

# 2010 SEA-CSSJ-CMS Trilateral Meeting on Clays



## BOOK OF ABSTRACTS GENERAL MEETING



June, 2010





**2010 SEA-CSSJ-CMS TRILATERAL MEETING ON CLAYS**

**BOOK OF ABSTRACTS OF  
THE GENERAL MEETING**





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June 8-10, 2010  
Seville, Spain

**Organized by:**  
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Clay Science Society of Japan (CSSJ)  
Spanish Clay Society (SEA)

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## Preface

The Clay Minerals Society (CMS), the Clay Science Society of Japan (CSSJ) and the Spanish Clay Society (SEA) hold this Trilateral Meeting in Spain in 2010 devoted to Clays and Clay Minerals. The aim of this 2010-Trilateral Meeting on Clays (**2010TMC**) is to offer a warm and friendly conference that will highlight innovative scientific and technical aspects of clays and related minerals. The 2010TMC will begin with a one-day Workshop on Clays & Materials in Madrid followed by a one-half day field trip to the Mg-clay deposits of the region (i.e., sepiolite and smectites). The 2010TMC has a format similar to that of the CMS Annual Meeting but in this case is celebrated jointly with the other two Clay Societies.

This book contains the presentations corresponding to the General Meeting of six Plenary lectures, being 3 of them introduced by the 2010 CMS Awarders (The Marilyn and Sturges W. Bailey Distinguished Member Award, The George W. Brindley Lecture Award, and The Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award) and the others by three relevant Invited Lecturers. In addition, two short General Lectures will be introduced by two CSSJ Awarders. Parallel Sessions are focused on the following topics: 1. *Structural Features and Crystal Chemistry*, 2. *Mineralogy and Geology*, 3. *Soils and Sediments*, 4. *Environment & Energy*, 5. *Biological Aspects & Health*, 6. *Industrial and other Applications* and 7. *Clays in Education Programs*. These Sessions are organized beginning for a Keynote Lecture followed by oral and poster presentations (about 200 Abstracts).

We would like to acknowledge the support from the Scientific Committee, especially Prof. E. Galán, Prof. J.L. Pérez-Rodríguez and Prof. J. Cornejo for their valuable effort and dedication reviewing and classifying of the abstracts. Thanks also to the three Societies for their support that have made possible this book. And finally we would like also to thank to the diverse committees for their hard work in the organization tasks as well as to the regional, national and international sponsors for financial support.

*Eduardo Ruiz-Hitzky*  
*General Chair of 2010-TMC*

*M. Carmen Hermosin*  
*Chair of General Meeting of 2010-TMC*



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# LECTURES





## **2010 CMS BAILEY AWARD**

### **CLAY SCIENCE: AN AREA OF INTERDISCIPLINARY RESEARCHS**

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Clay Minerals are solids that due to its peculiar characteristics (layer or porous structures, variability in crystal structure and chemical composition, differences in layer charge and in location of charges, etc) have attracted the interest of scientists of different areas (Chemistry, Physics, Crystallography, Mineralogy, Geology, Soil Science, Ceramics, among others). Due to the diversity of the field, clay research relies on, and profits greatly from, interactions among different disciplines and many techniques must be applied to a given problem.

Clay Science has been, in many cases, the antecedent of research and of technological applications as advanced materials, of other solids of similar structures (layered and nanostructured solids and porous materials as zeolites). Also, clay minerals due to its characteristics, constitute, in several cases, appropriated model systems in which specific properties and phenomena are particularly pronounced and can be isolated and investigated in depth. Cases concern: crystal structure, arrangement and reactivity of molecules in confined spaces, surface and colloid phenomena, among others.

A few significant cases will be presented.

## **2010 CMS BRINDLEY AWARD**

### **MOLECULAR SIMULATION AND THE NATURE OF THE CLAY-WATER INTERFACE**

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Interfaces play a critical role in many geochemical and clay mineral processes. Adsorption, dissolution, precipitation, nucleation, and growth mechanisms, in particular, are controlled by the dynamic interplay of structure, thermodynamics, kinetics, and transport at the clay mineral-water interface. These mechanistic details are typically beyond the sensitivity of experimental and analytical techniques, and so require accurate models and simulation methods to evaluate and characterize the important molecular processes. In this effort, we have developed and used classical and electronic structure methods to investigate the complex behavior of the clay mineral-water interface and its significance in the environment. Clay minerals and other phyllosilicates provide a unique opportunity to examine the behavior of water at well-defined interfaces. The wide variety of multicomponent low-symmetry phases having variable layer charge uniquely influences the structure and behavior of both interlayer and external surface water molecules. In addition, the adsorption of aqueous ions and molecules can be accurately simulated using molecular models. Bulk structures, swelling behavior, adsorption, and intercalation processes are evaluated and compared to experimental and spectroscopic findings. Classical molecular dynamics methods and *ab initio* molecular dynamics, in particular, provide valuable insights into the structure, dynamics, and reactivity of these complex materials and help to better understand and predict important geochemical processes.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

## 2010 CMS JACKSON AWARD

### CLAYS IN TEM

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Clays or clay minerals are generally in a fine particulate form whose size is generally at a micron or sub-micron order. Hence most analyzing techniques (XRD, IR, TG-DTA, etc.) treat numerous amounts of particles as a specimen and the obtained results are integrated or averaged ones over the particles. Only transmission electron microscopy (TEM) can analyze individual particles to derive information for their crystal structure, chemical composition, bonding state, etc. Hence TEM analyses are generally irreplaceable and often essential for the comprehensive understanding of the clay specimens. Of course TEM is not omnipotent. Especially the number of particles examined by TEM is so limited that the obtained results may not represent the specimen. This problem should be complemented with other “bulk analysis” techniques.

As mentioned, TEM is very powerful to investigate fine materials like clays, but everyone knows that it is not so easy to utilize TEM efficiently in their researches. TEM requires a considerable training time to operate it skillfully. Hence it is the best way to keep TEMs as a daily-use tool in a laboratory. The best results cannot be reached in some cases, with limited machine time by shared TEMs, or with division of the operator and researcher. However, modern TEMs are so expensive to purchase and maintain. If people would appreciate to some extent the author’s TEM results to date, it is only owing to his fortunate position in which he could almost exclusively occupy a TEM and become skilled year by year.

After 1996 when the author started TEM investigation of clays or related materials in university, several new TEM technologies have been developed and spread. Focused ion beam (FIB) sample preparation, Z-contrast imaging in scanning TEM (STEM), and spherical aberration (Cs) correctors for probe- or image-forming lens are among them. These new techniques will solve a plenty of remained problems in clay sciences in future. In this lecture, some results using these techniques will be presented. However, in spite of the appearance of new techniques, many types of clays are still difficult specimens for electron microscopists. Amorphization by beam radiation often prevent the atomic scale imaging of clays. Moreover, recently the author noticed that dehydroxylation of dioctahedral 2:1 phyllosilicates is almost inevitable. To overcome these problems, TEM technologies must be innovated more and more.

## CLAY-BASED NANOSTRUCTURED ECO-MATERIALS: FROM ENERGY STORAGE TO BIOMEDICAL APPLICATIONS

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Nanostructured solids derived from clay minerals are materials of increasing interest based on both, structural and functional characteristics. Among these materials, polymer-clay nanocomposites based on smectites (montmorillonites, saponites, etc) or microfibrinous clays (sepiolite and palygorskite) are currently being investigated to develop hybrid advanced materials useful for a wide type of applications, including energy storage, environmental and biomedical scopes.

This communication will be essentially focused on some recent examples of nanostructured clay derivatives emphasizing results from our own Laboratory. In this context, the following novel types of clay-based nanocomposites will be introduced and discussed:

1. Bio-nanocomposites, prepared by assembly biopolymers and other entities of biological origin to diverse types of inorganic solids. Examples include the case of biopolymers, such as polysaccharides, proteins and lipids, assembled to clay minerals. Interestingly, these materials, which can be conformed as powders, thin films or monolithic blocks, are biodegradable, biocompatible and exhibit additional properties, such as ion-exchange, fire retardancy, etc. Moreover, certain bio-nanocomposites can be prepared to show a cellular structure that provides ultra-lightweight characteristics. Applications: active phase of sensors, thermal and acoustic insulating materials and adjuvant of vaccines (1,2).
2. Inorganic-inorganic nanocomposites, consisting in clay-heterostructures as for instance the montmorillonite-sepiolite systems, and also the materials prepared by the assembly of metal-oxide nanoparticles (NPs) to clay minerals. Examples:  $\text{TiO}_2$  and  $\text{Fe}_3\text{O}_4$  NPs/clay systems, which are useful for environmental applications among others (3).
3. Graphene-like based nanocomposites, prepared by combination of carbon nanotubes with clays or generated from precursors of natural origin (e.g. sugar), using clays as templates. These materials have unique characteristics, as they simultaneously exhibit electrical conductivity and elevated specific surface area. Examples of applications: sensors and electrodes for rechargeable Li-batteries (4).

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## CLAYS FOR A HEALTHY SOIL-WATER ENVIRONMENT

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The presence of toxic chemicals in the soil-water ecosystem is viewed with great concern due to the inputs of enormous amounts of agrochemicals and huge amounts of industrial and urban residues. These situations can arise because the soil does not always act as a sink for organic molecules and consequently they leach to groundwater, volatilise to air and remain in the environment and frequently enter the food chain.

This lecture deals with two important aspects of clays properties: 1) the key role played by clays in the soil-water processes affecting contaminants fate, particularly in the sorption, degradation and transport of organic chemicals through the soil profile, and 2) the applications of clays as raw materials or after modifying their properties by means of several procedures to obtain different matrices to improve the soil-water environment.

Natural colloids are organomineral associations of multiple soil constituents, and are the main contributors to sorption and transport processes affecting pesticides and other organic contaminants in soil and water. In Mediterranean soils and subsoils, the amount of organic matter is scarce and the role of clay minerals in the dynamics of polar, ionic or ionizable organic compounds becomes very important. For these pesticides, it has been shown that the clay content was the soil characteristic better correlated to pesticide sorption (1). On the other hand, the contribution of the soil mineral surface is considered important on sorption of polycyclic aromatic hydrocarbons (PAHs) (2).

Looking for the role of clays on the fate of organic contaminants and pesticides in soils, it was derived the use of clays as sorbents for chemicals, especially when these are ionic, ionizable or polar, because of the hydrophilic character of these materials. The selective modification of these clays with organic cations containing appropriate functional groups has been used to maximize the affinity of the adsorbent for a given chemical (3). These organoclays are widely used as sorbents for diverse target molecules and for decontamination or contamination prevention purposes in soil and water environments, e.g: in clay-pesticide formulations. Factors influencing the release rate and extent of pesticides from clays and organoclays are still issues which need to be addressed. Interaction mechanisms of original and modified clays with organic molecules are discussed (3-5).

Organoclays based on large and small organic cations are proposed not only as carriers in pesticide formulations to retard pesticide leaching after soil application

and slow release of bioactive chemicals and photostabilizers, but also as filters or barriers for water decontamination. Even for emerging contaminants like drugs and pharmaceuticals, clays have been proved as good sorbents.

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## APPLICATION OF CHLORITE GEOTHERMOMETER TO LOW TEMPERATURE ROCK ALTERATION

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The geothermometry of clay mineral assemblages is an interested subject ongoing over decades. Among many methods proposed, the geothermometer utilizing the chemical composition of chlorite is useful because chlorite is ubiquitous in a wide range of geologic environments and displays a wide range of non-stoichiometric compositional variations depending on bulk rock composition and physicochemical conditions (T, P, pH, activities of metal and gaseous solutes in fluids etc) prevalent at the formation. Two types of approaches to the chlorite geothermometry have been proposed: (1) empirical calibrations based on the tetrahedral Al occupancies and/or the octahedral vacancies as a function of measured temperatures and (2) thermodynamic calculations based on the chlorite solid solution model. De Caritat et al. (1993) reviewed it and concluded that dogmatic application of a particular geothermometer is risky and it should be used with caution.

