Oxidation was performed (a) by addition of hydrogen peroxide to MgCl_2 solutions during the removal of interlayer potassium, and (b) by addition to the Mg-saturated vermiculite before replenishing it with potassium. Addition of the oxidant during potassium removal

(a) did not lead to the formation of interstratification, which could only be produced by (b) restoring interlayer potassium in vermiculite from solution.

After gradual oxidation of vermiculites mixed layering resulting from the intake of potassium into the interlayers became increasingly random at the expense of regular interstratification. At the lowest content of ferrous iron (1.24 % by weight) X-ray diffraction of K-treated samples revealed only a decrease of basal spacings from 1.46 to 13.5 nm with slight line broadening of the 001 reflections. The mineral remained in the expanded state even though the equivalent ratio between exchange capacity and the highest addition of potassium was in the order of 1 : 1 000.

The observed phenomena are discussed as being affected by the interaction of contractive and expansive forces depending on size and hydration energies of the ions involved in interlayer exchange reactions and on the distribution of charge within the silicate layer.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GRACOS: A COMPUTER PROGRAM FOR GRAPHICAL REPRESENTATION OF CRYSTAL STRUCTURES.

A. VEGAS AND E. VILA

Instituto de Química Inorgánica "Elhuyar".C.S.I.C. Serrano 113.
28006 Madrid (Spain).

"GRACOS" is a set of programs written in interpreted and compiled GWBASIC, for an Olivetti M-24 personal computer, with MS-DOS operating system, so that it can be also runned in another IBM compatible personal computers. It makes possible the graphical representation of crystal structures, in the stick and ball model, and has been envisaged as a usefull tool in both, research and teaching in crystallography, crystal chemistry and mineralogy, as well as in inorganic chemistry and metallurgy.

The program can create, read and modify permanent sequential files with all the information needed for graphical representation of structures. The input data are: unit cell dimensions, atomic coordinates of the asymmetric unit, symmetry operations, the limits of the x, y and z coordinates for the generation of the rest of the atomic positions, and the crystal system and centricity of the S.G. Together with this data, formula, space group and one bibliographic reference can be also stored in the permanent file.

This file serves as input for the graphical representation of the structure, projected along one crystallographic axis. To do this, the user must select the size and colour of the different atomic species.

Hereafter, the user dispose of several options:

- Rotate the structure around x, y and z, by giving the values in degrees of the rotation angles around each axis.
- Draw chemical bonds between selected atoms within the given limits in Å.
- Project the structure on a plane defined by three given points.

- Perspective drawing of the structure.
- Obtain a hard-copy in the printer.

Within the above options, the user can also modify the actual drawing in the following way:

- Magnify or reduce the size of the drawing.
- Magnify or reduce the size of the atoms.
- Change the colour of the atoms (with an option for not drawing some kind of atoms).
- Erase and redrawing the unit cell edges.
- Mark the origin of the unit cell.
- Divide the computer screen in two windows, allowing to represent two different projections of the same structure or projections of two different compounds to be compared.

Hardware and software facilities will be provided for a practical check of programs system.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

Crystallinity index of illite and smectite in the bottom sediments of Adriatic Sea- Sedimentological implications

VENIALE F., CAUCIA F. and TORTELLI M.

Dipartimento di Scienze della Terra, sezione Mineralogia, Petrografia e Geochimica - Università di Pavia, Italia.

The Adriatic Sea is an oblong land-locked basin, having two main different sedimentation environments: the northern shelf (paleo-delta of the Po river) with relatively shallow water (maximum m 50-70), and the southern deep (maximum m 1,200) "fossa", separated by the "meso-fossa" with some small basins at depth of m 270-280.

Distribution patterns of heavy and light minerals, and grain-size classification indicate a mainly longitudinal dispersion in the Po paleo-delta area, whereas a transversal one is prevailing in the "fossa" (PIGORINI B., 1968: "Sources and dispersion of recent sediments in the Adriatic Sea". Marine Geol. 8, 197-229).

Among the clay minerals (VENIALE F., 1976: "Clay mineralogy of bottom sediments in the Adriatic Sea". Proc. 7th Conf. Clay Miner. Petrol. Karlovy Vary, 283-298) no significative variations have been observed for illite. Smectite and kaolinite are generally decreasing in the direction shore --> open basin in the transversal profiles, and present delta --> paleo-delta edge in the longitudinal ones. Smectite dispersal is also reworked by the stream system, especially along the Italian coast. Such distribution suggest mainly a differential mechanical sorting and/or flocculation(?). The behaviour of chlorite is ubiquitous and might be interpreted either as partial regeneration of detrital clays, or as variation of its sedimentation rate. Vermiculite and mixed-layers are absent in the nearshore sediments (and also in the fluvial discharges), appearing only off-shore and open sea-ward; therefore, aggradation processes ("incipient" smectite --> well crystallized smectite --> mixed-layers, vermiculite, chlorite) are suggested, and they are better recognizable in the southern "fossa" supplied by volcanic ashes. On other hand, the clay components appear to be mainly detrital, indicating the different source areas: eastern alpine rivers with low content of smectite, Po river (from central and western Alps, and Apenninics affluents rich in smectite), volcanic region in southern Italy.

The crystallinity index of illite and smectite has been considered in order to classify source areas and diagenetic processes after deposition. The obtained results are compared with previous sedimentological and petrographical data, and allow to distinguish discharges from: i) Po river, ii) rivers from eastern Alps, iii) southern Italy volcanic area. Some mixing effects due to current transport are actually recorded in the northern basin facing Po delta, Venice lagoon and Triest gulf, as well as in the central "meso-fossa". The same is true along the shore of the Italian coast.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SCANNING ELECTRON MICROSCOPY APPLIED TO THE STUDY OF ANCIENT POTTERY
AND CERAMICS FROM NORTHERN ITALY ARCHEOLOGICAL SITES

F. VENIALE, S. MASSA (*), M. SETTI and M. TORTELLI

Dipartimento di Scienze della Terra, Università di Pavia, Italia
sezione Mineralogia, Petrografia e Geochimica

(*)Soprintendenza Archeologica della Lombardia, Milano, Italia

A teamwork set up by the mentioned scientific and archeological organisations is carrying out a co-operative programme concerning pottery and ceramic manufactures (amphorae, jars, dairy filters, jugs, basins, bowles, pans, lids, African red slip wares, Italian "terra sigillata", "terracotta" ornaments) from various archeological sites, historical monuments and buildings belonging to pre-late Roman and Middle Age, Renaissance and Baroque style, located in northern Italy: Milan, Parma and Brescia cities, Garda lake region, Certosa cathedral and Lomello near Pavia.

The aim of the research is to reconstructing pug mixtures, identifying raw materials provenance, inferring manufacturing technology, firing temperatures and conditions.

Among other analytical procedures (X-ray diffraction, thermal methods, thin sections under polarizing microscope, bulk and trace elements analyses) SEM observations are routinely applied.

Scanning electron microscopy (SEM) is a suitable tool for helping to understand firing conditions and manufacturing procedures.

Micro-fabric features of the clay matrix, reactions with coarse grains and neofomed phases, etc. can allow detailed informations concerning the nature of the processes occurred within a ceramic body.

Size and shape of clay particles in the matrix, their spatial arrangement (texture), reaction rims around shortner-chamotte grains, aspects of neofomation and/or decomposition phases, etc. are discussed in comparison with the results obtained by means of other analytical techniques.

Size of clay particles in the matrix is ranging from silt to clay dimension. Coarser grains of quartz, feldspar(s), mica(s), carbonate(s) and/or chamotte are both of primary origin (i.e. constituents of the used raw materials), or added as shortner of the ceramic body. Their composition and features resulted useful for identifying different provenance areas: Italian Alps and Apennines, north Africa, etc.

The spatial arrangement of clay particles is depending on manufacturing procedures: i) isoriented, especially the mica needles, near the external surface; ii) anisotropic in the core; iii) exfoliated by drying, etc.. On other hand, micro-texture is influenced by the firing temperatures which had been reached, and also by the duration of heating: i) porous, weakly cohesive for low values (450-500°C); ii) welding and sintering aspects for

temperatures around 600-700°C (within this range, chlorite-mica lamellae may be partly exfoliated); iii) vitrified and secondary alveolar, for heating at 750°C and higher, when also new-formed phases (as cristobalite, plagioclase, pyroxenoids) may appear. Remobilization of calcite, as "patches" or veinlets, has also been observed.

The presence of the so-called "black-heart" is also accompanied by different aspects of the clayey matrix: i) voids filled by Fe-oxy-hydroxides on the border, whereas the texture is more porous in the core.

Reaction rims around the coarser shortner-chamotte grains are appearing only in ceramic bodies fired at relatively high temperature (> 700°C). They show various aspects depending on the mineralogy: "corrosion" of carbonates, melting of micas, homogenization of twinned plagioclases, etc..

Such kind of observations allow to understanding manufacturing techniques (homogenization-depuration of the pug mixture, reducing-oxidizing and firing conditions), technological properties (hardness, imbibition-evaporation ratio), decay behaviour under frost-weathering-pollution agents, mobility of soluble salts and mechanical stress due to their precipitation, location and activity of micro-organisms.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

PETROLOGICAL AND TECHNOLOGICAL STUDY OF CLAYS FROM NORTHERN GREECE

V. VENTURI¹ AND C. FIORI²

¹Geoceramic Researches, Monte S. Pietro (BO). Italy

²C.N.R., Istituto di Recherche Tecnologiche per la Ceramica,
Via Granaloro 64, 48018 Faenza. Italy

Some wide clayish deposits of Northern Greece (Makedonia and Chalkidiki) were studied with the objective of evaluating their exploitation for ceramic tile production. After a geological and morphological description of the sedimentary formations to which these deposits are associated, data are given as regards chemical, mineralogical and grain size characteristics of seven clay materials.

The chemical data were employed for rational analysis by a computerized method; in such a way, the quantitative mineralogical composition of the samples, as reported in Table 1, was obtained. The thermal analyses carried out are: thermogravimetric (T.G.), differential thermal (D.T.A) and dilatometric. These analyses characterize especially the mineralogical association of quartz-illite-chlorite-montmorillonite-Na feldspar. The carbonate contents vary from 0 to 24%.

Laboratory tests were also carried out to examine the physical-ceramic behaviour of the single materials. Data regarding technological parameters of samples of green ware, obtained from wet-ground raw material and formed by dry-pressing, and of the same samples after firing are reported. The differences of physical-ceramic behaviour among the examined materials are remarkable. Some of them show very high plasticity (samples 1 and 2) and some show a very low one (samples 5 and 7).

Table 1

	1	2	3	4	5	6	7
quartz	33	22	20	28	32	23	24
Na-feldspar	16	9	7	16	1	20	1
K-feldspar	1	-	-	1	-	6	-
calcite	5	8	8	8	4	-	24
ankerite	-	4	-	-	-	-	-
illite + muscovite	26	25	22	23	16	24	38
chlorite	4	12	20	9	29	4	7
montmorillonite	10	14	15	10	11	17	-
Fe oxides	4	4	6	4	5	3	4
accessories	1	2	2	1	2	3	2

After firing at 1030 °C some sample are still expanding (samples 2 and 7), or practically don't show any change (samples 1 and 3), while some are strongly shrinking (samples 5 and 6). The color of the fired bodies varies from red to pink and beige.

The most interesting materials (samples 1 and 3) show water absorption lower than 20%, good bending strength and such a cubic expansion coefficient that they fit to a wide range of glazes. They are suitable in order to be used in glazed porous bodies mixtures ("cottoforte" and "maiolica" types) for paving and lining.

Excessive fine grain size (as in sample 5) or too high carbonate content (as in sample 7) are negative features. Also high portion of coarse grains, particularly of micas, is an unsuitable characteristic (as in sample 4). These negative characteristics don't exclude the industrial application of the corresponding clays in mixtures with other raw materials.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SEQUENCE OF THE PROCESSES OF GEOCHEMICAL WEATHERING IN THE NORTHERN

PIEDMONT OF THE CENTRAL SYSTEM (SALAMANCA, SPAIN).

M.A. VICENTE*, E. MOLINA** AND M.P. GARCIA-RODRIGUEZ*

* Centro de Edafología y Biología Aplicada de Salamanca.C.S.I.C.
Apdo 257 (Spain).

** Facultad de Ciencias. Universidad de Salamanca (Spain).

The zone studied is situated in the Northern Piedmont of the Central System with an altitude about 950 metres above sea level. In the zone it is possible to identify a basement of Paleozoic shales, quartzites and sandstones over which two geological units of different ages were developed: red alluvial fans from the Neogene and Raña deposits which have eroded the former. A study was made of the processes of weathering from the socle to the surface of the Raña, paying special attention on the importance of clays in such processes.

The shales of the basement exhibits two levels of weathering:

- The lower level of fresh green shale (10 YR 5/1), formed by ferrous chlorite (bavalite) and serpentine (berthierine), mica (mainly dioctahedral), quartz and feldspars.

- The upper level, formed of a reddened altered shale (10 R 4/4) composed of mica, kaolinite of low crystalline grade, quartz, feldspar and iron oxides (goethite and hematites).

Over this basement there is a Neogene alluvial fan, forming a conglomerate of quartzites and sandstones with a clay matrix. The set is red in colour (10 R 4/6), mottled in white (7.5 YR 7/0) that affects both the matrix and pebbles.

Studies by X-rays, DTA and TGA of the materials reveal that this conglomerate is composed, in its red part, of the following: quartz, mica, kaolinite, and iron oxides (hematites and goethite). The white mottling is localized in microcracks and fissures and is composed of quartz, kaolinite, and mica; part of the micas of

the white matrix are slightly vermiculitized.

The upper part of the same alluvial fan is affected by a weathering process that has given rise to a change in the colour of the materials towards an ochre (5 YR 5/8) and a disaggregation of the sandstones. Both in the case of the pebbles and the matrix, the major components, from greater to lesser proportions are as follows: quartz, mica, kaolinite and goethite; a white mottling is also found at this level.

The Raña is situated unconformably over these materials. This formation is assumed to be of Villafranchian age and in the zone studied has a thickness of some 2-3 metres. It is composed of a conglomerate of quartzites and sandstones tamped within a fundamentally silty-sandy matrix of variable colour.

Two horizons may be distinguished in the Raña:

- The lower one with pebbles whose major components are quartz, mica (to a small extent vermiculitized), kaolinite and goethite. The matrix has a similar composition but with a higher proportion of goethite.

- The upper horizon: formed by pebbles in which it is possible to observe a zoning from the interior (colour 5 YR 6/6) to the exterior (10 R 3/1) of them. The inner part is formed of quartz and lesser quantities of mica, kaolinite, feldspars, goethite and hematites. The outer part is mainly composed of quartz and hematites.

In summary, the following may be observed in this profile:

- 1.- A paleoweathering over the basement involving the destruction of primary materials with iron (chlorites and serpentines), together with the formation of kaolinites and iron oxides.
- 2.- Sedimentation of Neogene alluvial fans.
- 3.- Ochre weathering over the Neogene alluvial fans that has produced a complete arenization of the sandy clasts and the disappearance of hematites.
- 4.- Erosion of these alluvial fans and sedimentation of the Raña.
- 5.- Associated with the Raña, a process of weathering possibly due to oscillations of the earlier water tables, which in the lower part has given rise to a slight vermiculization of part of the micas and in the upper part to a massive evolution of

the iron oxides to hematites.

- 6.- In all the levels, excepting the upper part of the Raña, it is possible to observe a white mottling which appears to be the last of the processes studied and that has given rise to a strong leaching of iron and a small degree of evolution of the micas.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**COMPUTER PROGRAM FOR ANALYSING INTERSTRATIFIED STRUCTURES BY FOURIER
TRANSFORM BASED METHODS.**

E. VILA AND A. RUIZ AMIL

Instituto de Química Inorgánica "Elhuyar". C.S.I.C. Serrano, 113. 28006
Madrid. (Spain).

In this paper is described the preparation of a computer program (named INTER), written in GW BASIC (interpreted and compiled) for an Olivetti M-24 personal computer, with MS-DOS operating system and may also be runned in an IBM compatible personal computer. This program has been made for the analysis of two components interstratified structures by two different Fourier transform based methods:

1st one consist in the calculation of the X-ray diffraction intensity function and, in the 2th one (direct method), the distribution function of interlayer distances is calculated.

CALCULATION OF X-RAY DIFFRACTION INTENSITY FUNCTION METHOD.

The X-ray diffraction intensity is given by $I = \phi F^2 \Theta$, being ϕ the "mixing function"; F^2 the squared modulus of layer structure factor and Θ the angular factor. ϕ and F^2 are functions of the reciprocal spacing ($r^* = 2 \sin \theta / \lambda$), whereas Θ is a function of θ (Bragg angle) and depends on the experimental technique.

The INTER program allows to obtain ϕ , F^2 and Θ as functions of r^* . Calculation have to cover an r^* range from 0.001-0.5 Å^{-1} . and of 0.002 Å^{-1} between 0.5-1 Å^{-1} . The time required to calculate a diffraction intensity function, I , for the 750 resultant values of r^* is about 1-10 minutes.

a) "The mixing function", ϕ . The called "mixing function" represents the effect of the mixing of layer on the diffraction intensities. Mac Ewan's method consists of the calculation of the Fourier transform for a given distribution:

$$\phi(r^*) = K \sum_{n=1}^N \sigma(R_n) \cos 2\pi r^* R_n$$

where $\sigma(R_n)$ is the frequency of the occurrence in the crystallites of the interlayer distances R_n ; N is the total number of layer per particle and r^* is the reciprocal spacing.

For the particular case in which only two layer A and B are present, Φ depends on its fundamental spacings d_A , d_B and on the probability coefficients p_A , p_B , p_{AA} , p_{AB} , p_{BA} and p_{BB} .

It is only necessary to input into the INTER program the expected values of p_A and p_{AA} coefficients and d_A and d_B spacings. The program generates $\sigma(R_n)$ from p_A and p_{AA} and R_n from d_A and d_B spacings.

b) The layer structure factor. This factor is given by expression:

$$F_j = \sum_j f_j(r^*) \exp(2\pi i r^* z_j) \quad \text{and} \\ f_j = \sum a_i \exp(+b_i r^{*2} / 4) + c$$

a_i , b_i and c being characteristic coefficients of j th atom.

To calculate F of any layer it is only necessary to input in the INTER program the values of z_j coordinate and amount, for each class of atoms. This program calculates the f_j values for each atom from the ASF, DAT file; in this file are stored the coefficients a_i , b_i and c for the most usually class of atoms.

This data file may be listed, modified and increased by means of another program named TFA.

The structure factor for the mixed layer is $F = (F_A)^{p_A} (F_B)^{p_B}$. F_A and F_B being structures factors for the A and B layer, respectively, calculated by the above indicated expression for F , occurring in proportion p_A and p_B ($p_B = 1 - p_A$).

The function F may be corrected for temperature according to $F = F |\exp(-B r^{*2} / 4)|$, where B is the thermic coefficient.

The INTER program calculates F according to earlier expressions, being p_A the same value used to obtain the mixing function and B the thermic coefficient input.

c) The angular factor Θ . The INTER program use the angular factor (Lorentz polarization and geometrical factors) according to the equation $\Theta = f_c \Theta_c + f_p \Theta_p$, being f_c and f_p the proportion of Θ_c (for single crystal) and Θ_p (random powder), and $f_c + f_p = 1$.

It is only necessary to input in the program the radiation used in the X-ray diffraction diagram and the factor f_c .

DIRECT METHOD

The distribution function $W(R)$ of interlayer distances, R , is obtained from the observed diffraction intensities, I_s , and the basal spacing, d_s , by means of a Fourier transform:

$$W(R) = a/\pi \sum_s (I_s / \Theta_s^2 F_s^2) \cos 2\pi R/d_s$$

where Θ_s and F_s^2 are the values of the Θ and F^2 function at the position d_s .

The INTER program calculates the $W(R)$ function from d_s and I_s values.

In this program, the direct method is used, principally, in a preliminary survey of X-ray diffraction diagrams and gives a very valuable information about the possible values of p_A , p_{AA} , p_A and d_B . They can be used as starting inputs to calculate the X-ray diffraction intensity function.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

COMPUTER METHOD FOR QUALITATIVE AND SEMIQUANTITATIVE X-RAY FLUORESCENCE
ANALYSIS OF GEOLOGICAL SAMPLES.

E. VILA, J. BERMUDEZ-POLONIO AND M.T. GARCIA-GONZALEZ*

Instituto de Química Inorgánica "Elhuyar". C.S.I.C. Serrano 113.
28006 Madrid (Spain).

*Instituto de Edafología. C.S.I.C. Serrano 115 dup. 28006 Madrid
(Spain).

The X-ray fluorescence spectrometry is a well known technique for the quantitative analysis of large series of geological samples. Moreover, this technique is extremely well suited to qualitative and semiquantitative analysis of them, but its systematic application is rather limited, mainly in the wavelength-dispersive X-ray spectrometry, because of the long time required for the spectra interpretation step. This process can be simplified and accelerated by means of micro-computers.

In this paper we describe the preparation of a set of programs which might allow the use of small-capacity computers for this type of analysis without being on line with the spectrometer. In this method, the analyses are carried out starting from the spectra taken either from the spectrometer recorder or directly by the computer if this option is available.

The programs have been written in GWBASIC for an Olivetti M-24 personal computer (with MS-DOS operating system and may also be runned in an IBM compatible personal computer), and their main functions are: Input the spectra data. The data corresponding to the sample to be analysed are stored in a sequential "Sample Data File" and associated Subfiles. In the Sample Data File, the sample identification, X-ray tube used, number of recorded spectra and analysing crystals used, order of spectra analysis, etc., are stored. In the Subfiles, all data corresponding to each recorded spectrum and the results obtained in its qualitative analysis are stored. The X-ray data (peak position and intensity) can be loaded manually or automatically (only if the

computer can receive the intensity values obtained in the spectrum scanning). The FXAI program allows the automatic loading of intensity values of any X-ray spectrometer directly by means of a DT2805 analog and digital I/O board; this board allows analog inputs (i.e. the electric pulses that arrive to recorder) with no other interface.

Preparation of an X-ray emission lines and absorption edges table.

The FXT program allows to prepare and use the FXTAB.DAT file. In this data file, the Ka, Ka1, Ka2, Kb, Kb1, Kb2, La, La1, La2, Lb1, Lb2, Lb3, Lb4, Lb5, Lb6, Lg1, Lg2, Lg3, Ll, Ln, Ma1, Ma2, Ma and Mb emission lines (of orders 1 to 5, and relative intensity ≥ 1) and the AK, AL1, AL2 and AL3 absorption edges, whose wavelengths range between 0.2 and 25 Å, have been stored for the elements of atomic numbers 9 to 83, 90 and 92. The lines (emission lines and absorption edges) are arranged at increasing wavelength values.

Qualitative analysis. The FXQUAL program is designed for the qualitative analysis of fluorescence spectra recorded with any analysing crystal and using any wavelength-dispersive X-ray spectrometer. The analysis is carried out in four stages: (1) peak line assignment; (2) identification of the elements; (3) setting up the selection criteria for each identified element; and (4) final results list.

Semiquantitative analysis. The FXSQ program permits to compare, in the computer display, the recorded wavelength spectra of the unknown sample and prospective known materials.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAY MINERALOGY IN TECTOSEDIMENTARY ANALYSIS OF SOUTHERN SECTOR OF TER
TIARY EBRO BASIN (SPAIN)

J. VILLENNA^(*); F. LOPEZ-AGUAYO^(**); G. PARDO^(*); A. PEREZ^(*); A. MU-
ÑOZ^(*); J. GONZALEZ MARTINEZ^(**); J.M. GONZALEZ LOPEZ^(**) and C. FER-
NANDEZ-NIETO^(**).

(*) Estratigrafía. Fac. Ciencias. Univ. Zaragoza 50009 (Spain).

(**) Cristalografía y Mineralogía. Fac. Ciencias. Univ. Zaragoza 50009
(Spain).

The tectosedimentary analysis of this sector of the Ebro basin has shown the existence of various Tectosedimentary Units (T.S.U.) according to MEGIAS (1982), bounded by their correspondent sedimentary breaks. The three T.S.U. correlated with those established by PEREZ et al. (1985) in the Huerva river area, are studied.

From the sedimentological point of view, these T.S.U. have been deposited in alluvial fan environments and lacustrine associated areas. The lateral and vertical evolution of the latter are a consequence of the space-temporal variations in the depositional system, related with the tectonic activity on the basin margins.

The main mineralogical association in these materials consists of: quartz, calcite, dolomite, gypsum and clay minerals. Among these last ones there appear systematically: illite, smectites and chlorite, while less frequent are: kaolinite, palygorskite, sepiolite and interstratified clay minerals. The mineralogy of each T.S.U. changes laterally and vertically according to the spatial distribution of the sedimentary subenvironments, the source-area variations and the progradation-retrogradation processes which define the tectosedimentary evolution.

Lower Unit. It is a complex T.S.U. with cyclic evolution. The lower hemicycle, with positive evolution, presents sediments with characteristic facies of middle to distal alluvial fan environments associated with palustrine-lacustrine facies.

The clay minerals of this set are: illite, smectites, chlorite

and kaolinite. Vertical variations in the content of these minerals can be observed, which conform with the positive evolution of this hemicycle.

The upper hemicycle, with negative evolution, responds to a succession of distal to proximal facies of an alluvial fan. From the "Torcas" profile toward the E. the relative position of the studied profiles corresponds with progressively more distal alluvial fan domains.

The change of sign of this hemicycle is clearly indicated by the important increase in inherited clay minerals. In the "Torcas" profile it is interesting to emphasize the systematic increase of kaolinite, which can be correlated with a source-area change.

In the eastern extreme (Sastago profile) this hemicycle culminates with an interval of positive evolution. The occurrence of smectites, in important amounts, confirms the evolution change of this interval.

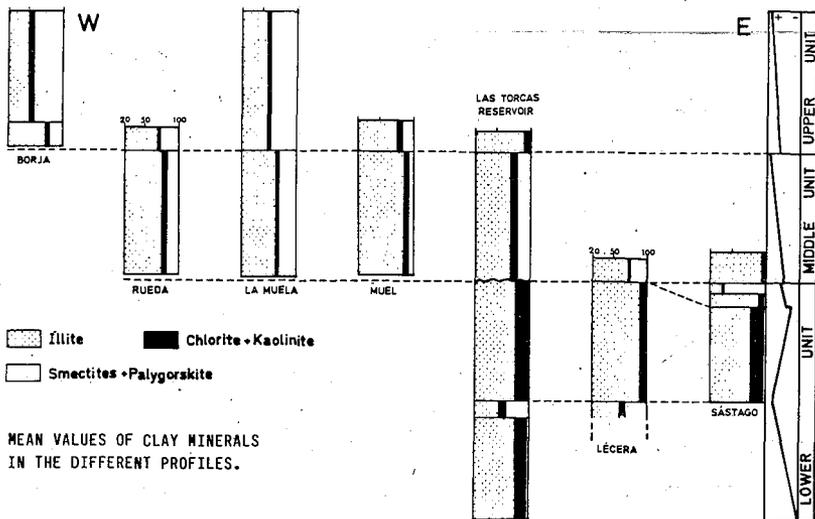
Middle Unit. It presents a positive evolution. The studied series correspond, in general, with a succession of lutitic and chemically precipitated sediments, which can be assimilated to distal sectors of alluvial fans and playa-lake areas.

The clay minerals association in this unit is fairly homogeneous, except for the "Sastago" and "Muel" profiles, whose content in smectites is clearly smaller. This variation should be related with a different relative position of these profiles in the depositional systems.

Upper Unit. It corresponds to a sequence of positive evolution built mainly by carbonatic sediments characteristic of palustrine and lacustrine domains.

In this unit two clay minerals associations, with a different percentage of smectites, can be distinguished. In the more western profile both associations can be observed, confirming the evolution type described for this unit. The smectites absence in the "Torcas" profile, together with the different illite crystallite size (313 \AA), confirms a more proximal position of this profile.

This work has been supported by the nº 826/84 project of CAICYT.



BIBLIOGRAPHY

Megias, A.G. (1982) Introducción al análisis tectosedimentario: Aplicación al estudio dinámico de cuencas. Actas V Cong. Latinoamericano de Geología. Argentina, 1: 385-402.

Pérez, A.; Azanza, B.; Cuenca, G.; Pardo, G. y Villena, J. (1985). Nuevos datos estratigráficos y paleontológicos sobre el Terciario del borde meridional de la Depresión del Ebro (provincia de Zaragoza). Estudios Geológicos. 41: 405-411.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

HIGH RESOLUTION ELECTRON MICROGRAPHS AND MICROCRYSTALLINITY OF
PSEUDOBOEHMITES

A. VIOLANTE, P. VIOLANTE and T. HENMI*

Institute of Agricultural Chemistry, University of Naples (Italy)

*Department of Agricultural Chemistry, Ehime University (Japan)

The primary purpose of this work was to study the morphology and microcrystallinity of pseudoboehmites by high resolution electron microscopy and electron diffraction.

Recent research data (2, 3) revealed that the sequence of the relative effectiveness of certain perturbing organic anions, commonly present in nature, in promoting the formation of pseudoboehmites over $Al(OH)_3$ polymorphs is as follows: phthalate = succinate < glutamate < aspartate < salicylate = malate < tannate < citrate < tartrate.

The optimal ranges of the ligand/Al molar ratios for the formation of pseudoboehmites at initial pH 8.0 vary from 0.005 to 0.015 for tartrate and from 7.0 to 14.0 for phthalate or succinate.

Pseudoboehmites were synthesized at room temperature at pH values from 5.0 to 8.0 by adding 0.1 M NaOH to stock solutions of $AlCl_3$ in the individual presence of aspartic, tannic, citric or tartaric acid. The final Al concentration was 5×10^{-3} M (Table 1) (3).

The electron micrographs showed that all the samples but J5 had fibrous morphology. However, there were differences in the degree of fiber development depending on the samples. Highly developed fibers were evident in the J3A sample. Many stripes were recognized in J3A which frequently appeared to be double lines with a separation of about 40Å. This suggests that the sample was mainly composed of very fine tubes resembling imogolite (1). The fibers were not so well developed in the J3B and J3C samples.

TABLE 1 - Pseudoboehmite samples formed in the presence of selected organic ligands, at different ligand/Al molar ratio (R) and initial pH

Sample	Ligand	R	Initial pH
J1	Aspartic acid	0.1	8.0
J2	Tannic acid	0.01	8.0
J3A	Citric acid	0.01	5.0
J3B	Citric acid	0.01	6.0
J3C	Citric acid	0.01	7.0
J3D	Citric acid	0.01	8.0
J4	Citric acid	0.02	8.0
J5	Citric acid	0.05	8.0
J6	Tartaric acid	0.01	8.0

In addition to fibers, thin plate-shaped objects, which showed strand pattern, resembling lattice image (the objects might be assemblage of poorly developed tubes) were found in the J3D and J4 samples. Only aggregates of fine particles appeared in the J5 sample. The morphological change from the fibers to the fine particles seems to be due to an increase in the concentration of citric acid.