It is known that chlorites formed at low temperature conditions such as diagenesis, low-grade metamorphism, and hydrothermal alteration display different features of compositional variations from those of higher-grade metamorphic chlorites; for instance, the former has higher Si, octahedral vacancy, and probably  $\text{Fe}^{3+}$ , and lower Fe+Mg contents than the latter. Taking into account these chemical characteristics of low-T chlorites, we developed a new convenient geothermometer (Inoue et al., 2009).

In this communication we will discuss the validity of the new geothermometer from the standpoint of the effect of  $\text{Fe}^{3+}$  content on the estimate of temperature of formation, using new analytical data of hydrothermal chlorites from an active geothermal field in Japan. The studied geothermal field involves a Pb-Zn-Mn epithermal vein-type ore deposit, called Toyoha deposit. Intensive chloritization of Miocene volcanogenic sediments occurs in the vein and the peripheral alteration zones. The present data set contains the proportions of ferric iron determined by X-ray photoelectron spectroscopy (XPS), in addition to SEM-EDS analyses and homogenization temperature data of fluid inclusions in quartz and calcite associated with chlorite. As well as in our previous results (Inoue et al., 2009), it was found that independent determination of ferric iron contents is indispensable to estimate correctly the formation temperature of chlorite even when it coexisted with iron sulfide minerals.

De Caritat, P. et al. (1993) *Clays Clay Minerals* 41, 219-239; Inoue, A. et al. (2009) *Clays Clay Minerals* 57, 371-382.



## 2010 CSSJ AWARD

### KINETIC STUDY ON INTERCALATION OF ORGANIC ANIONS IN LAYERED DOUBLE HYDROXIDE USING QUARTZ CRYSTAL MICROBALANCE

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Layered double hydroxide (LDH) is widely known as anionic clay, host-guest material and anion-exchanger. The general formula of LDH is represented by  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][Anion^{n-}_{x/n} \cdot yH_2O]$ , where  $M^{2+}$  and  $M^{3+}$  are metallic divalent cation ( $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , etc.) and trivalent cation ( $Al^{3+}$ ,  $Fe^{3+}$ , etc), respectively.  $Anion^{n-}$  signifies an exchangeable anion such as  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$  or various organic anions, and the  $x$  value is equal to the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$ , generally 0.20-0.33. LDH has various applications as catalyst, catalyst precursor, adsorbent, polymer stabilizer, antacid, antipeptin, etc. In addition, increasing attentions have recently been devoted to drug/LDH nanohybrids in the medical field. Hence, there are so many reports on the intercalation of anions in LDH. However, the kinetic study on the intercalation behavior of LDH has been limited so far, because of the experimental difficulty. Therefore, we focus on a quartz crystal microbalance (QCM)<sup>1-2)</sup> as analytical technique in aqueous solutions. In this study, the intercalation behavior of various organic sulfate anions in Mg-Al LDH by ion exchange has been investigated as well as the structural examination of the LDH films immobilized on QC electrode by X-ray photoelectron spectroscopy (XPS) spectra.

Mg-Al LDH containing magnesium acetate (Mg-Ac) in the interlayer was used as the starting LDH. This LDH was rapidly delaminated in water to form translucent dispersion liquid by supersonic wave treatment. First, the outside quartz surface surrounded central gold disc (4.9 mm<sup>2</sup> s.a.) of QC electrode was treated with fluorochemical to modify hydrophobic surface. Then, the LDH film was deposited on the gold disc part of QC electrode by dropping the Mg-Ac/LDH dispersion liquid and then by drying under reduced pressure at room temperature. After being measurement of the frequency of this LDH/QC electrode in air, the LDH/QC electrode was soaked in Milli-Q water of 8 mL in the cell. The intercalation reaction was started by adding the organic sulfate solution of 4  $\mu$ L in the cell with microsyringe and the frequency change was observed for 300 sec under stirring at 25°C.

From AFM observation, thin LDH film was immobilized on QC electrode by using the dispersion liquid of the delaminated Mg-Ac/LDH particles (100-200 nm in diameter and 1-3 nm in thickness). This LDH film was stable in water and observed

no peeling during the intercalation reactions. As the guest anions, alkylsulfates having n-alkyl chain ( $C_nH_{2n+1}$ ,  $n=5-12$ ; abbreviated as  $C_nS$ ) were used. In the cases of  $C_5S$  and  $C_7S$ , no frequency changes were observed. However, when the solution of  $C_{11}S$  having longer alkyl chain was injected in the cell ( $1.3-10 \times 10^{-5}$  M), frequency started to decrease with elapse of reaction time and reached the equilibrium after about 180 sec, supporting that the intercalation of  $C_{11}S$  anion by the ion exchange with  $OH^-$  and Mg-Ac of LDH occurred on the LDH/QC electrode. Almost the same result was obtained in the case of  $C_{12}S$ , and the decreasing rate and degree of frequency were found to be accelerated with increasing the  $C_{12}S$  concentration. These results mean that the intercalation rate and degree of  $C_nS$  are promoted with the guest anion concentration. Then, the rate equation based on reversible pseudo first order reaction was postulated for these intercalation reactions and the kinetic analysis was attempted. As the result, a linear relationship between the apparent rate constant ( $k_{obs}$ ) and guest anion concentration was found. From the slope and intercept of the linear line, the association rate constant ( $k_a$ ) and dissociation rate constant ( $k_d$ ) were obtained, respectively. Moreover, the equilibrium constant ( $K$ ) was calculated as  $1.44 \times 10^4$  M $^{-1}$  for the intercalation of  $C_{12}S$  anion. The same tendency was also observed when using dodecylbenzene sulfonate (DBS) as guest anion. Finally, the XPS spectra of the LDH films before and after the intercalation revealed that  $C_nS$  and DBS anions were intercalated into the interlayer of the LDH/QC electrode in aqueous solutions.

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## 2010 CSSJ AWARD

### EFFICIENT PHOTOCHEMICAL ENERGY TRANSFER REACTIONS IN CLAY-PORPHYRIN COMPLEXES

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<sup>\*\*</sup> PRESTO (Precursory Research for Embryonic Science and Technology), Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan.

Keywords: Porphyrin, Clay Minerals, Photochemistry, Energy Transfer, Electron Transfer

In green plants, photosynthetic reactions are realized by suitable alignment and orientation of molecules. Without the regulated structure of molecular arrangement, most of function in living object will be lost. Thus, we believe that exploring a technique to control molecular arrangement is important to develop “chemistry”.

Complexes composed of layered materials such as clay minerals and functional dyes have been studied extensively. Dyes in the complex have a possibility to exhibit unique arrangement and novel unique character. For example, absorption maxima of porphyrin are shifted to longer wavelength by about 50 nm, when porphyrin molecule is intercalated between clay mineral layers. Methylviologen becomes emissive on the clay surface, although it is not emissive in a solution. We have reported various unique complexes composed of cationic porphyrins and clay minerals. As a result, we found out that a precise matching of distances between the negatively charged sites on the clay mineral layers and that between the positively charged sites in the dye molecule is one of the most important factors to determine the structure of the clay-dye complex. We have termed this as the “size-matching rule”. These techniques could be useful to construct and control the nano-level structure of supramolecular complexes. In case of other types of dyes, it is difficult to examine their detailed adsorption structure at their high loading conditions, because of their irregular structure due to the aggregation. In this paper, the energy transfer reaction of porphyrin molecules on the clay surface was examined. The average intermolecular distance between porphyrin molecules on the clay surface turned out to be very important for energy transfer efficiency.

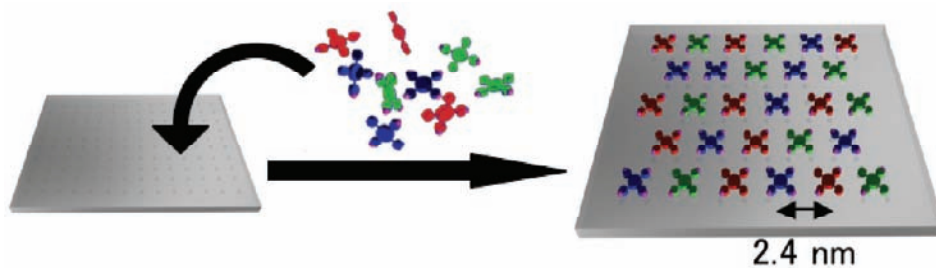


Figure Schematic view of porphyrin arrangement on the clay surface.

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# TOPIC 1

## *Structural Features and Crystal Chemistry*



# *ORAL PRESENTATIONS*





## A SPECTRAL INVESTIGATION OF THERMALLY TREATED SAUDI Ni-EXCHANGED MONTMORILLONITE

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Montmorillonite (MMT) clay from Khlays area in the western region of The Kingdom of Saudi Arabia was saturated with nickel and thermally treated at 120, 200, 300 and 400°C.

FT-IR analysis of Ni-MMT exhibited stretching vibrations of O-H at 3696 and 3625 cm<sup>-1</sup> that remained constant upon heating. A weak shoulder at 3650 cm<sup>-1</sup> appeared in the spectra heated to 300 and 400°C indicating a new species which may be attributed to Ni-OH vibrations and suggesting the migration of nickel ions into the empty octahedral sites. An increase in water O-H stretching vibrations from 3418 to 3450 cm<sup>-1</sup> reinforces this assumption. Stretching and bending vibrations of Si-O at 1033, 528 and 466 cm<sup>-1</sup> showed a gradual increase in their energies with temperature increase, proving that some Ni<sup>(II)</sup> ions inhabited the ditrigonal cavities of the clay structure.

These changes in structure were further studied using MAS-NMR spectroscopy of aluminum and silicon. <sup>27</sup>Al MAS-NMR spectrum of Ni-MMT exhibited a peak at 6.6 ppm representing the characteristic chemical shifts of Al<sup>(VI)</sup>, and two Al<sup>(IV)</sup> minor peaks at 84.4 and 61.9 ppm. The two Al<sup>(IV)</sup> sites may be attributed to different interactions of the tetrahedral sheets with interlayer water. Ni<sup>(II)</sup> fixation did not shift <sup>27</sup>Al peaks positions, which is expected when transition metals are incorporated in the MMT structure. The <sup>29</sup>Si MAS-NMR spectrum of natural MMT showed two major resonances at -91.2 and -106.5 ppm, attributed to Q<sup>3</sup>(Si1Al) and Q<sup>3</sup>(Si0Al) respectively. An increase in the intensity of the silicon signal (Si0Al) of Ni-MMT heated to 400°C was observed, in addition to a broadening of the peak. This change is due to charge reduction caused by Ni<sup>(II)</sup> ions in their vicinity; the ditrigonal cavities and/or in the vacant octahedral sites. Ni<sup>(II)</sup> ions are hence believed to be fixed upon heating; mainly in the ditrigonal cavities of MMT, and to a lesser extent in the empty octahedral sites of the structure.

## **SMECTITE FORMATION IN Fe-Mn-METALLIFEROUS SEDIMENTS COLLECTED IN THE HMS CHALLENGER EXPEDITION (1872-1876)**

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Three samples of submarine metalliferous sediments of hydrothermal origin, collected in the British HMS Challenger expedition (1872-1876), were studied to investigate the formation of smectite in such sediments. They were collected from the vicinity of the Pacific-Antarctic Ridge and the Chile Ridge. The samples were analyzed by means of XRD, chemical analysis, SEM-EDX, IR and TEM-AEM. After removal of biogenic calcite, the results from the above techniques indicated that they consist mainly of two amorphous or semiamorphous phases intimately mixed: Fe-Mn oxyhydroxides and a Si-Al-Mg-Fe phase of chemical characteristics similar to smectite and with variable proportions of the above elements.