Variations were also found in length and amount of the fibers and in the development of the plate-shaped objects with difference in the kind of ligands (J1, J2, J3D, J6).

Electron diffractions of all the samples showed d spacings which are included in the d spacings of boehmite (Table 2).

The relative intensity of the electron diffractions rings was different from one sample to another. Some samples lacked some diffraction rings indicating a variation of crystallinity depending on the synthesis conditions such as kind and concentration of ligands and initial pH values. The J5 sample had only two very diffuse diffraction rings with very weak or weak intensity. This indicates that the sample was very poorly ordered pseudoboehmite.

TABLE 2 - Electron diffraction analysis of pseudo-boehmite samples

Sample	d spacings Å								
J1	0.93 (vw)	1.13 (w)	1.31 (w)	1.44 (s)	1.74 (s)	2.37 (md)	2.82 (m)	3.15 (sd)	4.38 (s)
J2	0.94 (vw)	1.13 (w)	1.31 (vw)	1.44 (m)		1.85 (s)		3.16 (vd)	
J3A		1.14 (w)		1.44 (s)		1.86 (s)		3.16 (w)	
J3B		1.13 (w)		1.43 (sd)		1.86 (md)			
J3C		1.14 (vw)		1.43 (sd)		1.86 (sd)	2.59 (vsd)		
J3D		1.12 (wd)	1.30 (vwd)	1.43 (sd)		1.86 (sd)	2.34 (md)	3.11 (sd)	
J4		1.13 (wd)	1.30 (vwd)	1.42 (sd)		1.84 (sd)	2.35 (md)	3.17 (sd)	
J5				1.42 (vwvd)		2.35 (vwd)			
J6	0.93 (vw)	1.12 (m)	1.30 (w)	1.42 (s)		1.85 (s)	2.30 (w)	3.17 (m)	

v: very - s: strong - w: weak - m: middle - d: diffuse

The data obtained in the present study indicate that pseudo-boehmite samples formed in the presence of selected perturbing organic ligands differ significantly in their morphology and microcrystallinity.

REFERENCES

- 1) Farmer, V.C. and Fraser, A.R. (1979). Proc. Int. Clay Conf. 6th 1979:547-553.
- 2) Violante, A. and Violante, P. (1980). Clays Clay Miner. 28:425-434.
- 3) Violante, A. and Huang, P.M. (1984). Soil Sci. Soc. Am. J. 48:1193-1201.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

**SPECIATION OF METALS IN CLAYEY SEDIMENTS OF THE BOTHNIAN SEA:
SUCCESSIVE EXTRACTION AND DISSOLUTION KINETICS STUDY**

A. Vuorinen

Department of Geology, University of Helsinki,
P.O. Box 115, SF-00171 Helsinki, Finland

DESCRIPTION OF THE SEDIMENT CORE

A sediment core taken from the Bothnian Sea (61° 14.5'N, 20° 43.5'W, water depth 80m) was investigated.

The lowest part of the core consists of glacial till derived mainly from local Cambrian glauconitic sandstone and from Ordovician limestone (30.6% CaCO₃ and 1.17% MgCO₃). This is followed upwards by varved silt and clay accumulated during the marine Yoldia stage; black monosulphide-bearing clay of the lower fresh-water Ancyclus stage; pyrite-bearing homogeneous clay of the upper Ancyclus stage; greenish gyttja of the marine Litorina stage and finally by gyttja-banded clay which gradually changes into homogeneous sulphide-bearing clay.

The core was previously investigated for clay mineralogy and chemistry of sediments and pore water by L. Carlson (1983).

ANALYTICAL METHODS

The samples were kept in dark and at +4°C before analysis. The samples with a natural moisture content were subjected to the following successive extraction and dissolution kinetics study:

NH₄Ac (pH 7.3, 72 h, 30°C) for sample base and acid contents and for exchangeable and loosely bound metals

NH₄Ac (pH 4.8, 30°C) for sorbed and loosely bound metals and for carbonates

(10, 30, 60, 120 and 240 min)

HX1-HAc (30°C) for reducible loosely and moderately bound metals and Fe oxyhydroxides

(10, 40, 160, 320 and 640 min)

HX1-HAc (60°C, 6h) for reducible moderately bound and moderately bound metals of clay minerals

NaClO (60°C, 18 h, pH 13) for organically bound metals

NH₄Ac: 1 M ammonium acetate; HX1-HAc: 1 M hydroxylammonium chloride plus 2 M acetic acid; NaClO: 1 M sodium hypochlorite

The NH_4Ac extractions were performed under argon atmosphere. The concentrations of Na, K, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn and Pb in the extractants were analysed by flame-AAS methods (Perkin Elmer 403).

The sample base and acid contents were determined by measuring the pH of the NH_4Ac extractants (initial pH 7.3) and by reading the base or acid content value corresponding to mM NaOH or H_2SO_4 from an experimental diagram that was obtained by adding corresponding amounts of NaOH or H_2SO_4 to the blank extractant.

The relative chlorophyll content was determined by extracting the sample for 72 h with acetone and by measuring the absorbance at 670.8 nm after centrifugation (20 min, 3500 r/min). For more details about methods see Vuorinen et al. (1986).

RESULTS AND DISCUSSION

Iron and heavy metals (Co, Ni, Cu and Zn) were generally in moderately bound and silicate-bound forms in the sediments of the marine Yoldia stage. In contrast, a considerable proportion of Na, K, Mg and Ca was in exchangeable, sorbed and loosely bound forms. Further, the content of sorbed cations decreased in the sediments of the fresh-water Ancylus stage. The mode of occurrence of the metals is considered to reflect chemical equilibrium in the clayey sediments of varying salinity. The variation in salinity was reflected very clearly by the cations sorbed in different sites of clay minerals.

Owing to autochthonous phytoplankton production and river-borne colloidal organic matter to the Bothnian Sea, the sample base content, corresponding to about 10 mM NaOH per 1 g of sample in till, vanished and the acid content increased during the upper Yoldia stage. It continued to increase and at the end of the Ancylus stage it corresponded to ca. 13 mM H_2SO_4 per 1 g of sample. Framboidal pyrite spherules with marcasite margins have been identified from analogous sediments of the upper Ancylus stage of the Bothnian Sea. The formation of marcasite has been attributed to increased acidity of the sediments (Papunen 1968). However, the measured acidity in this study seems to be higher than the original one due to oxidation of sulphides during storing of the samples.

Loosely bound and sorbed forms of heavy metals increased in the sediments of the lower Ancylus stage as a consequence of elevated biological activity and biogeochemical processes. In particular, sorbed forms of Fe and exchangeable forms of Co, Ni and Zn increased. Cations associated with higher salinity have obviously caused flocculation of Fe, colloidal organic matter and Cu in association with Ni, Zn and Co (cf. Sholkovitz 1978). The flocculation was very spontaneous at the beginning of the marine Litorina stage. Successive extraction gave the following metal contents for these sediments: Fe 2.8%, Cu 88, Zn 85, Ni 50.9 and Co 11.9 mg/kg of dry sample. These were the maximum contents of the core, and

the order of organically bound metals was $\text{Cu} > \text{Fe} > \text{Ni} > \text{Zn}$, which is in agreement with the affinities of the metals for fulvic acid (Schnitzer and Skinner 1967). The relative chlorophyll content also showed a maximum (about 8 times the values of the upper core) in these sediments as did the sample acid content (corresponding to 25 mM H_2SO_4 per 1 g of sample).

The contents of loosely and moderately bound Na and Mg increased at a depth of 160-210 cm, reflecting an increase in salinity. Maxima in the contents of Co, Ni and Zn at this depth were evidently caused by flocculation of colloidal organic matter in association with the metals.

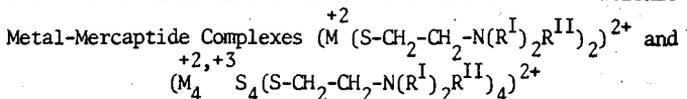
Exchangeable and sorbed forms of Ca had a distinct maximum at a depth of 207 cm in the sediments of the lower Littorina stage. Maxima of sorbed and moderately bound Mn and moderately and organically bound Pb were in association with this maximum of Ca.

In general, the contents of loosely and moderately bound Na and Mg correlated well with each other and negatively with the corresponding K contents. The Ca content of the successive extraction and to a lesser extent the corresponding K content correlated negatively with the sample acid content.

REFERENCES

- Carlson, L. (1983) Mineralogical and geochemical characterization of Bothnian Sea sediments. 5th Meet. Eur. Clay Groups, August 31 - September 3, Prague, Czechoslovakia, p. 34.
- Papunen, H. (1968) On the sulfide in the sediments of the Bothnian Sea. Bull. Geol. Finland 40: 51-57.
- Schnitzer, M. and Skinner, S.I.M. (1967) Organo-metallic interactions in soils: 7. Stability constants of Pb^{++} , Ni^{++} , Mn^{++} , Co^{++} , Ca^{++} , and Mg^{++} -fulvic acid complexes. Soil Science 103,4: 247-252.
- Sholkovitz, E.R. (1978) The flocculation of dissolved Fe, Mn, Al, Cu, Co, and Cd during estuarine mixing. Earth and Planet. Sci. Lett. 41: 77-86.
- Vuorinen, A., Alhonen, P. and Suksi, J. (1986) Palaeolimnological and limngeochemical features in the sedimentary record of the polluted Lake Lippajärvi in Southern Finland. Environmental Pollution, 41 A: 323-362.

Derivatives of Montmorillonite and Beidellite with Cationic



Armin Weiss und Angelika Beck

Institut für Anorganische Chemie der Universität München
 Meiserstraße 1, 8000 München 2

Catalytic activities of interlayer cations of smectites have been a major topic in clay chemistry research during the last years. In this context the existence of ferredoxinlike intercalation complexes is of general interest. The present study deals with metal-mercaptide smectite complexes with $(M(S-CH_2-CH_2-N(R^I)_2R^{II})_2)^{2+}$ (= a) and $(M_4^{+2,+3}S_4(S-CH_2-CH_2-N(R^I)_2R^{II})_4)^{2+}$ (= b) as interlayer cations.

(a): $M^{2+} = Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb$; $R^I = -CH_3$; $R^{II} = -CH_3, n-C_8H_{17}, n-C_{10}H_{21}, n-C_{12}H_{25}, n-C_{14}H_{29}, n-C_{16}H_{33}, n-C_{18}H_{37}$.
 (b): $M^{2+} = M^{3+} = Mn, Fe, Co, Mo, V$; $R^I = -CH_3$; $R^{II} = -CH_3, n-C_8H_{17}, n-C_{10}H_{21}, n-C_{12}H_{25}, n-C_{14}H_{29}, n-C_{16}H_{33}$.

Basal spacings and lattice expansions of these complexes have been studied in detail with nitriles, alkanols and amides. Complexes of $(Hg(S-CH_2-CH_2-N(CH_3)_2R^{II})_2)^{2+}$ -montmorillonite with nitriles $n-C_xH_{2x+1}CN$ of varying chain length exhibit a linear relationship between basal spacings $d_{(x)}$ and the number of carbon atoms in the nitriles

$$d_{(x)} = a x + b \text{ (\AA)}$$

independent of the chain length of the n-alkylgroup R^{II} in the cation. a, b and the correlation coefficient r^2 are listed in table 1. a is on the average 1,22 Å and close to the theoretical value for n-alkyl chains in all-anti-conformation with the chain axis almost

perpendicular to the silicate layers. b increases with increasing chain length of R^{II} .

Table 1:

a , b and r^2 for the linear relationship $d(x) = a \cdot x + b$ (\AA) of $(\text{Hg}(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2R^{II})_2)^{2+}$ - and $(\text{Pb}(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2R^{II})_2)^{2+}$ -smectite-complexes

a) -montmorillonite-complexes with nitriles

R^{II}	a (\AA)	b (\AA)	r^2
$-\text{CH}_3$	1,11	18,55	0,9986
$n-\text{C}_8\text{H}_{17}$	1,20	19,64	0,9992
$n-\text{C}_{10}\text{H}_{21}$	1,23	21,79	0,9997
$n-\text{C}_{12}\text{H}_{25}$	1,22	24,19	0,9995
$n-\text{C}_{14}\text{H}_{29}$	1,19	26,81	0,9989
$n-\text{C}_{16}\text{H}_{33}$	1,29	36,97	0,9998
$n-\text{C}_{18}\text{H}_{37}$	1,26	38,37	0,9999

b) -beidellite-complexes with nitriles

R^{II}	a (\AA)	b (\AA)	r^2
$n-\text{C}_{10}\text{H}_{21}$	1,30	22,78	0,9996
$n-\text{C}_{16}\text{H}_{33}$	1,29	36,98	0,9998

c) -montmorillonite-complexes with acid amides

R ^{II}	a (Å)	b (Å)	r ²
-CH ₃	1,08	12,15	0,9986
n-C ₈ H ₁₇	1,27	13,77	0,9999
n-C ₁₀ H ₂₁	1,32	14,75	0,9989
n-C ₁₂ H ₂₅	1,19	17,67	0,9986
n-C ₁₄ H ₂₉	1,11	20,84	0,9992
n-C ₁₆ H ₃₃	1,19	31,83	0,9997
n-C ₁₈ H ₃₇	1,29	34,26	0,9988

d) -beidellite-complexes with acid amides

R ^{II}	a (Å)	b (Å)	r ²
n-C ₁₀ H ₂₁	1,31	17,39	0,9999
n-C ₁₆ H ₃₃	1,19	31,84	0,9997

Basal spacings of $(\text{Hg}(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\text{R}^{\text{II}})_2)^{2+}$ - and $(\text{Pb}(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\text{R}^{\text{II}})_2)^{2+}$ -smectite-complexes are identical within the experimental limit of error.

The reddish brown complexes of $(\text{Fe}_2^{\text{+2}}\text{Fe}_3^{\text{+3}}\text{S}_4(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\text{R}^{\text{II}})_4)^{2+}$ -montmorillonite are oxidized by air to $(\text{Fe}_2^{\text{+2}}\text{Fe}_3^{\text{+3}}\text{S}_4(\text{S}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\text{R}^{\text{II}})_4)^{3+}$ -montmorillonite. They can be reduced by dithionite. The redox-reaction is reversible.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

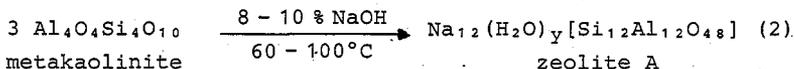
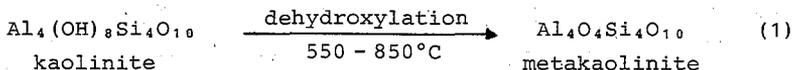
KINETIC STUDIES ON THE SYNTHESIS OF FORMED SHAPES
OF ZEOLITE A FROM KAOLINITE

ARMIN WEISS AND ELFRIEDE FRANK

Institut für Anorganische Chemie der Universität
Meiserstraße 1, 8000 München 2 (Germany).

Kaolinite can be used as a simple starting material for the synthesis of zeolite A. The reaction is extremely slow with crystallized kaolinite, but proceeds rapidly with dehydroxylated kaolinite (metakaolinite). In contrast to the zeolite synthesis from amorphous $\text{Al}(\text{OH})_3$ and $\text{SiO}_2 \cdot \text{H}_2\text{O}$ -gels the synthesis using kaolinite as starting material can be performed with preshaped bodies. This results from the high plasticity and dry strength of kaolinite bodies.

The synthesis proceeds via the following two steps:



Kinetic studies of step (2) were performed with regard to the synthesis of zeolite A spheres from preshaped spheres of kaolinite/metakaolinite. The corresponding rate law was determined and compared to the rate law of the synthesis of zeolite A powder from metakaolinite powder. Spheres and powder obey different time relationships. For spheres the experimental results are consistent with a three-dimensional diffusion-controlled process. In a linearized form the rate law can be written as

$$[1 - (1 - \alpha)^{1/3}]^2 = k (t - t_I)$$

with α : fraction of reacted material

t : reaction time

t_I : induction period

k : rate constant

(exp. cond.: concentration of NaOH: 10%).

This rate law has been shown to be valid for temperatures ranging from 62 to 92°C.

Relations between porosity of the metakaolinite bodies and reaction rate have been investigated. The total reaction remains diffusion-controlled and the rate constant k decreases with decreasing pore volume (tab. 1).

There is also a pronounced induction period at the beginning, which depends upon reaction temperature and porosity of the metakaolinite bodies (tab. 1).

tab. 1: Kinetic data of the diffusion-controlled synthesis of shaped zeolite A corresponding to equation (3).

reaction temperature [°C]	pore volume of the meta-kaolinite bodies	rate constant k [$10^{-3}h^{-1}$]	induction period t_I [h]
82	55%	3.5	4.8
82	60%	5.0	3.7
82	65%	8.9	3.3
62	65%	2.5	11.3
72	65%	6.1	6.3
92	65%	11.0	2.6

During the induction period aluminum and silicon is extracted from the "amorphous" metakaolinite structure. It could be shown that this dissolved aluminum and silicon play no significant role in a shortening of the induction period.

From systematic measurements the (apparent) activation energy of the synthesis of shaped zeolite A corresponding to equation (2) has been determined to be 300 kJ/mol.

Depending upon only minor alterations of the experimental conditions hydroxysodalite, zeolite A, zeolite P, zeolite X or mixtures thereof can be obtained.

Studies with oriented flakes (or highly distorted single crystals) as starting material were used in order to obtain information regarding topochemical relationships. These are, however, not very pronounced.

The results offer a cheap synthesis of preshaped zeolite A, P or X, which can be used for storage of solar energy, and, therefore, might contribute to modern environmental science.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

SULFATE INTERACTION WITH KAOLINITE AND GIBBSITE

RUNE WENDELBO

University of Oslo, Oslo, Norway

The purpose of the present work was to investigate sulfate ion interaction with clay minerals. This topic has attained little interest in the past, but is of interest in several aspects. The polluted acid rain contains more sulfate than pre-industrial rain, which may affect the ion-balance in soils. Sulfate is also a plant nutrient. Many investigators have studied sulfate interaction with bulk soils, and the general impression is that sulfate is retained by sesquioxides of iron and aluminum when present. Clay mineral hk-surfaces have surface functional groups similar to those on the sesquioxides, so a similar interaction with these surfaces should be expected. It seems that interaction studies with pure, well defined minerals are of more general interest than studies with bulk soils, because precise knowledge of each minerals contribution makes predictions for bulk soils possible when the mineralogy is known.

The aim of this work has been to determine whether sulfate is chemisorbed by kaolinite and gibbsite, by the formation of covalent bonds to hk-surface Al, or only retained by electrostatic attraction.

In order to limit the number of variables, the systems studied are the simplest possible; A CMS standard KGa-1 kaolinite ionexchanged with NaCl and washed free of excess salt, and a synthetic gibbsite. Equilibration with solutions of NaCl or Na₂SO₄ tagged with ³⁶Cl and ³⁵S respectively were performed in batch, centrifugated, and aliquots of the supernatant were counted in a liquid scintillation counter.

As expected it was found that at a given pH-value, more sulfate than chloride is retained by kaolinite and gibbsite. Separation of charge between bulk solution and solids is not possible, so the transfer of excess charge to the surface region in sulfate systems must be compensated by one or more of the following reactions:

- I) Co-adsorption of cations; salt retention.
- II) Desorption of other, previously adsorbed anions; ion exchange.
- III) Desorption of surface hydroxyl-groups; ligand exchange.
- IV) Charging of surface by potential determining adsorption of H^+ .
- V) Protonation of adsorbed sulfate to form bisulfate ions.

Other investigators have proposed that sulfate is chemisorbed by ligand exchange and formation of mono⁻ and bidentate surface complexes, in which a sulfate ion should be coordinated to one or two exposed lattice aluminium ions. This conclusion has primarily been based on the observation that between 1 and 2 OH^- are released for each sulfate ion retained, and the apparent similarity in shape with the phosphate ion for which this retention mechanism is well established.

In this work it was found that sulfate adsorption on kaolinite reaches equilibrium within 1 minute, and the same for isotopic exchange. Stern model approach shows a slight selectivity for sulfate over chloride, while the Gapon equation yields selectivity for chloride over sulfate. The total amount of sulfate adsorbed at a given pH exceeds the total amount of chloride, and the separation of charge by this unequal anion exchange is compensated by adsorption of H^+ .

There was found no evidence that sulfate ions form mono⁻ or bidentate surface complexes with any of the minerals investigated. This only means that the complex constants for these reactions are so small that the mechanisms do not contribute measurable to the total sulfate retention. It seems that the important mechanism for sulfate retention is electrostatic attraction, with some specificity as compared to a point charge model.

Precipitation of discrete phase $Al-SO_4$ -compounds did not take place in any of the experiments, regardless the solubility product of jurbanite was exceeded in some cases. This is probably a Kinetic problem. When K^+ was present the sulfate retention increased slightly on long time exposure, a slow reaction that could possibly be precipitation.

The following series of events can be proposed for the reaction of sodium sulfate with Na-Cl-exchanged kaolinite hk-surface, when pH and Na⁺-concentration is kept constant.

1. Anion exchange on equivalent basis in the double layer outside a positively charged surface of constant potential type.
2. Diffuse sulfate ions approach closer to the surface than chloride ions, in accordance with the Stern and Gouy-Chapman theories.
3. Surface charge density increases by potential determining adsorption of H⁺, in order to maintain a constant surface potential.
4. More anions adsorbed in order to maintain electroneutrality in the interface region.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

GENESIS OF CLAY MINERALS-KAOLINIZATION BY HYDROTHERMAL PROCESSES

P. WIEDEN

Former Geotechnical Institute, Bundesversuchs- u. Forschungsanstalt,
Vienna, Austria

The genesis of deposits of kaolin-kaolinization- and clay minerals is still a problem. There are two preponderant theories, "weathering" and "hydrothermal" as the most usual.

Formation of deposits of kaolin and clay is possible if the following conditions are met:

1. The mother soils (granite, granulite, porphyrite, trachyte, andesite, etc. must have such a petrographical and chemical composition to permit the formation of clay minerals.
2. There must be a tectonic or thermal fissuring (cracking) to produce a sufficient permeability to allow circulation of water or watery solutions.
3. These solutions shall have a PH-value of about 7 or weak acid, corresponding to an E_H potential, organic substances for bleaching or as a kind of collector (concentrator) for the weak solutions of ions (H. Harder) if the formation of clay minerals goes through an ionic phase. There must be such a temperature to permit the reactions to go on in a reasonable time to form useful deposits of kaolin or clays.
4. The kaolin deposits have to be protected by sedimentary overburden or by tectonic sinking or both together. To find out which is the current possibility for the genesis of a deposit, the conditions in the geological environment have to be studied.

"Weathering" in the classical sense is dominated by: Reaction with moderate temperatures of the agens water, reactions with different P_H and E_H and transformation of mostly feldspar ("feldspar kaolin"), a framework silicate to a layer silicate. The removal of iron (iron oxides) occurs by bleaching of organic materials such as humic and falvic acids.

The formation of clay minerals can be more easily explained by the assumption of the convection of surface water and magmatic water (watery solutions) influenced by a hotspot of a plutone.

Investigations of kaolin deposits in the Austrian part of the Bohemian Massif lead to the postulate (P. Wieden 1978) that in addition to the normal weathering agents, circulating ground water with variation of P_H , E_H and mineralization of this watery phase is the cause of kaolinization. H. Schröcke (1979) describes hydrothermal reactions by a system of groundwater streams rising round the intrusion (plutones). The source of energy is the capacity of heat of the magma. If the rocks, e.g. granites, have a permeability of 0.15 md (millidarcy) and the neighbouring rocks have one of 0.30 md there are about 100 circulations in the cooling time of the plutone in the range of about 10^5 years until 20 % of the starting temperature are reached.

This knowledge was supported by the paper of S. Sheppard 1969, 1971 through studies of isotope ratios of hydrogen and oxygen of layer silicates in connection with porphyric copper ore deposits. The D- and ^{18}O values correspond to the ones of surface water. Investigations of dickite of the Bohemian Massif have shown that surface water and hydrothermal water was involved in forming clay minerals.

The Conference "High Heat Production (HHP) Granites, Hydrothermal Circulation and Ore Genesis" in St. Austell (Cornwall, England, 1985) dealt with the following aspects: Water-rock interactions and origin of aqueous fluids, duration and timing of hydrothermal circulation; hydrothermal alteration and mineral zonation; exploration for and exploitation of ores, industrial minerals and thermal resources, etc.

Of special interest was the excursion to a typical Cornubia granite plutone of coarse, biotite granite and fine biotite granite, intrusion of granite porphyry, mineralization and kaolinization. The formation of kaoline and other clay minerals respectively by hydrothermal reactions in connection with vulcanism has not been contradicted.

Summarizing one can say that by intrusion into a sufficiently permeable rock system a mechanism of convection starts, bringing cold

water downwards and warm water upwards. A result of cooling of the plutone or batholite is fissuring (cracking), followed by greater permeability. The definition of weathering, hydrothermal by convection of groundwater or hydrothermal in connection with vulcanism is the cause of the genesis; this depends sometimes on the degree of investigation.

References

- Schröcke, H.: Geotechnik und Lagerstättenbildung; Fortschritte d. Miner. 55,2. 135-172, 1979.
- Sheppard, S.M.F. and al.: Oxygen and Hydrogen Isotopes Ratios of Clay Minerals from Porphyry Copper Deposits. Econ Geol. 64, 755-77.
- Wieden, P.: Genese und Alter der österreichischen Kaolinlagerstätten; Schriftenr. Geol.Wiss., 11, 335-342, 1978.
- Wieden, P.: Kaolinization by Circulating Surface Water in the Upper Part of Intrusions; Acta Min.-Petr.- XXIV/1980 Proc. of the 10th Kaolin Symp. in Budapest, S. 35-38, 1979, IGCP, Project Nr. 23.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

NMR STUDIES ON KAOLIN HYDROPHOBIZATION

P. WYSZOMIRSKI, S. SAGNOWSKI^x, L. STOCH

Academy of Mining and Metallurgy, Kraków /Poland/

^xInstitute of Nuclear Physics, Kraków /Poland/

Atmospheric moisture is being adsorbed by washed kaolins to a various degree, owing to the hydrophilic character of kaolinite. Its hydrophobization can be achieved mainly through adsorption of certain organic compounds, e.g. silanes and mercaptanes. It improves the properties of washed kaolins as fillers of rubber and plastics.

The ¹H NMR method is particularly useful in the studies on the hydrophobization process. A narrow resonance line /Lorentzian line/ originating from the protons of the adsorbed water which overlaps the broad line /Gaussian line/ corresponding to the protons in the kaolinite structure is observed in the obtained spectra. It follows from NMR spectra of some Lower Silesian kaolins that washed kaolin from Nowogrodziec is characterized by the least amount of moisture /Fig.1/. This is due to coarse-grained and highly crystalline character of its kaolinite /Stoch et al. 1978/. Hence this kaolin represents a most interesting material for the study of its hydrophobics.

Hydrophobization of the washed kaolin from Nowogrodziec was carried out using silane compounds /Si-69 made by Degussa, Germany, Polyvest-25 - HtIs, Germany, A-1120 - Union Carbide, USA, Z-6082 - Dow Corning, USA/ and mercaptan compounds /dodecylmercaptan/ in a chromatographic column at 25°C and 200°C until the sorption equilibrium was reached. Prior to that procedure a stream of helium was passed through the kaolin sample to remove water.

After hydrophobization the examined material was protected against moisture by immediately sealing it in a glass tube in a 10^{-3} Tr vacuum.

The best effect of the kaolin activation is obtained using Si-69 silane and dodecylmercaptan. This is indicated by the shape of the curves illustrating the dependence of the integral intensity of the Lorentzian lines - registered in the ^1H NMR studies of non-activated and activated samples of this kaolin - on the time period which has passed since the moment the activation was completed /Fig.2/. However, independently of the applied activator the water-repellent samples reveal certain hydrophilic tendency. It increases to various degree not attaining however the H_2O content in non-dried and non-activated kaolin. Water-resorbed is strongly bound to the kaolinite surface. The strong binding of water molecules is evidenced by the fact that vacuum drying / 200°C , 10^{-3} Tr/ of activated kaolin samples prior to NMR measurements never led to the loss in the amount of resorbed water /Fig.3/. It can be seen from the fact that the adsorption of H_2O by the water-repellent kaolin is the most intensive in the first stage. The equilibrium is attained after about 4 days. The reason for some hydrophilic character of the water-repellent kaolinite is most probably incomplete blocking /in spite of the attainment of sorption equilibrium/ of all the active centres in kaolinite by molecules of the activator. Judging by the great force with which the water molecules are being sorbed, these centres represent probably broken bonds on the edges of flakes, growth steps, dislocation boundaries and other discontinuities of the kaolinite surface. This is evidenced by the increase in the hydrophilic character with decreasing degree of the crystallinity of this mineral /Fig.1/. The water molecules localized in the pseudohexagonal holes within the tetrahedral framework /hole-water/ play - as it seems - a less important role.

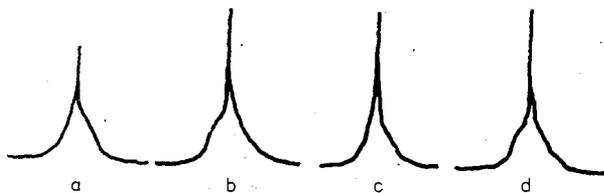


Fig.1. ^1H NMR spectra of washed kaolins from Nowogrodziec /a/, Żarów /b/, Wądroże Wielkie /c/ and Jętfowa /d/ deposits.

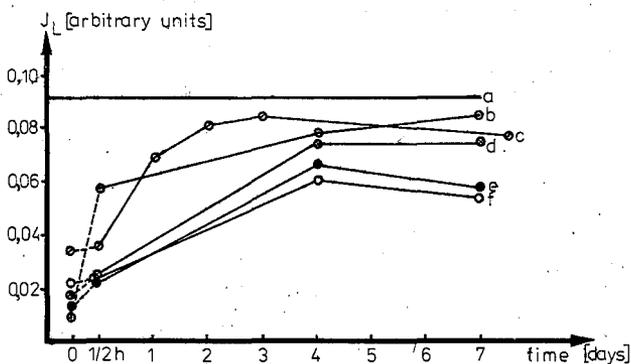


Fig.2. The integral intensity of Lorentzian line vs. time for washed kaolin from Nowogrodziec: non-dried and non-activated /a/, dried and non-activated /b/, activated with Polyvest-25 silane at 25°C /c/ with dodecylmercaptan at 200°C /d/, with Si-69 silane at 25°C /e/, with dodecylmercaptan at 25°C /f/.