TEM-AEM analysis, obtained from powders dispersed on holey C-coated formvar Au grids, showed the morphological and chemical characteristics of the several components of the sediment. The appearance of Fe-rich oxyhydroxides, as round-shape particles, is clearly different from that of the other phases. Mn-rich oxides and smectite have both the typical flaky and wavy morphology of smectite, with the particularity that Mn-bearing particles aggregate to form high-contrast clusters. XRD analysis identified the Mn-oxides as  $\delta$ -MnO<sub>2</sub>, related to birnessite, also a layered structure. The smectite particles always appear associated to Fe-Mn oxyhydroxides. Smectite composition corresponds in most cases to nontronite, frequently containing a trioctahedral (Mg-rich) component, although there are compositions corresponding to Fe-montmorillonite and Al-montmorillonite. No Mn-rich smectite was detected. Electron diffraction patterns confirm the poor crystallinity of both Fe-Mn oxyhydroxides and most smectite particles. These results are interpreted as representing smectite formation from Fe-Mn-rich metalliferous sediments as the Fe-rich gels react with solid particles and dissolved species. Possible sources of Si, Al and Mg are detrital silicate minerals, glass of basaltic origin, silica gel precipitated from hydrothermal fluids and, specifically for Mg, seawater.

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## EFFECT OF ACID LEACHING ON THE STRUCTURE OF PALYGORSKITE AND SEPIOLITE

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Moderate acid treatment is a common process for increasing the specific surface area of clay minerals by leaching out some of the octahedral ions and creating an amorphous hydroxylated silicate phase. This work employs near-infrared spectroscopy (NIR) to understand how acid leaching affects the structure of palygorskite and sepiolite (both non-expandable phyllosilicates with a discontinuous octahedral sheet and alternating ribbons and tunnels), as well as to provide spectroscopic indicators for detecting and monitoring the degree of leaching of these minerals.

Acid leaching has a rather minor effect on the spectra of ambient palygorskite and sepiolite. Upon leaching, the samples exhibit progressively weaker OH stretching combination and overtone modes, but their relative intensity which reflects the speciation of the octahedral sheet remains invariable. The SiOH groups of the amorphous silica phase are manifested by a broad overtone envelope at ca. 7320  $\text{cm}^{-1}$  and are identical to those reported earlier by Madejova for acid leached montmorillonite.

Similarly, the zeolitic dehydration of the leached samples does not lead to any significant differentiation of the spectrum of the structural hydroxyl groups in comparison to that of their unleached counterparts: The  $\text{AlAlOH}$ ,  $\text{AlFeOH}$ ,  $\text{FeFeOH}$  stretching overtone triplet of dry dioctahedral palygorskite is observed at 7076, 7012 and 6945  $\text{cm}^{-1}$  and the  $\text{Mg}_3\text{OH}$  mode of dry trioctahedral sepiolite appears at 7192  $\text{cm}^{-1}$  in the spectra of both raw and leached samples. Also, upon leaching, the silanol spectrum of the unleached samples (7250-7270  $\text{cm}^{-1}$ ) is substituted by the 7320  $\text{cm}^{-1}$  overtone, now appearing sharper and better defined.

On the contrary, the effects of leaching become very obvious at temperatures where the unleached clays are known to be in the folded dehydrated state (> 200 °C for palygorskite, >275 °C for sepiolite). XRD data demonstrate that none of the acid leached samples folds at these temperatures, in agreement with Valentin et al. (2007) who made the same observation on sepiolite and proposed that folding is a synergetic effect involving all ribbons simultaneously and therefore depends on the octahedral sheet integrity of a critical number of ribbons.

At folding temperatures (300 °C), palygorskite pre-treated with 2M  $\text{H}_2\text{SO}_4$  exhibits a new position of the dioctahedral stretching overtone triplet, now appearing at

7147, 7085 and 7020  $\text{cm}^{-1}$ , respectively, instead of the expected 7115, 7052 and 6980  $\text{cm}^{-1}$  of the unleached folded clay. A new  $\text{H}_2\text{O}$  species is present as seen from a sharp combination mode at 5265  $\text{cm}^{-1}$  instead of the expected 5180  $\text{cm}^{-1}$  wavenumber. Lower concentrations of acid yield spectra which can be described as a superposition of unleached and leached palygorskite.

Sepiolite SepSp-1 leached with 2M  $\text{H}_2\text{SO}_4$  and heated to 300 °C behaves quite differently than palygorskite. No new peaks are observed in the  $\text{H}_2\text{O}$  combination spectrum. The  $\text{Mg}_3\text{OH}$  overtone is observed at 7192  $\text{cm}^{-1}$  i.e. at the exact position of zeolitically dry sepiolite. Interestingly, this mode remains fixed up to 375 °C indicating that the phyllosilicate layer of the leached sample suffers no deformations over a very broad temperature range. For comparison, the 7192  $\text{cm}^{-1}$   $\text{Mg}_3\text{OH}$  mode of zeolitically dry but unleached sepiolite splits sharply at much lower temperature ( $280 \pm 10$  °C) to discrete components at 7218 and 7180  $\text{cm}^{-1}$  signaling the onset of folding and maintains this spectrum unchanged up to ca. 500 °C.

## STRUCTURES OF THE PALYGORSKITE-SEPIOLITE GROUP MINERALS: COMMENTS ON THE FORMATION OF THE POLYSOMES

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The palygorskite-sepiolite mineral group consists of palygorskite, sepiolite, falcondoite, kalifersite, loughlinite, raite, intersilite, tuperssuatsiaite, and yofortierite. The basic structure is characterized by a Si tetrahedral sheet, and this sheet is composed, in part, of a continuous basal oxygen-atom plane. An apical-oxygen atom of the tetrahedral sheet can point in one of two opposing directions. The apical oxygen atoms complete octahedral coordination with other anionic groups ( $\text{OH}$ ,  $\text{OH}_2$ ) around metal cations, and these octahedra link by edge sharing to produce a strip or ribbon pattern. An octahedral strip and the adjacent tetrahedra describe a "polysome".

A comparison of the palygorskite- and sepiolite-like minerals to phyllosilicates involves defining structure parameters similar to those that are used to compare phyllosilicate structures. These parameters include  $\alpha_{\text{polysome}}$  (defined as in-plane tetrahedral rotation within the polysome, which varies between  $0.81 - 12.62^\circ$ ),  $\alpha_{\text{interpolysome}}$ , which defines in-plane tetrahedral rotation between polysomes ( $0.53 - 10.82^\circ$ ), and  $b/2$ , which is an indicator of out-of-plane tilt (raite has the greatest out-of-plane tilt at  $b/2 = 8.800 \text{ \AA}$ , whereas palygorskite, sepiolite, and tuperssuatsiaite have near planar basal-oxygen planes at  $b/2 = 8.921 - 9.005 \text{ \AA}$ ). Comparison of average octahedral and tetrahedral bond lengths between mica structures (e.g., M-O:  $2.019 \text{ \AA}$ , T-O:  $1.632 \text{ \AA}$ ) and palygorskite (M-O:  $2.016 \text{ \AA}$ , T-O:  $1.623 \text{ \AA}$ ) suggests that misfit between the lateral dimensions of the tetrahedral sheet and the octahedral strip is not the cause of the polysome structure of palygorskite.

The octahedral strips in the palygorskite-sepiolite group minerals are terminated by OH and  $\text{OH}_2$  for anion completion of the octahedra at the polysome-channel interface. These terminations are consistent with an aqueous environment with a high  $a_{\text{OH}^-}$ . In support of this observation, the palygorskite-sepiolite group minerals form in high alkali environments ranging from low-temperature aqueous solutions (e.g., salt lakes) to high-temperature [e.g., agpaitic,  $(\text{Na} + \text{K})/\text{Al} > 1$ ] environments. These environments indicate alkali-rich aqueous conditions at near-surface to hydrothermal ( $<350^\circ\text{C}$ ) temperatures. Thus, there is a continuum of environments, where the activity of the polysome components is similar. In comparison, trioctahedral smectite, either stevensite (Mg) or saponite (Al), forms also in aqueous environments at conditions similar to but not necessarily identical to palygorskite and sepiolite. Furthermore, the formation of smectite requires a high value of  $a_{\text{OH}^-}$  also. Thus, unknown chemical parameters may affect the continuity of the octahedral sheet to produce palygorskite-sepiolite-like polysomes or a traditional layer structure like smectite. This parameter may relate to  $a_{\text{alkali}}$ ,  $a_{\text{SiO}_2}$ , and/or  $a_{\text{OH}^-}$ .

## SOLID-STATE NMR STUDIES ON ETHYLENE GLYCOL INTERCALATED KAOLINITE

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Many modern composite materials contain clay platelets as functional compounds, e.g. in polymer layered silicate nanocomposites (PLSNs). To avoid cracks in the composite material the interfacial interaction between the filler and the matrix needs to be optimized by the modification of the external surfaces of the clay. These modifiers should be irreversibly adsorbed onto the clay surface via electrostatic or covalent bonding. A very competitive and promising clay mineral for such an application via a covalent bond is the 1:1 layered silicate kaolinite  $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$  in combination with diols as modifiers.

For detailed examinations of the proposed reaction between the  $\mu$ -bridged OH-group of the kaolinite and the OH-groups of the diol we used ethylene glycol intercalated kaolinite as a model system. Although there are certain indications known<sup>[1]</sup> that a reaction may take place between the kaolinite and the ethylene glycol, neither a proof nor a quantification has ever been presented for a covalent Al-O-C bond. Solving this problem solid-state NMR is a very powerful method to obtain structural information on the local and intermediate length scale. In this study the postulated Al-O-C bond between the ethylene glycol and the kaolinite was examined.

$^{27}\text{Al}$  MQ-MAS measurements were performed for the pristine kaolinite, the DMSO intercalated kaolinite and the ethylene glycol intercalated kaolinite to gain more information about the chemical environment of the  $^{27}\text{Al}$  nuclei. The measurement of the DMSO intercalate, which forms only hydrogen bonds with the kaolinite, features just a small change of the chemical environment in comparison to the pristine kaolinite (Figure 1, left). However, the chemical environment of half of the  $^{27}\text{Al}$  nuclei has significantly changed in the  $^{27}\text{Al}$  MQ-MAS measurement of the ethylene glycol intercalated kaolinite (Figure 1, middle). Consequently, the MQ-MAS measurements clearly point out that the bond strength between the kaolinite and the ethylene glycol exceeds that of an hydrogen bond considerably.

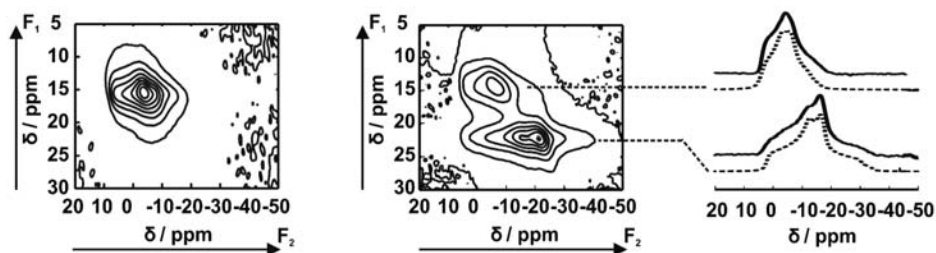


Figure 1:  $^{27}\text{Al}$  MQ-MAS measurements of kaolinite (left), ethylene glycol intercalated kaolinite (middle) and the fit (solid lines, right) of the cross-sections (dotted lines, right)

Additional examinations focused on the dynamic of the ethylene glycol molecules in the layer were accomplished by temperature dependent  $^1\text{H}$  static solid-state NMR measurements. Below 190 K the dynamic of the molecules is frozen, while the dynamic of the system is fully developed at temperatures above 360 K.