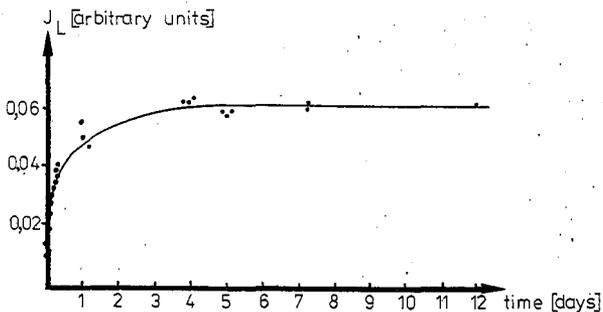


Fig. 3. The integral intensity of Lorentzian line vs. time for washed kaolin from Nowogrodziec activated with Si-69 silane at 25°C .



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

Polygonal Micro-Structures of Povlen Chrysotile
Observed by High Resolution Electronmicroscopy

Keiji Yada and Liu Wei*
Research Institute for Scientific Measurements,
Tohoku University, Sendai, Japan
*Institute of Physics, Academia Sinica

Rather strange structures showing polygonal cross sections have been predicted from X-ray diffraction analysis (Middleton and Whittaker¹⁾) for 'Povlen' variety of chrysotile and actually proved by electron microscopy (Cressey and Zussman²⁾) for Povlen chrysotile from several different localities. One of the present authors (Yada) has observed polygonal structure in a synthetic serpentine preparation as pointed out in the last part of reference 1. More recently, polygonal structures have been observed by electronmicroscopy (Liu and Jiang³⁾) for Povlen chrysotile from Guangyuanpu asbestos mine of Sichuan Province, China. They also studied the chemical composition of the sample by chemical analysis.

In such Povlen-type samples, polygonal structures are usually found for very thick fibers of about 2000 Å or more with a circular fiber in its core, tube-in-tube features, though thin normal chrysotile fibers are coexisting in each sample. Now, the polygonal serpentine has proved to be not uncommon but unsolved problems have remained in relation to their detailed morphology, crystal structure and growth mechanism. We observed ion thinned samples of Povlen chrysotile from Guangyuanpu asbestos mine with high resolution electronmicroscopes of 100 KV and 1 MV.

Considerable numbers of polygonal cross sections more than thirty were observed and it was found that numbers of segments of polygon are confined to certain values. Namely, more than half of the total was 15 in their segmental number, near a quarter 30 and the rest was not explicit but close to 15 or 30. Concentric lattice planes consisting of the polygonal walls were found, though clear-cut examples were small in number. Single helical lattice planes were also found but multi-helical ones seemed very few. Fig.1 shows an example of polygonal cross section having 30 segments and concentric lattice planes. The growth mechanism will be discussed based on these findings.

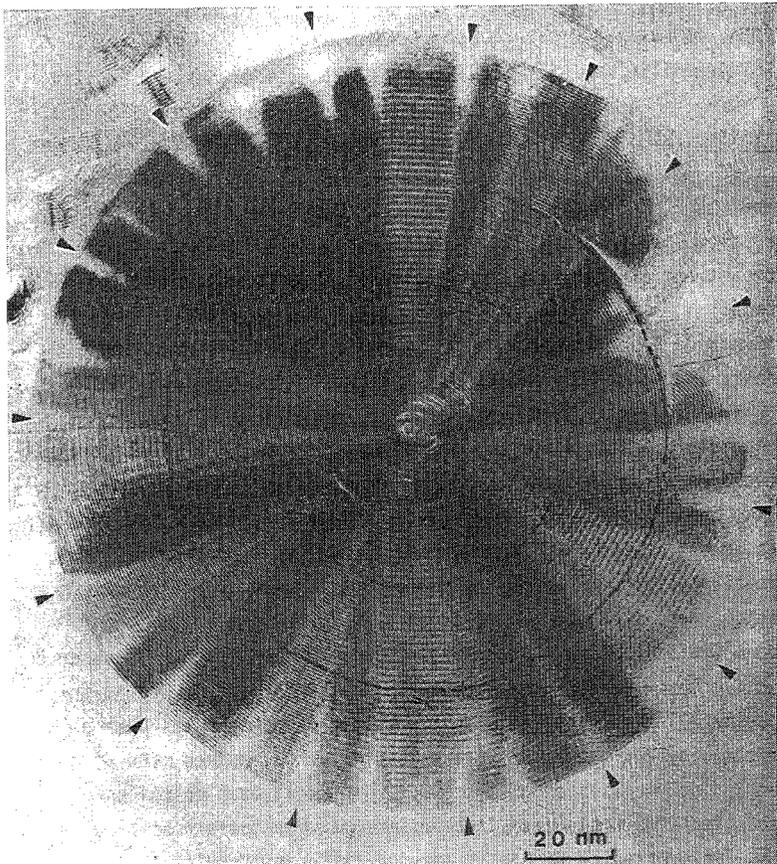


Fig.1 A typical example of polygonal cross section having 30 segments. Traces of dotted lines along the lattice planes show concentric or single helical structure. Some structure-disappearing parts along the circumference are due to electron beam damage, which suggests that the polygonal corners where lattices have a kind of defects or compositional irregularity are less resistive to electron beam damage.

References

- 1) A. P. Middleton and E. J. E. Whittaker, *Can. Mineral.* 14 (1976) 301
- 2) B. A. Cressey and J. Zussman, *Can. Mineral.* 14 (1976) 307
- 3) Liu Wei and Jiang Shaoying, *Acta Mineral. Sinica* 2 (1984) 111 (in Chinese)



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

METACHROMASY IN CLAY MINERAL SYSTEMS. ADSORPTION OF CATIONIC DYES, CRYSTAL-VIOLET AND ETHYL-VIOLET BY MONTMORILLONITE. SPECTROSCOPIC AND ELECTROPHORETIC MOBILITY STUDY.

S. YARIV*, L.G. HEPLER**, D.K. GHOSH AND L.L. SCHRAMM***

*Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem 91904, Israel.

**Department of Chemistry, University of Alberta, Edmonton, T6G 2G2, Canada.

***Syn crude Research Laboratory, Syncrude Ltd., Edmonton, Alberta, Canada.

The visible absorption spectra of aqueous solutions of the two cationic dyes, crystal-violet (CV) and ethyl-violet (EV), depend markedly on the concentration of the dye; very dilute aqueous solutions of these dyes absorb at 590 and 594 nm, respectively. This absorption band, which is called band α , is due to monomeric species. At larger concentrations band β due to dimers appears at lower wavelengths (about 550 nm). At very much larger concentrations band γ is observed at still lower wavelengths (about 490 nm); this band is due to polymeric or micellar species. This spectroscopic phenomenon has been called metachromasy and these dyes are called metachromic dyes. The dimerization and polymerization of these dyes in the aqueous solutions is associated with π electron interactions between the aromatic cations.

The adsorption of CV and EV by nine different homoionic montmorillonites was investigated by visible spectroscopy. The adsorption which takes place mainly through cation exchange is accompanied by metachromasy. Four types of bondings were identified from the electronic spectra. In types A and B, which are identified with the help of band α , monomeric dye cations are adsorbed through organophilic interactions and electrostatic attractions respectively; the former are located on the external surface of the tactoid whereas the latter are in the inter-layer space. In type C, which is identified with band β , monomeric

dye cations are bound to the oxygen plane of the alumino-silicate via π interactions. This type of interaction is responsible for metachromasy. In type D which is identified with band γ , polymeric dye species are located in the interparticle spaces of clay flocs.

The extent of formation of the different types of bondings depends on the exchangeable metallic cation, the dye and the degree of saturation. Type D is negligible with CV and is detected only to a small extent with EV. Type B is formed at low degrees of saturation, whereas type A is obtained at higher saturations. The lowest degree of saturation in which type A starts to appear is defined as the "transition saturation." These transition saturations are higher for CV than for EV. They are highest for the monovalent montmorillonites.

Larger amounts of type C are obtained with CV than with EV. For most systems highest stability of the π interactions (lowest wavelength of band β) is found slightly below the transition saturation.

The adsorption of both dyes leads to the flocculation of the clay. Maximum flocculation occurs with degrees of saturation smaller than the transition saturations. This degree of saturation is always smaller for EV than for CV and decreases with increasing charge of exchangeable cation.

Electrophoretic mobilities of several homoionic montmorillonites treated with various amounts of CV or EV were measured. The mobilities vary between -60 to 40 ($10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ v}^{-1}$). For both dyes the degree of saturation at which the point of zero charge (PZC) occurs, decreases with increasing valence of the exchangeable cation. Maximum flocculation occurs always before PZC. For most systems the transition saturation also occurs before the PZC. A flocculation peptization mechanism has been suggested.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

LATERITE AS CATALYSTS FOR HYDROTREATMENT OF HEAVY OIL.

I. IDENTIFICATION AND CHARACTERIZATION OF A VENEZUELAN LATERITE.

S. Yunes¹, P. Grange², A. Herbillon² and B. Delmon².

1. Micromeritics Instrument Corporation, One Micromeritics Drive, Norcross, Georgia 30093 U.S.A.
2. Université Catholique de Louvain, Groupe de Physico-Chimie Minérale et de Catalyse. Place croix de Sud 1, 1348 Louvain-La-Neuve. Belgium.

The use of laterite as a hydrotreatment catalyst has been recently initiated in Venezuela, since this country is one of the major heavy crude oil producers in the world. A careful characterization of the laterite was necessary on the first stage to determine its potential utilization as hydrotreating catalysts. However, it is important to synthesize and characterize the active phase responsible for the catalytic activity with a view to optimizing both activity and selectivity in the catalytic reaction. For this reason, an exhaustive and precise characterization was carried out on that naturally occurring material. In this study, different characterization techniques were used. In addition to elemental analysis and selective dissolution, we present X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), infrared spectroscopy (IR) measurements. It will be demonstrated that a combined use of all these techniques allows mineralogical identification of the parent laterite.

It was found that the nature and chemical composition of laterite depends upon its place of extraction and its particle size. In its initial state, the sample is composed of a heterogeneous assembly with two predominant species which impart yellow and red colors to the sample. The yellow fraction was mainly composed of gibbsite $\alpha\text{Al}(\text{OH})_3$ and the red fraction was predominantly formed by hematite $\alpha\text{Fe}_2\text{O}_3$ and goethite αFeOOH .

The sample studied here was extracted from the "Serranía de los Guaicas" in Venezuela.

The elemental analysis showed that the laterite is briefly composed by 50% in weight of Fe_2O_3 and 30% of Al_2O_3 with a residue of TiO_2 and SiO_2 . The alumina content decreased with the increase in particle size, while iron oxide content increased.

Thermogravimetric analysis presented a weight loss of 17.3% and 550 °C and 1000 °C for fraction of laterite containing gibbsite, but only a weight loss of 9.8% is presented for a gibbsite-free sample. This indicates about 7.5% weight loss due to gibbsite dehydration and 9.8% weight loss due to goethite dehydration.

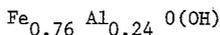
X-ray diffraction showed that the raw material is composed essentially of gibbsite $\alpha\text{Al}(\text{OH})_3$, goethite αFeOOH and hematite $\alpha\text{Fe}_2\text{O}_3$. It was also found by X-ray diffraction that the d(III) goethite peak presents a shift from 2.45 Å (for pure goethite) to 2.42 Å. This phenomenon was reported in the literature when similar studies were carried out, and this corresponds to a certain amount of Al substituted Fe in the goethite. According to the calibration curve of Thiel, this shift corresponds to a substitution of 24 moles % of AlOOH in the goethite.

The dithionate-citrate-bicarbonate (DCB) for selective iron extraction showed that for samples where gibbsite was previously extracted after successive extractions of iron, a value of 0.225 as $\text{Al}/\text{Al} + \text{Fe}$ was reached. This result indicates that there is about 22 to 24 moles % of AlOOH in the goethite. There is an agreement with the value obtained by X-ray analysis as has been shown above.

All results above obtained by the different analysis techniques together with the knowledge of the elemental analysis of both the gibbsite-free and gibbsite-containing samples, lead to the conclusion that the laterite in study is composed by:

Aluminous Goethite	Hematite	Gibbsite	TiO_2	Total
64.412	1.437	29.54	2.70	98.10

and the composition of the goethite can then be represented by the following formula:





Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

LATERITE AS CATALYSTS FOR HYDROTREATMENT OF HEAVY OIL

II. INFLUENCE OF CHEMICAL AND THERMAL

TREATMENTS ON THE HDS AND HDM ACTIVITY

S. YUNES¹, P. GRANGE, B. DELMON.

Groupe de Physico-Chimie Minérale et de Catalyse
Université Catholique de Louvain
Place Croix du Sud, 1
B-1348 Louvain-la-Neuve - Belgium.

1. Present address: Micromeritics, 1 Micromeritics Drive, Norcross,
GA 30 093, U.S.A.

Effects of thermal treatment and iron extraction by the dithionate method (DCB) on the pore size distribution of laterite, and influence of iron and molybdenum impregnation on hydrodesulfurization (HDS) and hydrodemetallization (HDM) of natural DAO Morishal feedstock, were investigated.

The more important conclusions of this work can be summarized as follows:

1) The surface area and pore volume of the studied material depend strongly on the calcination temperature, even though no parallelism is shown between them.

2) The dithionate - citrate - bicarbonate dissolution method for iron extraction seems to have a moderate effect on the pore volume to be increased. Furthermore, after a long treatment, it may be supposed that the obtained solid behaved differently due to a complete texture and structure modification.

3) All different impregnated materials showed no relevant differences in pore volume and surface area values. The pretreatment with water vapor at high temperatures decreases the surface area of the material: even the pore volume seems to be increased.

4) Hydrodemetalization activity of the samples studied presented a moderate value when compared with those corresponding to a commercial catalyst, i.e., NiMo/Al₂O₃. This phenomenon was related to the pore size distribution of the sample in question.

5) The poor hydrodesulfurization activity of the samples can be explained by the poor active metal (iron) phase dispersion, although some impregnated samples, i.e., 1% Fe₂O₃ impregnation and MoO₃ impregnation, present an improvement in HDS activity. This effect was related to the active metal phase dispersion, due to the impregnation phenomena and the presence of a very active metal as MoO₃ in HDS activity.

6) Laterite as a raw material can be used as a hydrotreating catalyst, although careful manipulations and pretreatments notably enhance both HDM and HDS activities.

In any case, even if the efficiency of such raw material is lower than commercial hydrotreating catalysts, one major advantage is that such catalysts could be used and removed easily since they are more economically suitable than commercial HDT catalysts.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

DIAGENETIC TRANSFORMATION OF EARLY PERMIAN MARINE SEPIOLITE AND ITS
RELATIONSHIP WITH COAL METAMORPHISM IN SOUTHERN CHINA

YANG ZHENGQIANG

Yichang Institute of Geology and Mineral Resources, Chinese Academy of
Geological Sciences. P.O.Box 502, Yichang City, Hubei, China.

INTRODUCTION

Sepiolite in China was first reported in Chinese geological literature in 1947. In 1963 the association of talc and quartz with Permian marine sepiolite in Leping County, Jiangxi, was identified by DTA and XRD, but no explanation was given of why talc can occur as a sedimentary mineral which is mixed with sepiolite in sedimentary rocks because talc was merely regarded as a metamorphic mineral at that time. However, in recent years the knowledge in this aspect has been deepened and also minor stevensite (magnesium montmorillonite) has been found. According to experimental evidence and observation in the laboratory, now it is believed that both talc and stevensite are products of phase-transformation and that the talc is actually the final result of deep burial (anadiagenesis). Therefore, sepiolite transformation in the Early Permian of southern China provides a rare natural example of Mg-clay transformation during burial diagenesis.

SEPIOLITE TRANSFORMATION INDICATED BY RANK OF COAL

Both clay minerals and organic matter are very sensitive to burial conditions (temperature, pressure and time) throughout diagenesis. Coalification can serve as a reliable, irreversible record indicating the maximum temperature that the clay mineral and sediments in rocks associated with coal seams had ever reached under deep burial. The rank of the Permian coal in southern China determined by some parameters, including the amount of volatiles and vitrinite reflectance, is useful in studying the thermal diagenesis of sepiolite, no matter whether the coal seam overlies or underlies the sepiolite-bearing group (P_1^2).

According to the volatiles in the coal seam (P_1^1 or P_1^2), all sepiolite are related with the low-middle rank of coal (subbituminous-high volatile coal). The volatile values cover a range of 30-52%, averaging about 40%, which is favourable for the preservation of sepiolite, whereas the reflectance of vitrinite of coal seams, plant fragments or coal material measured in Permian sedimentary rocks varies approximately over the range of 0.4-0.8% in many sepiolite areas. The continuous rise of vitrinite reflectance and volatile indicates that clay minerals have been transformed into stevensite and talc already.

Regionally geological data for coal samples collected from the Leping depression and its vicinity allow the author to distinguish the corresponding coalification stages in the light of representative values of V_r for 108 coal mines and input the values into the VICTOR-9000 microcomputer for calculation. The volatile data can be successfully shown on the two-dimensional triple-trend surface plot and/or four-trend surface plot by trend surface analysis. It is interesting that the results shown in the plots indicate that the extents of low coal rank evidently coincide with the distribution areas of sepiolite. In contrast, only high V_r value areas are located in the talc districts.

However, the major factors affecting the diagenetic process are geological time, pressure and geothermal heat, which are essential to both coal and clay minerals. The favourable palaeotemperature for the conversion of sepiolite into stevensite and talc is over 120°C, which can be determined by the vitrinite reflectance of coal or coaly fragments preserved in sepiolite-bearing rocks in correspondence to related palaeotemperature. Thus the transformation temperature of sepiolite in nature is much lower than previously measured from experiments (i.e. 310°C). That is because lower temperatures seem more important to slow heating rates (gradual subsidence) than to rapid heating rates (in experiments).

CONCLUSION

The burial diagenesis in southern China has just reached the anadiagenesis stage. The geotemperatures around 60-100°C are essential to the preservation of sepiolite in the strata.

In order to find out the potential areas of sepiolite deposits, the author proposes that the preservation of sepiolite has a synchronous relationship with the rank of Permian coal. There is such a possibility so that new occurrences of sepiolite marked with the distribution of the lower coal rank can be predicted. It has been successfully used in my own experience of field-research work.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

CLAYS AND ENVIRONMENT

PÉRSIO DE SOUZA SANTOS

Depto. de Engenharia Química - Escola Politécnica da Universidade de São Paulo, São Paulo, Brazil

Clays are a natural component of the environment: their role in Agriculture and Geotechnics, as well as raw materials for the Chemical Process Industries, show the very positive contribution of clays and clay minerals to society, with a significant influence on the environment. The question is: can clays be "hazard's" or "risks"? According to Marshall, a "hazard" is a potential for harm and a "risk" is the probability that harm may be realized.

The International Labour Office (ILO) conference in Geneva, in June 1986, considered "all respirable asbestos fibres". According to Costa, asbestos and more 150 fibres, all mineral, are a natural constituents of the environmental air because they exist in Nature. The clay mineral chrysotile, the white asbestos, is considered as belonging to the Health Group Hazards because it produces a serious non-malignant disorder to human beings called asbestosis, similar to silicosis; it may also produce lung cancer and a rare type of cancer of the pleura or peritoneum called mesothelioma; that disease is more frequent to those exposed to dust from the amphibole asbestos crocidolite and amosite; the other asbestos tremolite and actinolite are usual contaminantes of the clay mineral talc. The health hazards of asbestos are linked to inhalation, not to swallowing; according to Churg "exposure to chrysotile asbestos from urban air or in public buildings will not produce detectable disease. The U.S. National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety Health Agency (OSHA) concluded, in spite of substantial epidemiological data in contrary, that a threshold limit for asbestos does not exist for clinical effects to be observed and proposed a maximum limit of 0,1 fibre/ml in environmental air. A respirable asbestos fibre is defined (ILO) as a particle of asbestos with less than 3µm diameter and with a length/diameter ratio greater or at least 3:1. In January 29, 1986, the U.S. Environmental Protection Agency (EPA) proposed a regulation to ban

the use of any type asbestos in the USA, by prohibiting the production and the importation of asbestos; second, in the next ten years, by substituting by alternates all industrial products contains asbestos, like asbestos-cement; thermal insulations; floc paints and brake linings. If the law pass the demolition of huge amounts of asbestos containing materials on buildings is going to be made and, in consequence, enormous amounts of hazardous asbestos-containing wastes must be treated to avoid occupational and environmental pollution. According to Selikoff, "if asbestos fibres and other environmental sources of cancer are properly controlled, they do not have to be banned to protect society". The "controlled-use" approach to asbestos regulation was adopted in 1983 by European Communities, which was a factor for publication of the 1984 ILO's draft entitled "Code of Practice of Safety in Use of the Asbestos"; the 1986 ILO's conference approved that proposal, which was also recently supported by the 6th Asbestos International Association Conference in Montreal in May, 1987.

Preliminary laboratory testing for the mutagenicity of surface treated chrysotile indicated that it was less biologically reactive than untreated chrysotile; the treated chrysotile was produced by exposing the fibres to $POCl_3$ or PCl_5 . According to Dunningan, all alternative fibrous respirable minerals, organic and inorganic fibres, naturally occurring or man-made, should be treated with the same care as the various asbestos minerals as potential hazards to man and its environment; examples of fibres as hazardous as asbestos are the clay minerals palygorskite and sepiolite; the ceramic fibres (kaolin, alumina, glass, rock); wollastonite; xinolite; synthetic fibres of calcium sodium metaphosphate and of the organic polymer aramid.

Earth liners have been used worldwide for several decades for lining landfills, ponds and lagoons to retard the movement of pollutant leachates or liquids to the ground; they may be constructed from naturally occurring clay soils or from mixture of soils with sodium bentonite; they are often referred as "clay liners", because the clay fraction controls the hydraulic properties of the liners.

Landfills have been used historically for disposing of a multitude of different types of chemical and industrial was-

tes. According to Henstock, "pollution equals waste". Hazardous wastes are defined by the U.K. Control of Pollution Act as "poisonous, noxious or polluting matter, which relates the creation of an environmental hazard; itself defined as causing material risk of death, injury or impairment of health to persons or animals, or as threatening pollution or contamination of surface or underground water supplies". Bentonite, or more specifically sodium smectites, have been used for decades to impede or reduce the flow of water, leachates and liquid effluents through permeable soils: that property has been widely used by drilling and construction industries. On the other hand, adsorption on solids is increasingly being used for the removal from liquid effluents, leachates and/or polluted waters of toxic materials, of "refractory" organic chemicals, colour and to reduce the BOD to values to the 3-10mg/l range; activated clays, bauxites and zeolites have been used for that purpose. Smectite clay minerals can exchange, as shown by Farmer and Mortland, for organic ammonium cations, giving rise to strong acidic sites; in the case of ethylammonium cations, when additional amine is adsorbed, bonding occurs between the neutral amine and the ethylammonium cations; similar bondings occur with several other organic molecules. Clay/aromatic interactions have become of importance due to attenuation of pesticides and other toxic organic chemicals by soils, sediments and clays, specially after the realization that clay minerals can catalyse the degradation of many aromatic compounds and pesticides. Perry, Büchler, Warren and Ckark, after reviewing the clay-aromatic interactions with a view to their use in hazardous waste disposal, suggested tetramethylammonium-smectites as clay liners of vinasse ponds, which are used as waste disposal in the production of ethanol, for the attenuation of the organic load by adsorption. That organic-laden smectites could be, later on, disposed by encapsulation in cement based monolithic masses. Clay minerals have been used also by the nuclear energy industry for waste disposal of metal and cationic species in similar processes.

On the other hand, up to early 1980's, the consensus among ground water specialists seemed to be that clay liners were working fairly well; however, according to U.S. EPA, it was shown in laboratory and field conditions, that some concen-

trated organic chemicals "attacked" the compacted clay and increased its permeability, thus rendering the clay essentially useless as a barrier to the migration of liquid pollutants. Similar effect was also observed in the kaolinite clay barrier in red mud ponds due to the deflocculation caused by the alkaline water. According to Daniel, "until earth scientists and engineers build a data base that demonstrate that clay liners are performing well, doubts about the effectiveness of clay will persist"; thus synthetic polymers liners are being proposed as alternates.



Summaries - Proceeding
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

APPLICATIONS OF KAOLINS

IVAN HAY

Research Chemist, Dept. of Inorganic Chemistry
Kemira Oy Espoo Research Centre
Luoteisrinne 2, SF-02270 ESPOO, FINLAND

Reference to 'this materialistic age' is frequently made under the popular misconception that material things have an inherent power in their effect on man instead of realising fully that those effects are dependent on the use man makes of them.

This paper is concerned with china clays and their quality which sets them apart and have become essential to modern industry as food is to mankind.

Because china clay is one of the most versatile industrial pigments this paper will deal with its uniqueness in some of the industrial applications that it is used in and how those applications are based upon a combination of its predominantly physical characteristics. It will also review some of the more rapidly growing markets that call for high quality china clays along with special processed grades - showing how as products have been introduced to the market new application technology has been created, even though there is now a wider choice of white pigment minerals available china clay is still very much in demand.

AUTHIGENE KAOLINITE FROM THE KAOLIN SANDS IN NE BULGARIA

N.P. RUSKOVA, E.D. MANDOVA

Geological Institute, Bulgarian Academy of Sciences,
Sofia (Bulgaria)

Morphology of kaolinite crystals is studied by numerous observations on a Jeol T-300 scanning electron microscope. The samples come from several deposits of kaolin sands near the village of Kaolinovo (Northeast Bulgaria). An interesting aspect of their study is that besides the terrigenous clastic minerals and the common kaolinite crystals of almost isometric, pseudohexagonal, irregular and rare triangular shapes, typical wormlike kaolinite and stacks of kaolinite platelets indicating an authigenic process have been observed for the first time. In the samples their content vary from few grains to numerous crystals. (Ph. 1).

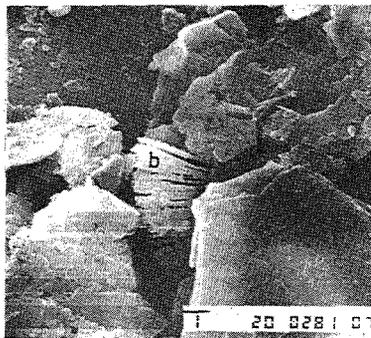
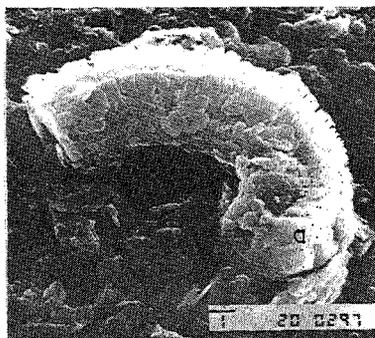
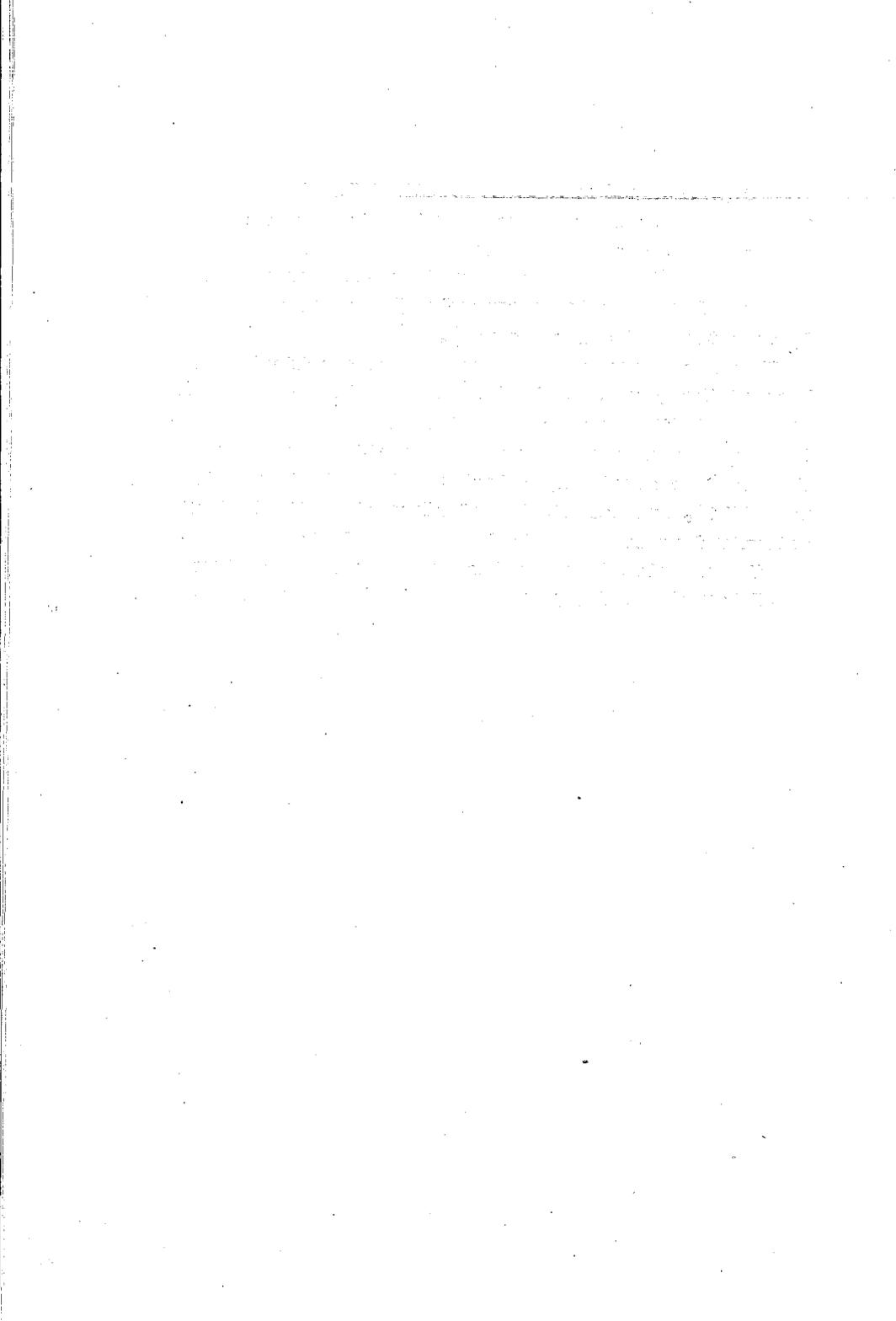


Photo 1: a - wormlike kaolinite; b - stack of kaolinite platelets.

X-ray microanalyses with the aid of Li-Al semiconductor detector were made parallel with the morphological observations. The spectrograms obtained show a value of Al:Si = 1:1 (from the number of impulses counted) but in part of the kaolinite crystals Al predominates greatly over the Si (to a ratio 2:1).