Furthermore, by using the REAPDOR<sup>[2]</sup> (rotational echo adiabatic passage double resonance) effect we successfully determined the  $^{13}\text{C}$ - $^{27}\text{Al}$  distances of the  $^{27}\text{Al}$  nuclei of the kaolinite and the  $^{13}\text{C}$  nucleus of the bonded ethylene glycol. According to these distances a covalent bond could be unequivocally proven. Additionally based on different simulation models informations about the orientation of the molecules within the layer were obtained.

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## WATER UPTAKE CAPACITY OF BENTONITES

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One of the most important properties of bentonites is the water uptake capacity which can be measured by a set of different methods. In principle the water can be added either as vapour or as liquid.

The present study was conducted in order to compare the water uptake capacity of bentonites from the vapor phase with the water uptake capacity in contact with liquid water (Kaufhold et al., 2009). The latter was measured with the Enslin-Neff method (Neff, 1959). The comparison of both water uptake tests was thought to improve the understanding of the dominant water adsorption mechanisms.

The water vapor uptake capacity is often measured gravimetrically after equilibration of a clay powder at a given relative humidity. Occasionally these values are used for the calculation of the total specific surface area ( $SSA_{WA}$ ). For the calculation of the water uptake value ( $SSA_{WA}$ ) either  $\approx 50$  or  $\approx 70$  % relative humidity is used.

Other studies suggest that water is mainly taken up by the exchangeable cations which results in a dependence of the  $SSA_{WA}$  on the layer charge density (Kaufhold, 2005). In addition some water is believed to adsorb at micro- mesopores which would render it impossible to determine correct SSA values unless the “pore water” can be quantified.

The present study proved that water is adsorbed both by exchangeable cations and in micro- mesopores. Considering the porosity and the CEC of 36 different bentonites suggests that the ratio of water adsorbed to exchangeable cations to the water in pores varies from 0 to 1. In the case of the Enslin-Neff method, however, the amount of exchangeable  $Na^+$  is more important than microstructural features.

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## NEAR-INFRARED SPECTROSCOPIC ANALYSIS OF ACID TREATED ORGANO-MONTMORILLONITES

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Investigation of clay minerals modified with organic surfactants is an attractive research area because of their wide application in industry and environmental protection. This work introduces the potential of the infrared spectroscopy in the near infrared (NIR) region to study the alterations in the organo-montmorillonites structure upon their dissolution in HCl. Ca-form of SAz-1 montmorillonite (Cheto, Arizona) and the alkylammonium salts with different alkyl chain lengths were used to prepare tetramethylammonium (TMA-), tetraethylammonium (TEA-), tetrapropylammonium (TPA-), and tetrabutylammonium (TBA-) montmorillonites.

Acid dissolution proceeds via replacement of the exchangeable cations with protons penetrating into the mineral layers and attack the OH groups. Following dehydroxylation connected with the release of the central atoms from the octahedral sheets results in formation of amorphous, partly protonated silica phase. The interpretation of the first overtone ( $2\nu$ ) and combination ( $\nu+\delta$ ) bands of OH and CH groups in the NIR spectra is based on the stretching ( $\nu$ ) and bending ( $\delta$ ) vibrations observed in the middle infrared (MIR) region. The NIR spectra of acid-treated samples show a pronounced decrease of the intensities of the structural OH overtone ( $\sim 7060\text{ cm}^{-1}$ ) and combination ( $\sim 4520\text{ cm}^{-1}$ ) bands indicating gradual degradation of the SAz-1 structure. A strong band in the  $5240\text{--}5250\text{ cm}^{-1}$  range is due to  $(\nu+\delta)\text{H}_2\text{O}$ ; its intensity decreases for TEA-, TPA- and TBA-forms reflecting more hydrophobic surface of the samples. Dissolution reduces the intensity of the  $(\nu+\delta)\text{H}_2\text{O}$  band for Ca-, and TMA-SAz-1 in contrary to other organo-forms for which the intensity decreases at first and later gradually increases. It is clear that this band sensitively reflects the changes in the amount of adsorbed water. A new band at  $7315\text{ cm}^{-1}$  observed in the spectra of acid-treated samples related to  $2\nu\text{SiOH}$  is an important indicator of the montmorillonite surface acidification and/or creation of partly protonated silica phase. The  $\text{CH}_3$  and  $\text{CH}_2$  overtone and combination bands appear in the  $6100\text{--}5500\text{ cm}^{-1}$  and  $4500\text{--}4000\text{ cm}^{-1}$  regions, respectively. Gradual decrease of the intensities of the  $2\nu\text{CH}$  and  $(\nu+\delta)\text{CH}$  bands reflects the reducing content of the alkylammonium cations as the extent of dissolution progressed. The sensitivity of the NIR region to detect the alkylammonium cations is very high. For example, no  $\text{CH}_3$  or  $\text{CH}_2$  vibrations can be distinguished in the MIR spectra of TEA-SAz-1 treated for 8 hours, only the bands of amorphous silica (near  $1100$ ,  $800$  and  $470\text{ cm}^{-1}$ ) are present in the spectrum. In contrary, the NIR spectra clearly show the overtone and the combination bands of  $\text{CH}_3$  and  $\text{CH}_2$  groups along with

the ( $\nu+\delta$ )OH bands of the structural OH groups. This proves that though the solid reaction product contains mainly amorphous silica, some fragments of the SAz-1 layers protected by the TEA<sup>+</sup> cations survive the acid attack. The content of the alkylammonium cations present in the organo-montmorillonites was followed also by thermal analysis (TA). Mass loss observed in the temperature range of 200-850 °C is assigned mainly to the surfactant decomposition and to the dehydroxylation of the montmorillonite layers. The mass loss determined for untreated samples increases in order TMA-SAz-1<TEA-SAz-1<TPA-SAz-1<TBA-SAz-1 confirming the rising amount of organic cations loading with increasing number of carbons. Upon acid treatment the organic cations and structural OH groups are released from the clay mineral which decreases the mass loss of the sample in the studied temperature range. The comparison of TA results for Ca-SAz-1 with other samples shows that TMA<sup>+</sup> cations are completely leached out after 8 hours of dissolution, while ~1.2 % of TEA<sup>+</sup>, 2.5 % of TPA<sup>+</sup> and 9.2 % of TBA<sup>+</sup> still remain in the samples.

The NIR spectroscopy and TA show that the dissolution rate of TMA-SAz-1 is only slightly lower in comparison with Ca-SAz-1, moderate deceleration has been found for the TEA- and TPA-forms, while degradation of the montmorillonite structure is significantly reduced for TBA<sup>+</sup> cations. This observation proves that longer-chain cations covering the inner and outer surfaces of montmorillonite prevent free access of protons to the layers and thus protect them from the acid attack.

## REPULSIVE INTERACTIONS IN AQUEOUS DIOCTAHEDRAL SWELLING CLAY MINERALS AT LOW IONIC STRENGTH

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Natural swelling clay minerals are negatively charged platelets whose charge is compensated by exchangeable cations. Swelling clay suspensions homoionized by monovalent cations form gels at low volume fractions  $\phi$ . Such a property is used in numerous industrial (drilling fluids, thickeners and anti-settling agents) or health (gastrointestinal protectors, antidiarrhoeaics) applications. Despite this importance, and though numerous studies have focused on colloidal dispersions of natural or synthetic clay platelets, the structure of the gel and the mechanisms of gelation are still under debate since the 1930's. Two conflicting views have been opposed: (i) The so-called "house of cards" model, based on electrostatic attraction between the edges and faces of the platelets, leading to a tridimensional network and (ii) the stabilization of the gel structure by a repulsive process between the interacting electrical double layers of the platelets. For studying this problem, we have chosen to work with four natural dioctahedral swelling clays of the montmorillonite group, one Beidellite SBld-1 and three Montmorillonites, SWy-2, SAz-1, Milos. After size-selection, osmotic stress experiments were performed to obtain a wide concentration range of clay suspensions varying from the liquid to the gel phase. Using such an approach, it is possible to tune various parameters such as size, shape, anisotropy, ionic strength and charge, which can control the phase behaviour of charged colloidal platelets. All samples were further analyzed by combining TEM observations and Small Angle X-Ray experiments.

SAXS experiments revealed the presence of correlation peaks whose position depends on the volume fraction. The evolution of the correlation distances between platelets allows deriving swelling laws that display a crossover from local lamellar order ( $\phi^{-1}$ )

to isotropic volumic swelling ( $\phi^{-1/3}$ ) close to the sol-gel transition. Furthermore, the average thickness of the individual objects derived from the swelling laws is closed to that of a single clay sheet (0.65 nm). In parallel, we applied a geometrical effective approach based on excluded volume interactions of hard spheres to determine these average interparticle distances by combining the morphological parameters derived from TEM and SAXS experiments. The good agreement between model and experiments fully validates this approach and reveals that excluded volume effects play an important role in such conditions. Finally, combinations of osmotic pressure measurements and SAXS results reveal that the pressure of the system can be approached from a simple Poisson-Boltzmann treatment based on the charge of infinite parallel platelets whatever the size of the particles. The agreement between calculated and experimental osmotic pressure is quite satisfactory, especially for ionic strength of  $10^{-5}$  and  $10^{-4}$  M/L and proves that at low ionic strength, all clay suspensions are purely repulsive even if values of the effective charge vary from a factor 10 between beidellite and montmorillonites.

## **SIMULTANEOUS RIETVELD REFINEMENT OF MULTI-DEVICE AND/OR MULTI-SPECIMEN XRD DATA OF MIXED LAYERED STRUCTURES**

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The structural characterization of clay minerals is an important tool for the interpretation of diagenetic or hydrothermal processes for example. Most analytical techniques are based on X-ray diffraction measurements with different sample preparations (oriented mounts and random powder samples), following diagnostic pretreatments of these materials. These pretreatments like heating or the intercalation of molecules lead to structural changes of individual clay minerals. These structural changes cause distinct effects in the powder patterns like change of peak positions, intensities, and breadths. One way to extract structural information from these patterns is the comparison with calculated patterns using software codes like Newmod (Reynolds, 1985), Wildfire (Reynolds, 1994) or DIFFaX (Treacy et al., 1991). In the ideal case, the interpretation should lead to a structure model which is consistent with all treatment states of the mineral (Sakharov et al., 1999).

Several approaches for the automatic refinement of disorder parameters exist (Leoni et al., 2004, Aplin et al., 2006, Casas-Cabanas et al., 2006), among them Rietveld compatible approaches for turbostratic disorder (Ufer et al., 2004), mixed layering and rotational or translational misfits of individual layers in a stacking sequence (Ufer et al., 2008). Recent developments of the Rietveld code BGMN (Bergmann et al., 1998) allow the simultaneous refinement from multiple measurements, e.g. synchrotron and in-house measurements of the same material. In addition, it is possible to refine global structural parameters which are served to individual structural models of different sample pretreatments, e.g. different interlayer cations and basal spacings of swelling minerals. Even the combination of the information contained in the diffraction patterns of oriented mounts and random powder preparations is possible.

The aim of the presentation is to show that the multi-device and multi-specimen refinements lead to more reliable and unique results. The applicability of this approach is demonstrated by a refinement of patterns of clay minerals, which contain different kinds of stacking disorder. The results are compared to that of individual refinements.