This study reveals new aspect of the complicated problem of the genesis of kaolin sands in Northeast Bulgaria. First, the presence of authigene kaolinite indicates directly at processes of neoformation (until now they were presumed only - Ruskova, 1968; Ruskova & Tzonev, 1971), and second, Si deficiency from the kaolinite determined probably by the karst type of the deposits and the associated enhanced water percolation in them (as Kukovskii, 1973, presumes for the similar cases).



OTHER ANNOUNCED PAPERS



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE ADSORPTION AND DESORPTION OF TRACES OF RADIUM AND
URANIUM ON SOME COMPONENTS OF FRESHWATER SEDIMENTS

ZDENĚK BOROVEC

Department of Petrology, Charles University, Albertov 6,
128 43 Prague 2, Czechoslovakia

AN ATTEMPT TO FORMULATE 2-3 DIMENSIONAL MODEL OF ILLITE
MONTMORILLONITE MIXED LAYER STRUCTURES

L. ČICHOVSKÝ, J. JIRÁNKOVÁ, R. ŠTROUF, O. VESELÝ[†]

Department of Spec. Geol. Sci., Mathematical Department,[†]
Geoindustria n.c., Přístavní 24, 170 04 Prague 7- Hole-
šovice, Czechoslovakia

ALTERATIONS IN ANTIGORITE AND LIZARDITE IN ALKALINE
ENVIRONMENT

L. ČICHOVSKÝ, R. ŠTROUF,

Department of Spec. Geol. Sci., Geoindustria n.c., Přístav-
ní 24, 170 04 Prague 7- Holešovice, Czechoslovakia.



Summaries - Proceeding

THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS

Seville, Spain, 1987. Sociedad Española de Arcillas

NATURAL CLAY OF GEORGIA AS CARRIER OF CATALYSTS FOR HYDRATION AND OXIDATIVE DEHYDRATION

G.O. CHIVADZE

Institute of Physical and Organic Chemistry, Georgian
Academy of Sciences, Jikia 5, Tbilisi 380086, (USSR)

CLAY ROCKS AND MINERALS WITHIN THE DEPOSITS OF THE SAME AGE HAVING DIFFERENT LITHIFICATION HISTORY

M. FAIER

Department of Geology, Moscow State University, Lengory,
119899, Moscow, USSR

Characterization of oxovanadium (IV) species adsorbed on montmorillonite

B.A. Goodman, D.B. McPhail and M.C. Mitchell

Macaulay Land Use Research Institute, Aberdeen AB9 2QJ, U.K.

Evidence for the multiphase nature of smectites from Mossbauer and EPR
spectroscopy.

B.A. Goodman^a, P.H. Nadeau^a and J. Chadwick^b

^a Macaulay Land Use Research Institute, Aberdeen AB9 2QJ, U.K.

^b Department of Physics, University of Liverpool L69 3RX, U.K.

Identification of oxide impurity phases and distribution of structural iron in
some diagenetic illitic clays as determined by Mossbauer spectroscopy.

B.A. Goodman and P.H. Nadeau

Macaulay Land Use Research Institute, Aberdeen, AB9 2QJ, U.K.

PROCESSES OF AUTOCHTHONOUS CLAY MINERAL FORMATION AND ORE GENESIS

Yu.P. KAZANSKY

Institute of geology and geophysics of Siberian division
of the Academy of Sciences of the USSR, 630090, Novosi-
birsk



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

MIXED-LAYERED CLAY MINERALS IN MESOZOIC AND CENOZOIC DEPOSITS OF AZERBAIJAN

M.B.Kheirov, A.G.Seidov

GEOLOGICAL INSTITUTE OF THE AZERBAIJAN SSR ACADEMY OF SCIENCES, 29A NARIMANOV PR., 370143 BAKU (USSR).

NEW MODIFICATIONS OF ASKANA BENTONITE AND PROSPECTS OF THEIR USE IN MEDICINE

E.I. KOBAKHIDZE, A.L. BATSANADZE, TS.S. GABELIA, and
T.G. ANDRONIKASHVILI

Laboratory of Colloidal Chemistry, Institute of Physical and Organic Chemistry, Georgian Academy of Sciences, Dzhikia 5, Tbilisi 380086 (USSR)

CLAY MINERALS AND GEOCHRONOLOGICAL SCALE

I.V. NIKOLAYEVA, M.JU. KAMENEVA, I.T. KOVALYOVA,
JU.N. LEBEDEV, L.K. ANOKHINA*, R.U. GABITOVA* &
R.I. TCHALABOV*

Institute of Geology and Geophysics, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, U.S.S.R.

* Physics Institute of Dagestan Branch of the USSR Academy of Sciences, Makhatch-Kala, U.S.S.R.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

ON THE DIFFERENT THERMODYNAMIC STABILITY OF DI-AND TRIOCTAHEDRAL MONTMORILLONITES AND THE MIXED-LAYERED FORMATIONS CONNECTED WITH THEM

A.G.SEIDOV, D.D.KOTELNIKOV* Z.A.KRIVOSHEEVA*

Geological Institute Azerb.SSR Academy of Sciences, Narimanov avenue 29A, Baku 370143 (USSR)

*Geological Department, Moscow State University, USSR

SOME PROPERTIES AND MINERALOGICAL COMPOSITION IN FOSSIL SOILS /PERIOD DENEKAMP?/ FROM THE NIZINA WIELKOPOLSKA REGION

SZERSZEŃ L., CHODAK T.

Department of Soil Science, Agricultural Academy,
Wrocław, Poland

Study of The Clay Minerals from Several Kinds of Oil-bearing Basins, China

Zhao Xingyuan

The Geological Lab Center , Scientific Research Institute of Petroleum Exploration and Development, Beijing, China



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

THE APPLICATION OF NMR SPECTROSCOPY TO THE STUDY OF CLAY
MINERALS AND RELATED COMPOUNDS

J.M. SERRATOSA

Instituto de Ciencia de Materiales, CSIC. MADRID (Spain)

Nuclear magnetic resonance spectroscopy has been successfully applied to elucidate several aspects of the structure and properties of clay minerals. This technique gives information on the local environment of the nuclei and can be applied to both crystalline and amorphous materials because it does not require the presence of long range order in the atomic distribution. In this lecture, examples are presented that illustrate the possibilities of this technique in clay research covering the following aspects: 1) structural characteristics, 2) surface properties and 3) reactivity and thermal transformations.

Specific examples included are:

- a) Distribution of four and six coordination of Al and identification of different structural sites for Si.
- b) Analysis of Si,Al distribution in phyllosilicates 2:1. ^{29}Si NMR data show that Al is homogeneously dispersed in the tetrahedral sheet and no evidence has been found of partial long range order.
- c) Structural characterization of layer silicic acids: identification of SiO_4 tetrahedra with different "connectedness" to neighbouring tetrahedra; characterization of surface OH groups, their evolution during thermal treatment and their reactivity with organic molecules.
- d) Structural characterization of "pillared" clays and identification of the reaction taking place between the intercalated Al polymers and the tetrahedral sheet of phyllosilicates.
- e) Characterization of adsorbed molecules in the interlayer space of phyllosilicates and study of their reactivity.
- f) Study of the structural changes that occur during the thermal decomposition of kaolinite and the subsequent formation of mullite.



Summaries - Proceedings
THE SIXTH MEETING OF THE EUROPEAN CLAY GROUPS
Seville, Spain, 1987. Sociedad Española de Arcillas

LABORATORY INVESTIGATION ON BENTONITE AS SEALING AGENT FOR WASTE DISPOSAL

A. CANCELLI, R. COSSU⁺, & F. MALPEI[^]

Dept. of Earth Sciences, University of Milano, and Dept. of Struct. Eng. Politecnico, Milano, (Italy)

⁺Inst. of Hydraulics, University of Cagliari, and Inst. of Sanitary Eng. Politecnico, Milano, (Italy)

[^]Sanitary Civil Engineer, Milano, (Italy)

Land disposal of municipal or industrial, hazardous wastes has become an ever more common practice in the most developed countries. From the standpoint of protecting the environment from pollution, the generation of leachate, which subsequently moves downward and outward to the underlying aquifer, is the main problem one is concerned with. Leachate is essentially formed by a liquid, containing dissolved or suspended, organic and inorganic components, as well as chemicals and metals.

All this turns into the problem to find reliable and safe liners, to prevent any migration of leachate from the disposal site.

When soils have to be used as waste confinement liners, one of their fundamental properties must be to have low hydraulic conductivity. In engineering practice, fine-grained clayey soils are generally assumed to be "impervious"; on the contrary, when water and pollutant movements are expected to occur over periods of hundreds of years, the fine-grained soils cannot be simply assumed as impervious. Therefore, it becomes necessary to measure the hydraulic conductivity of compacted clays in presence of pollutant fluids, and to investigate how this and other characteristics of the soil are affected by a long-term exposition to leachates. Laboratory investigations are in progress, to study the effects that different wastes produce on the permeability of sand-bentonite mixtures, and on some properties of the bentonite itself.

Particular consideration is given to relationships between the dielectric constant of the waste fluid and the hydraulic conductivity of the soil. It's well known that the behaviour of clays is strongly influenced by the nature of the pore fluid, and that the double layer thickness decreases with increasing of the dielectric constant of pore fluid. This

fact may particularly affect the structure and properties of bentonite, owing to the high ratio of double layer thickness to the thickness of smectite laminae (up to 20 times).

For the testing program, a sand/bentonite mixture is used, having the following composition (by dry weight):

- fine to medium sand, passing to no. 10 ASTM sieve: 95 %;
- commercial bentonite (68 % finer than 2 μm): 5 %.

The Atterberg limits of the bentonite (determined by remoulding dry bentonite with tap water), are: liquidity limit $w_L = 546$ %; plasticity limit $w_P = 42$ %; plasticity index $I_P = 504$ %.

Samples of the mixture were compacted, according to the Standard Proctor procedures, at the optimum water content, and placed into the permeability testing apparatus, essentially consisting in a triaxial cell; a back pressure was applied, up to 300 kPa, so that a degree of saturation $S_r > 95$ % could be attained. The constant head permeability tests were carried out under a hydraulic gradient $i = 13.3$.

Results of a first set of tests are shown in fig. 1. Curve 'A' refers to tests performed with deaired tap water: the hydraulic conductivity has

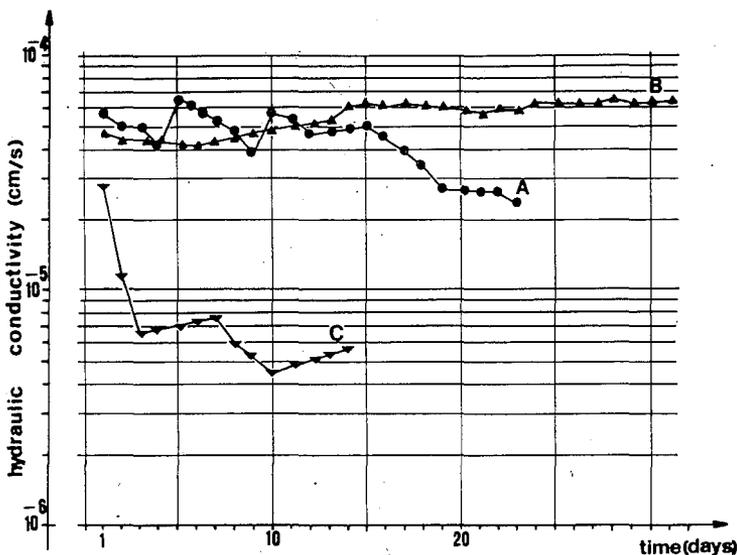


Fig. 1. Results of permeability tests on compacted sand/bentonite mixture: A) deaired tap water; B) filtered and C) non-filtered leachate.

a tendency to decrease with time, reaching a value of $2.3 \cdot 10^{-5}$ cm/s after 22 days. Successively, the water was replaced by a leachate, taken from a municipal sanitary landfill and previously filtered; the hydraulic conductivity was initially about $4.7 \cdot 10^{-5}$ cm/s and gradually increased to about $6.3 \cdot 10^{-5}$ cm/s; the total duration of the test was 33 days (curve 'B'). Finally, unfiltered leachate was used, and the hydraulic conductivity sharply decreased to less than $6 \cdot 10^{-6}$ cm/s (curve 'C').

As a preliminary comment, the presence of chemical solutes into leachate is effective in increasing the hydraulic conductivity of compacted clay soils; of course, suspended particles may cause pore clogging, and, consequently, may induce a decrease of hydraulic conductivity.

Atterberg limits were also performed on bentonite, by using waste leachate instead of water, in order to detect changes in its physical behaviour; an evident decrease of w_L and I_P was observed.

Industrial leachate, dilute acetic acid and propanol will be used for permeability tests further on; dielectric constant, viscosity and specific weight of each fluid will be determined as well.

AUTHORS INDEX

Abreu, M^a.M. 59
 Ackermann, H. 61
 Acosta, A. 183
 Adams, J.M. 63
 Alonso, B. 66
 Alonso, O.E. 69
 Alvarez-Berenguer, A. 160, 163, 486
 Allan, J.E.M. 71
 Amigó, J.M. 74, 490
 Amouric, M. 427
 Anadón, P. 304
 Andreoli, C.Y. 76
 Andrés Gómez de Barreda, A. de^a 79,
 387
 Andronikashvili, T.G. 619
 Anokhina, L.K. 619
 Aragón de la Cruz, F. 79, 470
 Aramburu, C. 490
 Arco, M. del 81
 Arduino, E. 84
 Arias, M.G. 213
 Armenteros, I. 404
 Aróstegui, J. 86
 Axelos, M.A.V. 521
 Aza, S. de 381
 Aznar, A.J. 88
 Azzaoui, M. 91
 Bailey, S.W. 21
 Bain, D.C. 276
 Balenzano, F. 94
 Baltar, C.R. 154
 Ballesteros, C. 160
 Barbarick, K.A. 208
 Barberis, E. 84
 Bartoli, F. 95, 98
 Barrese, E. 385
 Barrios, J. 101
 Barrón, V. 101
 Bastida, J. 74, 490
 Batsanadze, A.L. 619
 Beck, A. 581
 Bergaya, F. 509
 Bermúdez-Polonio, J. 570
 Bertolani, M. 104
 Besson, G. 106, 474
 Bezvodova, B. 109
 Bielicki, T.A. 381
 Bigeriego, M. 339
 Bini, C. 112
 Bittencourt Rosa, D. 95
 Bloodworth, A.J. 115
 Bodine, Jr. M.W. 118
 Boero, V. 84, 121
 Boguslawski, E.V. 545
 Boirón, M.C. 124
 Bonnin, D. 127, 363
 Borggaard, O.K. 129
 Borghini, M. 537
 Borovec, Z. 617
 Bottero, J.Y. 131, 178, 521
 Bottino, G. 135
 Brell, J.M. 203, 260
 Brigatti, M.F. 138
 Briggs, D.A. 115
 Brime, C. 69
 Bruant, M. 131
 Brusewitz, A.M. 140
 Bühmann, D. 142
 Buondonno, A. 145
 Burtin, G. 98
 Caballero, E. 148
 Cabral, J.M.P. 59, 446, 448
 Calas, G. 176, 178, 363
 Calle, C. de la 151
 Campillo, G. 154
 Cancelli, A. 622
 Canet, D. 131
 Carlson, L. 46, 157

Carrasco, F. 465
 Carretero, M^a.I. 432
 Casa, G. de 385
 Casas, J. 160, 378
 Cases, J.M. 131
 Castaño, R.M. 370
 Castells, R.P. 163
 Castelltort, F.X. 370
 Cathelineau, M. 124, 167
 Caucia, F. 559
 Cenens, J. 170
 Cichel, B. 173
 Cichovski, L. 617
 Coey, J.M.D. 71
 Cohen, E. 373
 Comas Minondo, M.C. 342
 Combes, J.M. 176, 178
 Conde-Pumpido, R. 154
 Coninck, F. de 180
 Córdoba, M.A. 183
 Corma, A. 390, 392
 Cornejo, J. 185, 223, 548
 Corral, M.P. 381
 Costa, D. 281
 Cossu, R. 622
 Chacón Montero, J. 349
 Chadwick, B. 618
 Chagnon, A. 188
 Chamley, H. 9
 Chenu, C. 542
 Cherubini, C. 189
 Chivadze, G.O. 618
 Chodák, T. 620
 Dameme, A. 445
 Daynyak, L.G. 106
 Daza, L. 192
 Decarreau, A. 106
 Delgado Calvo-Flores, G. 244
 Delgado Calvo-Flores, R. 195, 244
 Delmon, B. 216, 600, 602
 Delvaux, B. 198
 Dell'Anna, L. 94, 199
 Demai, J.J. 98
 Desjardins, M. 188
 Díaz, M^a.C. 201
 Díaz-Barrientos, E. 357, 360
 Dickson, D.P.E. 276
 Doff, D.H. 71
 Doi, H. 301
 Doirisse, M. 95
 Donati, F. 220
 Doube, M. 180
 Doval, M. 203, 260
 Driard, J. 445
 Drita, V.A. 23, 106, 474
 Dubinska, E. 205
 Dufey, J. 198
 Eberl, D.D. 208
 Fabbri, B. 210, 213, 220
 Faier, M. 618
 Farfán-Torres, E.M. 216
 Felleca, D. 145
 Fenoll Hach-Alí, P. 342
 Fernández García, P. 462
 Fernández-Nieto, C. 562
 Ferrell, R.E. 298
 Ferretti, O. 218
 Ferron, J. 154
 Figueiredo, M.O. 59, 446
 Fiori, C. 220, 562
 Fontaine, C. 203
 Forteza, J. 481
 Forteza, M. 223
 Franci, M. 229
 Frank, E. 584
 Fretigny, C. 127
 Fukushima, Y. 226, 301
 Fusi, P. 229

Gabbutt, A.J. 63
 Gabelia, TS.S. 619
 Gabitova, R.U. 619
 Galán, E. 223, 232, 236, 240
 Galván, B. 467
 Galván, J. 74, 378, 467
 Gámiz Martín, E. 195, 244
 Gangas, N.H.J. 71
 Garbarino, C. 249, 251
 García, I. 392
 García Agramunt, M.J. 74, 490
 García-González, M.T. 253, 570
 García-Ramos, G. 256, 270, 273
 García-Rodríguez, M.P. 564
 García Romero, E. 260
 Garzón, G. 462
 Gautheyrou, J. 456
 Ghosh, D.K. 598
 Giresse, P. 263
 Gomes, C.S.F. 265
 González, I. 236, 240
 González-García, F. 256, 270, 273
 González López, J.M. 572
 González Martínez, J. 572
 Goodman, B.A. 276, 618
 Graf von Reichenbach, H. 368, 555
 Grange, P. 216, 600, 602
 Grassi, G. 135
 Greco, A. 189
 Guadagno, F.M. 278
 Guignard, J. 281
 Gutiérrez, E. 284
 Gyepesova, D. 173
 Hasenpatt, R. 287
 Havrda, J. 525
 Hay, I. 611
 Heinemann, M. 142
 Helios, E. 218
 Hem, S.L. 51
 Henmi, T. 289, 575
 Hepler, L.G. 598
 Herbillón, A.J. 198, 600
 Hermosín, M^a.C. 185
 Hernández-Blanco, M. 81
 Hervio, M. 459
 Herrero, C.P. 292
 Herrero, F. 378
 Höding, T. 295
 Hoyos, M.A. 378
 Huard, E. 445
 Huertas, F. 148
 Hurst, A. 298
 Ianovici, V. 297
 Iden, I.K. 298
 Inagaki, S. 301
 Inglés, M. 304
 Izvonar, D. 525
 Jama, A.M. 180
 Janackovic, J. 528
 Janackovic, T. 528
 Jaunet, A.M. 459
 Jeanroy, E. 98
 Jiránek, J. 307, 310
 Jiránková, J. 310, 617
 Johns, W.D. 26
 Justo, A. 314
 Kaiser, P. 127
 Kallai, L. 355
 Kameneva, M.Yu 474, 619
 Kamigaito, O. 301
 Kahr, G. 502
 Kazansky, Y.P. 618
 Kheirov, M.B. 619
 Kimpe, C.R. de 317
 Klika, Z. 319
 Kobakhize, E.I. 619
 Komadel, P. 173, 322
 Köster, H.M. 325
 Kotelnikov, D.D. 620
 Kovalyova, I.T. 619

Kraus, I. 326
 Krivosheeva, Z.A. 620
 Kromer, H. 61, 329
 Kühnel, R.A. 331
 Kuzvart, M. 27
 Lacka, B. 263
 Lagaly, G. 30
 Lai, T.M. 208
 Landi, L. 453
 Latouche, C. 334
 Laviano, R. 94, 199
 Ledeleev, JU.N. 619
 Leguey, S. 335, 443
 Leydeckers, J.P. 445
 Lieres, A.V. 545
 Linares, J. 148
 Lippmann, F. 338
 Liso, J. 339
 Liso, M.J. 339
 López, J. 339
 López-Aguayo, F. 572
 López Galindo, A. 342, 346, 349
 López Munguira, A. 352
 Lorenzo, L.F. 481
 Lorenzoni, P. 451
 Loschi Ghittoni, A.G. 104
 Lupo, M. 189
 Luque, F.J. 462
 Luque, J.M. 548
 Mackenzie, R.C. 355
 Madrid, L. 357, 360
 Maillet, N. 334
 Maldera, R. 213
 Malla, P.B. 456
 Malpei, F. 622
 Manceau, A. 127, 176, 178, 363
 Mandova, E.D. 612
 Maqueda, C. 314, 432, 435
 Marañes, A. 365
 Marcks, Ch. 368
 Marfil, R. 370
 Margulies, L. 373
 Marino, O. 375
 Martelloni, C. 453
 Martín, C. 81
 Martín-Pozas, J. 404
 Martín de Vidales, J.L. 195, 378
 Martínez, R. 381
 Mas, R. 462
 Mascolo, G. 375
 Massa, S. 560
 Mattei Scarpaccini, F. 112
 Mattias, P. 385
 Mayoral, E. 236, 240
 McPhail, D.B. 618
 Medina, J.A. 335
 Melo, F. 390
 Meloni, S. 346
 Mellor, A. 55
 Mendioroz, S. 192
 Menéndez Aparicio, P. 79, 387
 Mengel, K. 545
 Mesa, J.M. 232
 Meyer, R. 95
 Mifsud, A. 390, 392
 Miles, N. 317
 Minato, H. 395, 397
 Minguzzi, V. 399
 Miras, A. 240
 Mitchell, M.C. 618
 Molina, E. 564
 Mongelli, G. 401
 Morandi, N. 210, 399
 Moresi, M. 401
 Morgan, D.J. 115
 Morillo, E. 435
 Moya, J.S. 381
 Muller-Vonmoos, M. 502

Muñoz, A. 572
 Murad, E. 46
 Murray, H.H. 35, 403
 Nadeau, P.H. 618
 Naidja, A. 503
 Nannetti, M.C. 210
 Navarrete, I. 404
 Neacsu, G. 297
 Neacsu, V. 297
 Neuzil, J. 406
 Niccolai, I. 218
 Nikolayeva, I.V. 619
 Nieto, F. 86, 408
 Novakova, L. 173
 Oddone, M. 346
 Olivera Pastor, P. 412, 414
 Ortega Huertas, M. 37, 86, 365,
 408, 418, 478
 Otsu, M. 397
 Padalino, G. 249
 Pajares, J.A. 192
 Pais Lopes, F. 416
 Palacios Lacasa, J.M. 387
 Palanques, A. 417
 Palomba, M. 249, 251
 Palomo, I. 418
 Paola, E. di 422
 Papirer, E. 425
 Pardo, G. 572
 París, E. 385
 Párraga Martínez, J. 244
 Parrón, C. 427
 Paterson, E. 98
 Pavlovic-Terzic, L.J. 525
 Pekkala, Y.O. 429
 Peña, F. 101
 Peralta, M. 404
 Pérez, A. 572
 Pérez-Castells, R. 486
 Pérez Rodríguez, J.L. 232, 314, 432,
 435, 438, 456
 Pezerat, H. 281
 Philippart de Foy, F. 213
 Philippy, R. 95, 98
 Plana, F. 417
 Polvorinos, A. 232
 Pons, C.H. 76, 91, 151, 539
 Poyato, J. 440
 Pozo, M. 335, 443
 Pozzuoli, A. 531
 Prost, R. 445
 Prudencio, M.I. 446, 448
 Quantín, P. 451
 Quienne, P. 521
 Qvale, H. 298
 Radojevic, Z. 528
 Raigón-Pichardo, M. 256, 270
 Ramunni, F.P. 189
 Ranger, J. 456
 Raso, E. 112
 Rautureau, M. 203
 Recio, P. 253
 Reksten, K. 298
 Reyes, E. 148
 Ristori, G.G. 112, 229, 453
 Rius, J. 417
 Rivas, P. 418
 Rives, V. 81
 Roaldset, E. 12
 Robert, M. 76, 456, 459
 Rodas, M. 462
 Rodríguez, P. 465
 Rodríguez-Castellón, E. 412, 414
 Rodríguez Fernández, J. 467, 478
 Rodríguez García, A. 412, 414
 Rodríguez Gordillo, J. 418
 Rodríguez-Pascual, C. 467
 Romero Acosta, V. 273

Rose, D. 329
 Röseler, A. 295
 Rossberg, R. 519
 Rozen, H. 373
 Rub, A. 502
 Ruiz-Abrio, M^a.T. 256, 270
 Ruiz Amil, A. 470, 567
 Ruiz Cruz, M.D. 465
 Ruiz-Hitzky, E. 88, 284
 Ruskova, N.P. 612
 Ruzo, L.O. 373
 Sagnowski, S. 593
 Sakharov, B.A. 474
 Salomoni, A. 531
 Salvadori, C. 477
 Samama, J.C. 95
 Sánchez, C. 478
 Sánchez-Camazano, M. 481, 484
 Sánchez-Martín, M.J. 484
 Sánchez-Soto, P.J. 256, 270, 438
 Santaren, J. 163, 486
 Sanz, A. 74, 490
 Sanz, E. 390
 Sanz, J. 292
 Sastre, J.L. 160
 Schoonheydt, R.A. 43, 170
 Schramm, L.L. 598
 Schüller, K.H. 329
 Schwertmann, U. 46, 121, 157, 492
 Sebastián, E.M. 183, 494
 Sebastián Pardo, E. 352
 Seidov, A.G. 619, 620
 Serrato Rodríguez, J. 406
 Serratos, J.M. 292, 621
 Setti, M. 560
 Shaikh, N.A. 497
 Shimosaka, K. 226
 Shuali, U. 502
 Sieffermann, G. 535
 Siffert, B. 503
 Simón, M. 365
 Sindelar, J. 505
 Smolyar, B.B. 474
 Soria, F.J. 494
 Souza Santos, H. de 416, 477
 Souza Santos, P. de 494, 508, 607
 Sparvoli, E. 112, 453
 Srasra, E. 509
 Srodon, J. 48, 511
 Stafferi, L. 135
 Steffens, D. 545
 Steinberg, M. 502
 Stepkowska, E.T. 513
 Stoch, L. 516, 593
 Stoch, Z. 516
 Störr, M. 15, 295, 519
 Stösser, D. 519
 Strouf, R. 617
 Stucki, J.W. 322
 Suárez, M. 404
 Suquet, H. 151
 Sutanto, R. 180
 Szerszen, L. 620
 Tardy, Y. 539
 Tateo, F. 399
 Tchalabov, R.I. 619
 Tchoubar, D. 521
 Tchoubar, K. 474
 Tecilazic-Stevanovic, M. 525, 528
 Tenaglia, A. 531
 Tessier, D. 91, 456, 539, 542
 Thomas, G. 381
 Tjojudo, S. 535
 Tobias, M.M. 440
 Tomadín, L. 537
 Tortelli, M. 559, 560
 Torrent, J. 101, 201
 Touray, O. 539

Trebol, M.E. 542
Tributh, H. 545
Trillo, J.M. 440
Ulibarri, M.A. 548
Uras, I. 249
Urban, H. 551
Utermann, U. 555
Valentini, G. 278
Van Damme, H. 509
Van der Gaast, S.J. 331
Varela, A. 154
Vázquez, M.A. 240
Vegas, A. 557
Velasco, F. 86
Velilla, N. 408
Veneau, G. 459
Veniale, F. 189, 218, 559, 560
Venturi, I. 220
Venturi, V. 562
Vesely, O. 617
Vicente, M.A. 81, 564
Vielvoye, L. 198
Vigil, R. 335
Vila, E. 470, 557, 567, 570
Villena, J. 572
Violante, A. 145, 575
Violante, P. 575
Vuorinen, A. 578
Wachsmuth, H. 368
Waerenborgh, J.C. 59, 448
Wedemeyer, U. 551
Wendelbo, R. 587
Wei, L. 596
Weiss, A. 581, 584
White, J.L. 51
Wieden, P. 590
Wiewiora, A. 52, 205, 263
Wilkinson, H.T. 322
Wilson, M.J. 55
Wyszomirski, P. 593
Yada, K. 596
Yariv, S. 502, 598
Yunes, S. 600, 602
Zalma, R. 281
Zhengqiang, Y. 604

ORGANIZING COMMITTEE

Chairman:

Prof. Dr. EMILIO GALAN, Univ. Sevilla

Secretary:

Prof. Dr. JOSE LUIS PEREZ-RODRIGUEZ, C.S.I.C., Sevilla

Treasurer:

Dr. Juan CORNEJO, C.S.I.C., Sevilla

Chairman Scientific Committee:

Prof. Dr. JOSE M. SERRATOSA, C.S.I.C., Madrid

Members:

Prof. Dr. PURIFICACION FENOLL, Univ. Granada

Dr. MATILDE FORTEZA, Univ. Sevilla

Dr. ISABEL GONZALEZ, Univ. Sevilla

Dr. M. CARMEN HERMOSIN, C.S.I.C., Sevilla

Dr. ANGEL JUSTO, C.S.I.C., Sevilla

Prof. Dr. FRANCISCO LOPEZ-AGUAYO, Univ. Zaragoza

Dr. CELIA MAQUEDA, C.S.I.C.

Dr. JOSE M. MESA, Univ. Sevilla

Dr. MAGDALENA RODAS, Univ. Madrid

Prof. Dr. CARLOS SERNA, C.S.I.C., Madrid

Excursion Committee:

Prof. Dr. JOSE AGUILAR, Univ. Granada

Dr. MERCEDES DOVAL, Univ. Madrid

Prof. Dr. SANTIAGO LEGUEY, Univ. Autónoma Madrid

Prof. Dr. JOSE LINARES, C.S.I.C., Granada

Dr. MIGUEL ORTEGA, Univ. Granada

Dr. EMILIO REYES, C.S.I.C., Granada