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## *POSTER PRESENTATIONS*



## PREDICTING THE FORMATION OF PLYGORSKITE THROUGH THE SYNTHESIS EXPERIMENT

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Twenty four mixtures were tested to form palygorskite in order to determine its origin. The mixtures were exposed to wetting and drying cycle for three months in oven at 45 and 70°C. The mixtures were done by using tap water and gels with different Mg/Al ratios and Si gel. Different chemical materials were added to the mixture such as gypsum, calcite and magnesium oxide in different ratio and forms. The EC was elevated by using sodium chloride. All sample solutions were brought up to the initial amount after drying. The synthesized mixtures were tested after first, second and third months. The samples were dried and prepared on glass slide. X-ray diffraction was used to analyze the samples at 0.02 step from 3-15  $2\theta^\circ$  in order to get the 10.5 Å peak.

The results showed that palygorskite was the only fibre crystalline phase synthesized. Further analyses were done in order to confirm the results. The samples were tested by Analytical Transmission Electron Microscopy (ATEM) of individual particles showing a fibre. Homogeneously fine size and fibre shape crystals were successfully synthesized in a single phase. The chemical composition of the final product was similar to the one found in the study area and also was compared with others forms from the literature.

The results conclude that forming palygorskite requires three main things: alkaline environment, enough supply of Mg and Silica and enough temperature in order to crystallize a single crystal.

## THE $\text{NH}_4$ FOR K SUBSTITUTION IN MICAS SYNTHESIZED AT 200°C

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Tobelite (the ammonium mica equivalent to K-white mica) (Higashi, 1982) has been frequently described in low-temperature environments, especially in sedimentary terrains rich in organic components, where it coexist with illite. (e.g. Juster *et al.* 1987; Daniels and Altaner, 1990).  $\text{NH}_4$ -mica formation is related in these cases to N liberation during the thermal decomposition of organic matter, and fixation, as  $\text{NH}_4^+$ , in diagenetic clay minerals, kaolinite being the most common precursor. Coexistence of tobelite and illite strongly suggested the existence of a miscibility gap between both end-terms (e.g. Nieto, 2002).

Synthesis of tobelite from kaolinite is easy and had been carried out previously (e.g. Shigorova *et al.*, 1981; Sucha *et al.*, 1998). In this work we have used different chemical systems ( $\text{K}_2\text{O}-(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{K}_2\text{O}-(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{HCl}-\text{H}_2\text{O}$ ), and different  $\text{NH}_4$ :K ratios with the aim of test the existence of such miscibility gap at low temperature. A solution/solid ratio = 1:15 was used in all the reactions. The hydrothermal treatments were conducted in 50 cm<sup>3</sup> Teflon-lined reactors (Parr 4744), which were maintained at a constant temperature of 200°C ( $\pm 3^\circ\text{C}$ ), with reaction times from 1 to 90 days.

In the system  $\text{K}_2\text{O}-(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , tobelite was formed at high  $\text{NH}_4$ :K ratios, whereas at lower ratios only zeolites formed. In the system  $\text{K}_2\text{O}-(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{HCl}-\text{H}_2\text{O}$ , a complete series of mica (except for  $\text{NH}_4$ :K ratio = 0:1) formed. The crystallinity of the newly formed mica increases in parallel to the  $\text{NH}_4$ :K ratio, and the basal spacing also increases, from 10.135 Å (for  $\text{NH}_4$ :K = 0.1:0.9) to 10.365 Å (for  $\text{NH}_4$ :K = 1:0). The obtained values do not show a linear correlation (Fig. 1).

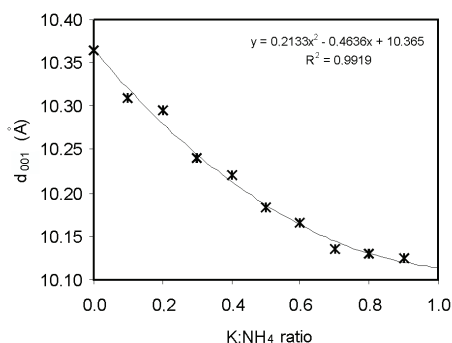


Figure 1. Basal spacing of the mixed  $\text{NH}_4$ :K micas as a function of the  $\text{NH}_4$ :K ratio.

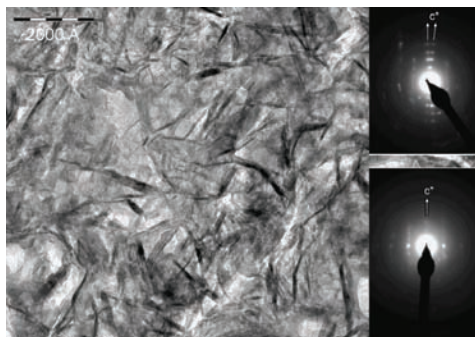


Figure 2. TEM image of tobelite ( $\text{NH}_4$ :K ratio = 0.7:0.3) and SAED images.

The TEM/AEM study confirmed that both K and  $\text{NH}_4$  occupy the interlayer positions in a ratio similar to that present in the original system. Tobelite form small and curved particles, and the SAED patterns indicate the prevalence of 1M and disordered polytypes (Fig. 2). Our results clearly indicate that a miscibility gap is lacking in micas synthesized at low temperature (200°C)

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## SYNCHRONOUS NEAR- AND MID INFRARED INVESTIGATION OF THE DEHYDRATION OF SEPIOLITE

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The modular structure of sepiolite is built of alternating ribbons and tunnels and results in a large internal and external surface which is decorated by various types of adsorbed  $\text{H}_2\text{O}$  molecules. A sequence of dehydration events of surface, zeolitic and coordinated  $\text{H}_2\text{O}$  has been reported. As the ribbons of sepiolite are held together by Si-O-Si linkages, the change of the interlayer spacing in response to varying  $\text{H}_2\text{O}$  content is constrained. Hence, dehydration imposes structural rearrangements within the layers themselves. The best known such rearrangement is the folding of the structure at ca. 300 °C.

This work combines near- and mid- infrared spectroscopy (NIR, MIR) to monitor in detail the structural aspects of the dehydration of sepiolite SepSp-1 (CMS source clay from Valdemoro, Spain), over a broad range of environments from ambient temperature and 100% RH to 500 °C, with particular emphasis on the poorly studied range of zeolitic dehydration.

The synchronous NIR and MIR monitoring allows for establishing a self-consistent set of assignments facilitated by the early seminal infrared work of Serna. Based on these assignments NIR can be employed as an independent, sensitive and convenient tool for the structural study of sepiolite.

The wavenumber of the  $\text{Mg}_3\text{OH}$  overtone (fundamental) stretching mode is found to respond to very subtle changes of the layer structure, usually unnoticed by XRD. The full occupation of the zeolitic  $\text{H}_2\text{O}$  sites at ambient temperatures requires elevated relative humidity. In this “zeolitically wet” state, the  $\text{Mg}_3\text{OH}$  mode is sharp and degenerate at  $7213\text{ cm}^{-1}$  (fundamental at  $3690\text{ cm}^{-1}$ ). At ambient RH and temperature, this mode broadens and splits, and a second weak component (which could be confused for a  $\text{Mg}_2\text{FeOH}$  mode) appears at  $7183\text{ cm}^{-1}$  ( $3670\text{ cm}^{-1}$ ). In the zeolitically dry state, the spectrum reverts to a single mode at  $7192\text{ cm}^{-1}$  ( $3680\text{ cm}^{-1}$ ). This degeneracy is removed again at ca. 280 °C and the onset of the folded state is manifested by two sharp modes of nearly equal intensity at  $7218, 7180\text{ cm}^{-1}$  ( $3692, 3673\text{ cm}^{-1}$ ) which persist up to ca. 500 °C and then broaden. Throughout these changes, the anharmonicity of the  $\text{Mg}_3\text{OH}$  stretch remains fixed ( $X=83.5\pm0.5\text{ cm}^{-1}$ ). This complex dependence of the layer structure on  $\text{H}_2\text{O}$  content is not observed in true trioctahedral phyllosilicates such as talc and saponite which exhibit the corresponding  $\text{Mg}_3\text{OH}$  modes at  $7186\text{ cm}^{-1}$  ( $3677\text{ cm}^{-1}$ ) with little or no

dependence on hydration. It is therefore considered as a unique characteristic of sepiolite.

Unlike dioctahedral palygorskite which dehydrates in a single step, the zeolitic dehydration of sepiolite is a two-step process with a well defined transient intermediate state corresponding to the partial hydration of the tunnels. This state is best detected via a single sharp  $\text{H}_2\text{O}$  combination mode at  $5270\text{ cm}^{-1}$ , which grows upon progressive dehydration at the expense of the doublet characterizing the wet state ( $5260, 5200\text{ cm}^{-1}$ ) and then vanishes giving place to the doublet of the zeolitically dry state ( $5225, 5160\text{ cm}^{-1}$ ).

Independently, but parallel to the above, the well-known surface dehydration of sepiolite manifests itself by the disappearance of the surface  $\text{H}_2\text{O}$  mode at  $5317\text{ cm}^{-1}$  and the concomitant appearance of sharp  $\text{SiOH}$  combination and overtone modes at  $4570$  and  $7270\text{ cm}^{-1}$ , respectively.

It is argued that the NIR monitoring of the dehydration of sepiolite can be standardized as a routine structural characterization technique yielding significantly richer structural information than ambient or spot temperature infrared measurements. It is anticipated that this background investigation of SepSp-1 will be useful in comparing sepiolites of variable octahedral composition, such as those reported as deviating from the ideal trioctahedral formula.

## PARTICLE SIZE AND SOLVENT EFFECTS ON INFRARED BAND POSITIONS OF LAYER MINERALS OBSERVED WITH POLARIZED ATR-FTIR

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It has been observed that particle size plays an important role in the infrared band positions of vibrations perpendicular to the basal surfaces of kaolin minerals due to self-induced electric fields by the vibrations. For example, reducing particle size shifted the in-phase OH vibrations of kaolinite and the apical Si-O band of nacrite to higher frequencies. Particle size should have the same effect on other layer minerals. Moreover, this effect should be weakened by strong polar solvents or dispersion matrixes. The objectives of this study were to systematically investigate the effects of particle size and the polarity of dispersion matrix on band positions of common layer hydroxides and silicate minerals.

Polarized attenuated total reflection FTIR spectra of typical layer silicate and hydroxide minerals were recorded with a Perkin Elmer Spectrum 100 FTIR. The infrared spectra of a highly-crystalline Keokuk kaolinite, different size fractions of a Georgia kaolinite, a dickite, a hectorite, a montmorillonite, a gibbsite, and a brucite were investigated in air, in water, and during drying process. The samples were mounted on a universal ATR accessory composed of zinc selenide (ZnSe) and diamond crystals. For each spectrum, 32 scans were recorded with a resolution of  $1\text{ cm}^{-1}$  in the  $4000\text{-}650\text{ cm}^{-1}$  range. A polarizer was employed to investigate the vibrations perpendicular to the basal surfaces of the layer minerals. In addition, infrared spectra were recorded using traditional transmission method (KBr pellet and ZnS-supported films).

Similar to the blue shifts observed on kaolin minerals, the gibbsite showed a nearly  $30\text{ cm}^{-1}$  blue shift on one of its five OH bands when its particle size was reduced. Grinding brucite resulted in a  $7\text{ cm}^{-1}$  blue shift on the OH band. The apical Si-O vibration of  $< 0.2\text{ }\mu\text{m}$  fraction of the Georgia kaolinite showed at  $1109\text{ cm}^{-1}$  in air when recorded in the transmission mode but shifted to  $1100\text{ cm}^{-1}$  in water when measured in the ATR mode. No distinct band shift was observed on Keokuk kaolinite during drying process. Drying the smectite (hectorite and montmorillonite) caused the OH band shift to higher frequencies. We speculate that the  $3630\text{ cm}^{-1}$  band in wet hectorite is due to the OH group of the mineral but not due to the adsorbed water as reported in the literature. We are investigating the band positions of the apical Si-O in the smectites during the drying process with the polarized infrared beam.



The preliminary results indicate that the vibrations perpendicular to layer hydroxides and silicate minerals were affected by particle size for the same reason as in kaolin minerals. The particle size effects were compensated by strong polar solvents and dispersion matrix. The band shifting with solvents suggest that the infrared band positions of the perpendicular modes of fine layer minerals can be used to study the physical reactions of mineral with solvents at the surfaces and can be used to refine the infrared band assignments of minerals.

## Al/Fe-, Al/Cu- AND Al/(Fe-Cu)-PILLARED CLAYS: STRUCTURAL FEATURES AT LOW ATOMIC ACTIVE METAL RATIOS (AMR)

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A set of Al/Fe-, Al/Cu- and Al/(Fe-Cu)-pillared clays were prepared from a Colombian bentonite in sodium or natural (Ca/Mg) form as starting materials. The effect of the loading of the second metal(s) (Fe and/or Cu) related to Al (AMR) in the intercalating solutions at low range of values  $\leq 10\%$ , on the main physicochemical properties was investigated. The insertion of the active metals raised almost linearly with AMR for both binary, Al/Fe- and Al/Cu- mixed metal systems. For the three-metal Al/(Fe-Cu)- mixed system, the stabilization of copper behaved randomly as a function of AMR, while the stabilization of Fe was almost not affected by the presence of Cu. On the basis of the ionic radii of the metals involved, a possible competition of the two active metals for the octahedral sites available in the  $Al_{13}$  polycationic structure is proposed for the three-metal system (ionic radii values:  $Al^{3+} = 0.68 \text{ \AA}$ ;  $Fe^{3+} = 0.67 \text{ \AA}$ ;  $Cu^{2+} = 0.73 \text{ \AA}$ ), but also as a good explanation for the efficiency of stabilization for iron around 15 times higher than copper in the binary metal systems. A clear dependence of the compensation of the cationic exchange capacity by polycations with the AMR value was found only for the system Al/Fe-, which was explained in terms of the opposite changes in the final pH obtained in the intercalating solutions, induced by the active metals in the Keggin-like polycations. The change in the basal spacings obtained in the XRD patterns from oriented glasses as a function of AMR was interpreted in terms of the opposite effect expected on the molecular size of the polycations as higher amounts of Fe or Cu would isomorphically substitute Al into the  $Al_{13}$  framework, allowing to propose that both, iron and copper are able to carry out such a substitution, although in different extent.

The hydrogen consumption in the  $H_2$ -TPR analysis of the materials was mainly distributed between two broad peaks: one from about  $250^\circ\text{C}$  to  $580^\circ\text{C}$ , and a second one from about  $750^\circ\text{C}$  to  $950^\circ\text{C}$ . Despite the several metal oxide species that are possible to form, the first signal in samples modified with the Al/Fe- system may correspond with the sequential overlapped reduction of  $Fe_2O_3$  in up to three steps: (1)  $Fe_2O_3 \rightarrow Fe_3O_4$ ; (2)  $Fe_3O_4 \rightarrow FeO$ ; and (3)  $FeO \rightarrow Fe$ , and to two sequential reduction effects in the range of  $210\text{-}260^\circ\text{C}$  for  $Cu^{2+} \rightarrow Cu^+$  and  $Cu^+ \rightarrow Cu^0$  at higher temperatures of ca.  $400^\circ\text{C}$  to  $700^\circ\text{C}$ . In the Al/Fe- system two shoulders were

observed at around 600°C and 850°C, whose intensity grow as the active metal loading increases, seem to be related to two kinds of metal sites repeatedly claimed in the literature as responsible for the high catalytic activity displayed by these materials in Fenton-like reactions; Fe “decorating” Al pillars and true mixed Al/Fe pillars, respectively.

The textural analysis of the natural modified samples suggest that at AMR below 5.0 %, a discrete maximum exist for the systems Al/Fe- and Al/Cu- over which the sorption capacity starts to be significantly affected. Simultaneous thermal analysis (DSC/TGA) demonstrated that the addition of a second metal in the intercalating system enhanced more the fraction of physisorbed water and decreased the maximum temperature for such a thermal event than intercalation with simple Al- polycations. SEM micrographs showed significant changes in morphology of the particles as AMR increased from 2.0 to 5.0%; as the amount of iron and/or copper added to the system increased, a greater amount of tiny particles deposited on the clay surface was seen, may be corresponding with external oxide aggregates. Likewise, the ratio Fe/Al obtained from the semi-quantitative surface chemical EDX analysis of the samples modified with the system Al/Fe- indicated that the AMR increasing also leads to higher fraction of the iron inserted represented in intercalated, possibly less aggregated mixed species in the materials.

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## EVIDENCE FOR A HOFMANN-KLEMEN TYPE MECHANISM IN THE FORMATION OF Li-Al-RICH MICAS

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It has long been known (Hofmann&Klemen 1950) that interlayer Li may get trapped in the 2:1 layer of dioctahedral phyllosilicates during dehydration at 250-300°C. The dehydration, which is easily recognized through the collapse of the  $d_{001}$  layer spacing down to about 10 Å, is reversible for beidellite but not for montmorillonite, a fact which is commonly used (Greene-Kelly 1953) in clay mineralogy to distinguish between octahedral (montmorillonite  $M_x(Al_{2-x}Mg_x\Box)[Si_4O_{10}(OH)_2]$ ) and tetrahedral (beidellite  $M_x(Al_2\Box)[Al_xSi_{4-x}O_{10}(OH)_2]$ ) charge deficiency. Despite considerable research efforts there is still much controversy about the mechanism of Li fixation (e.g. Komadel et al 2005), and up to date there is little knowledge about the positions where Li might get trapped and how they depend on the chemistry of the silicate.

In the present study, we were interested in the formation of lepidolite  $K(Li,Al)_{5-6}[(Al,Si)_3Si_3O_{10}(F,OH)_2]$  from muscovite under hydrothermal conditions. Natural  $2M_1$  muscovite  $K(Al_2\Box)[AlSi_3O_{10}(OH)_2]$  was mixed with LiF and  $SiO_2$  and heated to 600°C in  $H_2O$  at ~1 kbar for several days. The reaction products were characterized for their chemical composition using SEM electron microprobe analysis, and powder X-ray diffraction was used for mineralogical identification as well as for Rietveld structure refinements of the mica phase(s), with particular reference to the occupancies at the *trans* ( $B_t$ ) and *cis* ( $B_c$ ) octahedral and the interlayer cation sites.

Results show that for reaction times up to 8 days, muscovite is preserved almost unaltered. After 18 days, some Li entered the muscovite structure although the original  $2M_1$  polytype is still retained, except for one experiment where a  $1M$  lepidolite was found to coexist with the  $2M_1$  structure. For most of the longer experiments, non-mica silicates (e.g. eucryptite  $LiAlSiO_4$ , petalite  $LiAlSi_4O_{10}$ ) were found among the products, indicating that recrystallization processes do occur and may also explain the formation of  $1M$  lepidolite.

A more detailed analysis of the Li-containing  $2M_1$  structures shows a continuous transition which extrapolates from muscovite towards a hypothetical end member with the composition  $K_{0.6}(Li_{1.8}Al_{1.2})[(Al,Si)Si_3O_{10}(F,OH)_2]$ , i.e. the initially vacant *trans* ( $B_t$ ) octahedra are filled up with Li and nearly half of the Al ions in the *cis* ( $B_c$ ) octahedra are substituted by Li. This corresponds closely to the cation chemistry in polyolithionitic lepidolite  $K(Li_2Al)[Si_4O_{10}F_2]$ , except for a significantly lower number of interlayer potassium (0.6 instead of 1). Actual compositions come very near to the end member, but the recrystallized  $1M$  structure shows the normal polyolithionite composition with full occupancy of the K-site.

These observations suggest that the early steps of the transformation reaction are topotactic implying an interlayer  $K \rightarrow Li$  exchange followed by migration of Li into the octahedral sheet. It is interesting to note, however, that the overall charge of the octahedral cations *decreases* (from 6 to 5.4), in contrast to the classical HK model for montmorillonite where the octahedral charge *increases* (from 5.6 to 6, approximately).

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## VOLUME FRACTION VERSUS ORDER IN NEMATIC FLUOROHECTORITE DISPERSIONS

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The present abstract concerns nematic ordering in suspensions of Na-fluorohectorite in water and the investigation of this system by x-ray scattering, x-ray absorption and ellipsometry. Dispersions of hard platelets are known to form liquid crystalline phases when the concentration of the platelets crosses a certain threshold beyond which the decrease in entropy seen when the particles order is outweighed by a simultaneous increase in the entropy of the excluded volume [1]. Na-fluorohectorite particles dispersed in water undergo such an isotropic-nematic liquid crystalline phase transition [2,3,4,5,6] when the particle concentration is increased through the critical concentration threshold either due to gravity, centrifugation forces or evaporation. A higher degree of order than at the phase transition point is obtained by further concentration increases, and this order can be mapped as a function of the clay volume fraction by techniques such as x-ray scattering, x-ray absorption and ellipsometry. From the anisotropy of x-ray scattering from nematic phases it is possible to obtain quantitative measures for the nematic order parameter [7]. From x-ray absorption, knowing the composition of the solvent and of the dispersed phase, it is possible to calculate the clay volume fraction [8,5]. Finally, ellipsometry is a suitable technique for precisely measuring the specific optical retardance of ordered clay dispersions. We present results that show the development of order as a function of an increasing volume fraction, and demonstrate the advantageous role that solvent evaporation can play in the establishment of highly ordered nematic monodomains of Na-fluorohectorite dispersed in water.

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## FLOW INDUCED ORDERING IN NA-FLUOROHECTORITE DISPERSION

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We present studies on the synthetic clay Na-Fluorohectorite, which is a swelling trioctahedral smectite that has gotten some attention in recent years [see e.g. 1-4] due to its swelling properties and its ability to form liquid crystalline nematic phases when dispersed in water. If aqueous dispersions are left to sediment in gravity, several regions with different orientational properties are formed within a single sample tube, due to gradients in concentration and particle size. The present study is concerned with flow induced ordering of clay particles in dispersions that are orientationally isotropic at static conditions (Figure 1). We have studied the degree and type of ordering both as function of clay and salt content, as well as flow speed. Employed experimental techniques include rheology, and experiments performed in parabolic flight [5].



**Figure 1.**  
Strong and colorful birefringence in dispersions of Na-Fluorohectorite produced by turbulent flows after shaking.

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## COMPUTATIONAL ELASTIC PROPERTIES OF MICAS

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Crystal structure, elastic stiffness constants and pressure effects on the structure of 2M<sub>1</sub> muscovite-paragonite series have been calculated by means of quantum-mechanical methods based on Density Functional Theory, with specially adapted numerical LCAO basis sets, and norm conserving pseudopotentials [1]. These properties have calculated for five members of K<sub>1-x</sub>Na<sub>x</sub>Al<sub>2</sub>(Si<sub>3</sub>Al<sub>1</sub>)O<sub>10</sub>(OH)<sub>2</sub>, being x = 0, 0.25, 0.5, 0.75 and 1. The first, third and fifth are calculated with 1x1x2 supercells as 2M<sub>1</sub> polytype, and x = 0.25 and 0.75 are calculated with 2x1x2 supercells. The crystal structure, bond distances and bond angles of muscovite-paragonite series agree with the known experimental values. Equations of State are fitted to the pressure results, studying also axis compressibilities [2]. Elastic properties agree with the known experimental values of muscovite-paragonite series. Elastic properties of the polycrystalline aggregates are also studied. Average bond and structural feature deformations are analysed as a function of normal strains and pressure. Normal strains and the effect of pressure propagate along crystal structure according to the bonding of atomic groups. Deformation of interlayer space is the largest of the crystal structure. This methodology let us to know the elastic properties, EoS and bonding in the crystal structures in pure samples and series, without compositional and order/disorder interferences.

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## MOLECULAR DYNAMICS SIMULATIONS OF CLAY MINERAL-WATER/AQUEOUS SOLUTION SYSTEMS USING ATOM-ATOM POTENTIAL MODELS

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Clays and clay minerals, as well as zeolites, are major mineral components in the earth's surface environment. These minerals interact with the atmosphere, natural water, inorganic and organic components in soils and sedimentary rocks, etc. The physicochemical processes in the surface region are very complex and difficult to understand because of the complicated "molecular" structures and the ambient conditions under wet circumstances. We have investigated the structure and properties of the systems of minerals - surrounding gasses and liquids by means of molecular simulation methods, molecular dynamics and Metropolis Monte Carlo methods. Swelling of smectites, adsorption of cations and gas molecules in smectites and zeolites, etc. are simulated and analyzed in terms of the atomic and molecular processes.

To make such calculations, we have developed atomic and molecular interaction models for the use of molecular simulations. The model composed of electrostatic, short range repulsive, van der Waals, and covalent (radial and angular) terms for all the atoms and atom pairs appeared in the mineral-water systems. Using the model for  $\text{H}_2\text{O}$  molecule, structure and physical properties, such as density, diffusion coefficients, etc. of ices and water are well reproduced. Alkali halide aqueous solutions and gas hydrates and their solutions also reasonably simulated. Clay mineral - water interactions are particularly important to understand the mechanical and chemical processes in the earth's environments and to develop nano-composite materials, and also to use clays in engineering applications. The

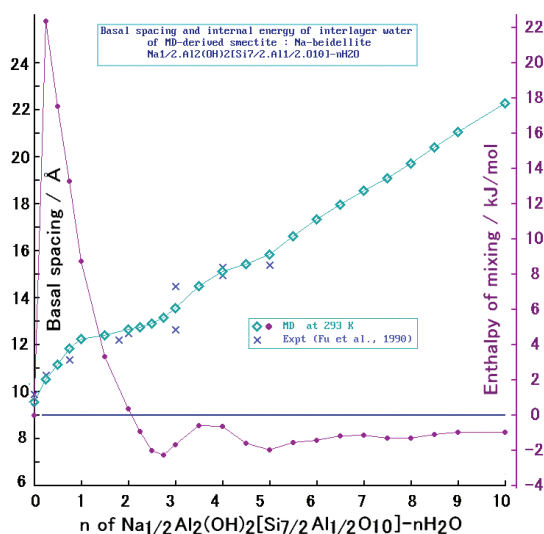


Fig 1. Swelling curve and enthalpy of mixing of Na-beidellite-water system.

absorption and swelling are the most remarkable properties of clay minerals, specially, smectite. We have investigated these properties by means of molecular simulation methods. The swelling curves, the relation between water content and basal spacing were reproduced (Fig.1), and nano-scale structural and dynamic properties of interlayer aqueous solutions were obtained.

Wetting of clay mineral surfaces determine the mechanical properties of clays, soils, and sedimentary rocks. We investigated the wetting properties of smectite, kaolinite (Fig.2), pyrophyllite, brucite, etc. The wetting property of these minerals were quite different each other. The origin of these differences was investigated by our molecular simulations.

Our purposes of studying clay nano-properties are to know the fundamental nano-mechanics of clays, and to apply the nano-properties to predict long term behavior of clay-based materials, such as mechanics of soil and sedimentary rocks, and engineering barrier for radioactive waste disposal. For this purpose, unified nano-micro-macro approaches have been established (Ichikawa, et al. (1999) Engineering Geology, 54, 21-31. Choi, et al. (2008) Int. J. Numer. Anal. Meth. Geomech., DOI:10.1002/nag.744.)

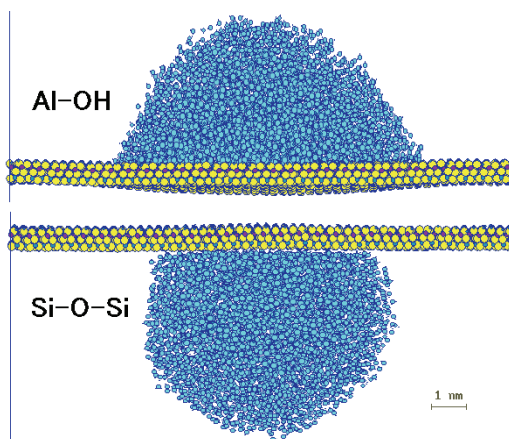


Fig 2. Wettig of kaolinite surfaces

## STRUCTURAL HETEROGENEITY OF ALKYLAMMONIUM-EXCHANGED, SYNTHETIC SWELLING FLUOROMICAS

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Swelling fluoromicas can be synthesized from the mixture of suitable oxides and fluorides melted at 1300-1500°C or from talc using an intercalation procedure. These silicates are produced on an industrial scale and, in comparison to natural clays, show a greater degree of crystallinity. Their chemical composition and physico-chemical properties can be controlled in a wide range.

Alkylammonium derivatives of clay minerals have been extensively studied. In contrast, surprisingly few investigations have been reported on the adsorption of organic ammonium ions on synthetic layered silicates. In this work, two synthetic swelling micas: Na-fluorotetrasilicic mica (TSM) and Li-fluorotaeniolite (TN) were used as starting materials. Their cation exchange capacities (CECs) determined by adsorption of alkylammonium ions are 92 and 124 meq/100 g.

Organo-micas were prepared by ion exchange with dodecyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium (C12, C14, C16 and C18) bromides. Concentration of the ammonium salt varied from 0.25 to 4.0 CEC of the mica. The products were characterized using  $^{23}\text{Na}$  MAS NMR spectroscopy, X-ray diffraction (XRD) and C and N determinations.

As shown by  $^{23}\text{Na}$  MAS NMR, up to 25% of the total amount of  $\text{Na}^+$  ions in the TSM were non-exchangeable, even if a large excess of the organic salt was used. The maximum amount of the alkylammonium ions bound to the mica was 92 meq/100 g. However, at high concentrations of the C16 and C18 surfactants, the salt molecules were adsorbed on the silicate in addition to the organic ions, resisting washing with water but being removable with ethanol.

The XRD patterns of the samples obtained show that the alkylammonium ions are distributed inhomogeneously within the mica interlayers. As a consequence, the organo-TSMs contain several phases consisting of randomly and regularly interstratified layers differing in terms of the amount of the alkylammonium ions adsorbed. The largest basal spacings (40.8-50.4 Å) indicate the presence of a superstructure, composed of two different layers. However, these layers swell in ethylene glycol in the same manner and form new interlayers with identical spacings. From the XRD patterns it is clear that the organo-TSMs do not contain the Na-TSM phase and the interlayers are presumably filled with both organic and  $\text{Na}^+$  ions in various ratios.

The maximum amount of the alkylammonium ions adsorbed on the TN was 124 meq/100 g. By reacting the mica with an excess of the C16 and C18 salts, the surfactants were adsorbed in both cationic and molecular forms as it was found for TSM. Thus, the interlayer  $\text{Li}^+$  ions were also only partially replaced by the alkylammonium ions.

The XRD patterns of the organo-TNs show a series of reflections suggesting that the samples obtained are polyphasic. The strong peaks in the range 23.3-28.7 Å may be ascribed to the random interstratifications of the TN layers with diversified amount of adsorbed alkylammonium ions. The peaks with very low intensity corresponding to the basal spacings of 42.3-51.2 Å indicate that small amounts of regularly interstratified layers are present.

This study also shows that adsorption of ethylene glycol, well known and widely used in clay mineralogy, may be successfully applied to XRD characterization of alkylammonium-exchanged silicates, especially those with mixed-layer structure.

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## CATION MIGRATION IN CELADONITE AND CIS-VACANT ILLITE BY ELECTRON RADIATION IN TEM

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Cation distributions in the octahedral sheet of dioctahedral 2:1 phyllosilicates in fine particles are still in debate. It is known that the crystal structures of muscovite, paragonite, margarite, pyrophyllite, etc., for which sufficiently large and high-quality crystals for single-crystal structure analyses are available, adopt a *trans*-vacant (*tv*) octahedral sheet where the *trans*-octahedra is vacant. On the contrary, Méring and Oberlin (1971) first proposed that a montmollironite specimen adopts the vacancy sites not at the *trans*-octahedra, but at the *cis*-octahedra (*cis*-vacant: *cv*). Drits and his group suggested several criteria to discriminate between *tv*- and *cv*-dioctahedral layers. After that, many studies reported the existence of the *cv*-dioctahedral 2:1 layer in montmorillonites, illite, mixed-layer illite-smectite (I-S), etc. However, details of the structures of phyllosilicates containing the *cv* layers seem still obscure. A way for further investigation is to observe the structure directly using high-resolution electron microscopy (HRTEM) with the beam direction parallel to the layers. Discrimination of the *cv* and *tv* layers from the HRTEM contrast using conventional TEMs is theoretically possible. However, we have not observed and no one has reported so far HRTEM contrasts that indicate the *cv* layer in the illite or smectite specimens in which the *cv* layers are dominant. On the other hand, celadonite, a dioctahedral mica with trivalent iron and magnesium as major octahedral cations, originally has a *tv* octahedral sheet but the HRTEM images indicated a different cation distribution (Kogure *et al.*, 2008). The present paper describes these results in detail and the origin of the discrepancy between expected and actually recorded images is discussed.

The  $\beta$  angle for the celadonite (1*M* polytype) derived from the HRTEM images is ca. 98.5° which is considerably smaller than those (ca. 100.5°) reported from XRD. The HRTEM contrast for each 2:1 layer is also not corresponding to the calculated one for the *tv*-dioctahedral layer. In previous works, cation migration from the *tv* configuration to *cv*-like one and decrease of the *b* angle after dehydroxylation of celadonite by heating were reported (Muller *et al.*, 2000). Furthermore, Kogure (2007) suggested that paragonite is dehydroxylated by intense electron beam radiation in TEM, without sample heating. The same phenomenon, dehydroxylation and subsequent cation migration, probably occurred in celadonite during TEM investigation. However, the new cation distribution models derived from HRTEM images along the [100] and [110] directions are not in agreement.

On the other hand, the contrast in a number of HRTEM images from a 1M-illite specimen from Canada in which *cv*-illite is dominant (Drits *et al.*, 1993), is almost the same as that for the *tv*-dioctahedral layer. This result is also interpreted as cation migration accompanied by dehydroxylation in TEM, similarly to heated *cv*-illite (Drits *et al.*, 1995). The increased  $\beta$  angle (ca. 102.5°) from that in the natural state (101.5°) estimated from the HRTEM images also supports this interpretation. This phenomenon will be a large obstacle to investigate phyllosilicates containing Al-rich *cv* and Mg, Fe-rich *tv* 2:1 layers, using HRTEM.

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## PORPHYRINS INTERCALATED IN Zn/Al, Mg/Al LAYERED DOUBLE HYDROXIDES: STRUCTURAL ARRANGEMENT AND PROPERTIES

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The arrangement of porphyrin molecules (5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin – TPPS) and Zn-(5,10,15,20-tetrakis(4-sulfonatophenyl porphyrin)) – ZnTPPS) in the interlayer space of Mg<sub>2</sub>Al and Zn<sub>2</sub>Al layered double hydroxides (LDH) prepared by a coprecipitation technique with hydrothermal treatment has been studied. The samples exhibit various loadings of guests in the interlayer space (70–80 % of AEC in case of Mg<sub>2</sub>Al LDH and about 90 % of AEC in case of Zn<sub>2</sub>Al LDH).

The structural arrangement and properties of prepared samples were characterized by combination of molecular dynamics simulations and experimental techniques (X-ray powder diffraction, diffuse reflectance UV-VIS spectroscopy, thermogravimetric analyses, high-resolution transmission electron microscopy and time-resolved near-infrared luminescence). The calculated X-ray diffraction patterns of optimized models with various loadings were compared with experimental measurements. Mg<sub>2</sub>Al LDH-TPPS samples were represented by two phase structure models [1] with overall TPPS loading of 75 %, 83 % and 92 %, while Zn<sub>2</sub>Al LDH-ZnTPPS samples were described by one phase models with 100% loading of the guests [2].

The interlayer space is filled with nearly parallel porphyrin units with a dihedral angle varying between 0 and 10°. The guests exhibit a disorder arrangement without any aggregation. The porphyrin units are inclined with respect to the hydroxide layers with the average angle between the porphyrin plane and the layer normal of about 14°. The sulfonate groups are about 4 Å from the center of the hydroxide layers with hydrogen bonding interactions between sulfonate groups and OH groups of the layers with the contribution of water molecules. In agreement with HRTEM measurements the central zinc atoms of ZnTPPS are located in the middle of the interlayer space and their horizontal positions are disordered. In comparison to Mg<sub>2</sub>Al LDH, Zn<sub>2</sub>Al LDH-ZnTPPS system exhibits a very good crystallinity. We obtained a good agreement between the positions of nonbasal diffraction lines which indicate that the layer stacking in the intercalate corresponds to the original layer stacking order in the original nitrate form. The calculated XRD patterns of Mg<sub>2</sub>Al LDH-TPPS

are compared with experimental measurements and the influence of guest loadings on the X-ray diffraction pattern is shown. The LDH-TPPS hybrid systems are suggested as new photofunctional materials. The photophysical experiments showed that TPPS in MgAl LDH systems produce singlet oxygen with long effective lifetimes, while no measurable amount of this species was found for ZnAl based hybrids.

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## CRYSTAL CHEMISTRY OF KEROLITE-STEVENSITE MIXED LAYERED MINERALS FROM THE URAL REGION (RUSSIA)

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This work reports on two weathering products of serpentinized Mg-rich ultramafic rocks (Ural, Russia), presented as aggregates of small, white or green plates. The samples are studied by X-ray diffraction, mid- and near-infrared spectroscopy, differential thermal and thermogravimetric analysis, scanning electron microscopy and electron microprobe analysis.

According to chemical analysis, the samples can be distinguished in Ni-poor (I) and Ni-rich (II). The DTA and TGA curves for both samples are similar and exhibit three of water loss events: 100-200°C – adsorption water (7.5 and 7.7%) with  $t_{\max} = 100^\circ\text{C}$ , 200-780°C – structural water (2.8 and 3.5%) with  $t_{\max} \approx 380^\circ\text{C}$ , and 780-1050°C – structural hydroxyls (4.3 and 3.8%) with  $t_{\max} = 850^\circ\text{C}$ , for samples I and II, respectively.

The Ni-poor sample exhibits FTIR spectra typical of hydrated talc-like minerals and these have been assigned mainly to kerolite  $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ , a 2:1 Mg-phyllsilicate with structure and composition similar to talc, though more disordered and with a higher degree of hydration [1-3]. The Ni-rich sample exhibits additional  $\text{Ni}_3\text{-OH}$  spectral features, and is therefore considered as a member of the kerolite-pimelite series. Of interest is the NIR monitoring of the mild dehydration of the Ni-poor sample which reveals the presence of surface Si-OH defects, as well as of new  $\text{H}_2\text{O}$  combination modes at 5300 and 5180  $\text{cm}^{-1}$ . The latter are not common to phyllosilicates and point to the existence of distinct species of chemisorbed water, in close interaction to some very specific (but unknown) feature of the clay.

The powder XRD patterns of both non-oriented and oriented samples in the air-dried state exhibit 001 reflections at 11.6 Å shifting to ca. 9.7 Å after heating to 550-600°C (to be compared with ca. 9.65 Å for kerolite and 9.38 Å for talc). Ethylene-glycol solvation leads to the emergence of new reflections at 25.0, 13.0, 9.3 and 5.3 Å for the Ni-poor and 24.0, 17.0, 9.0 and 5.3 Å for the Ni-rich sample, and reveals the mixed layer nature of both samples.

Based on these data, the samples can be described as mixed-layer members of the kerolite (pimelite) – stevensite series  $(\text{Mg}_{3-y}\text{Ni}_y\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O} \cdots (\text{Me}^{+}_{2x})(\text{Mg}_{3-x}^{2-})_x)$

$\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot m\text{H}_2\text{O}$  [3-5], with chemical formulas based on a +22 total cation charge:  
 $[\text{Na}_{0.02}\text{Ca}_{0.02}][(\text{Mg}_{2.91}\text{Ni}_{0.02}\text{Fe}_{0.02}\text{Al}_{0.01})\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot 0.7\text{H}_2\text{O}$  (I), and  $[\text{Na}_{0.02}\text{Ca}_{0.03}]$   
 $[(\text{Mg}_{2.07}\text{Ni}_{0.87}\text{Fe}_{0.08}\text{Al}_{0.04})(\text{Si}_{3.76}\text{Al}_{0.24})\text{O}_{10}(\text{OH})_2] \cdot 0.9\text{H}_2\text{O}$  (II).

This work was supported by the Russian Foundation for Basic Research (Grant № 09-05-00302) and the National Hellenic Research Foundation.

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## FLEXIBLE STRUCTURE OF SILICALITE (MFI) BY GAS ADSORPTION

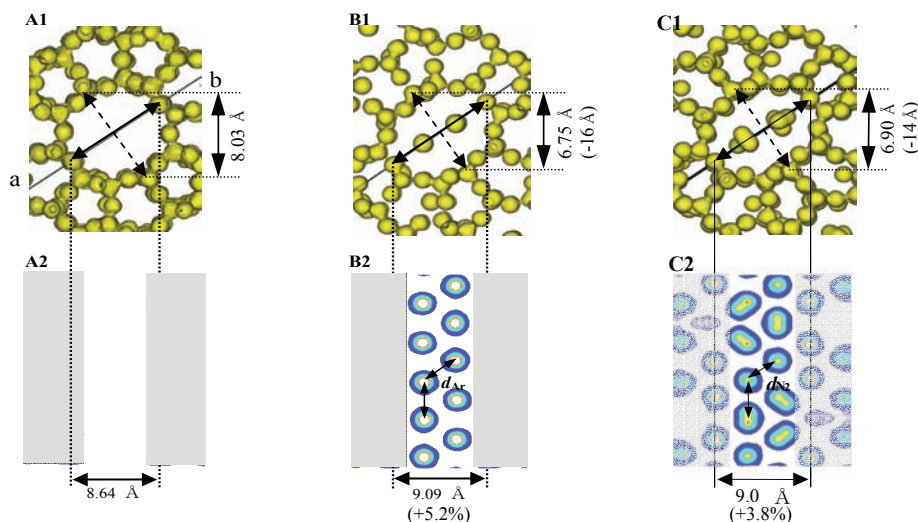
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The MFI zeolite has two crystal forms (monoclinic and orthorhombic) [1], and has straight channels and zigzag channels. Effect of temperature on the phase transition of the MFI zeolite from monoclinic to orthorhombic has been examined by the calorimetric method, and the transition temperature ( $T_v$ ) decreases with the increase of Al content in MFI [2].

In this study, the Synchrotron-Radiation Powder Diffraction experiments of the MFI zeolites (Si/Al=500) were carried out by the *in situ* gas adsorption measurement system, which is installed in the BL02B2 beam line of Super Photon Ring 8 GeV (SPring-8). This SRPD data of the three samples are used in MEM/Reatveld analysis (Fig.1). It indicates that the phase transition from monoclinic ( $P2_1/n$ ) to orthorhombic ( $Pnma$ ) is brought about by adsorption of Ar @77K and N<sub>2</sub> @65K. The adsorbed amounts of Ar and N<sub>2</sub> in the channels are evaluated to be 32 molecules/unit cell



**Fig. 1.** Isodensity surface contour (1.0 eÅ<sup>-3</sup>) (upper) and MEM electron density distribution (from 0.15 to 8.0 eÅ<sup>-3</sup>) (lower) of MFI zeolites (A: vac @ 65 K, B: Ar @ 77 K, C: N<sub>2</sub> @ 65 K). Upper parts (A1, B1, C1) are viewed from top of straight channel of MFI zeolite, while lower parts (A2, B2, C2) are viewed from parallel to the straight channel in a-b plane.

from SRPD data, whose value matched with the high resolution gas adsorption isotherm from BELSORP-max and BELCryo[3].

The shape of the straight channels (10-ring) of MFI is changed from circle to oval by the adsorption of Ar @77K and N<sub>2</sub> @65K. Ellipticity of main strait channel pore has sensitive adsorbed molecule size. In addition to channel shape, we can determine the precise positions of adsorbed molecules in the channels. The arrangement of Ar or N<sub>2</sub> in the straight channels can be regarded as the closest packing structure which mean adsorbed molecule take more dense crystal structure.

Furthermore, the average center-center distances of Ar or N<sub>2</sub> in the MFI channels are found to be shorter than those of the bulk distances. That is, the average Ar-Ar distance ( $d_{Ar}$ ) in the channels is 3.72Å, which is shorter than those of liquid (4.09Å) and solid (3.85Å), and the average N<sub>2</sub>-N<sub>2</sub> distance ( $d_{N_2}$ ) is 3.73Å, which is shorter than those of liquid (4.33Å) and solid (4.00Å). This means adsorption density is much higher than solid which infers a high pressure adsorption state.

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## NEW POROUS CLAY HETEROSTRUCTURES (PCH) FROM HIGH CHARGE-MICA TYPE MATERIALS

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True micas are 2:1 layered aluminosilicates with charge density as high as 2 negative charge per unit cell, with non hydrated cations compensating the layer charge in the interlayer space. Classically, natural micas have any capacity of swelling due to the strong electrostatic attraction between the layers. A new family of swelling synthetic micas has been successfully synthesized with an unusual cation exchange capacity -up to 468 meq/100g of clay in Na-4-mica- with up to four monovalent hydrated cations accommodated in the ditrigonal holes in the external surface of the tetrahedral layer [1]. Despite the large negative charge originated by isomorphic substitution of silicon by aluminum in the tetrahedral layer, high charge micas unlike brittle micas, exhibit unexpected structure stability.

In a more general point of view, layered clays have been extensively used as precursors of porous acidic materials for catalysis because of their intrinsic acidic properties. In that direction, porous clay heterostructure (PCH) are a new class of solid acids firstly proposed by Pinnavaia et al. with pore sizes in the rarely observed supermicropore to small mesopore region [2]. They are formed by the surfactant-directed assembly of mesostructured silica within the two dimensional galleries of a moderate charged layered clay. Most of the silicates used for this application are smectite type with up to 1.2 negative charges per unit cell. Although several efforts have been made to increase the acidity of the PCH, the most popular methods involve tedious post and pre treatments [3,4]. Swelling high charge micas are ideal materials to be explored regarding this application; in first place due to the extraordinary number of intrinsic acidic places in their structure, attributed to the high level substitution of aluminum for silicon in the tetrahedral layer mentioned above, and in second place because synthetic micas, unlike smectites, have shown high thermal stability of the structure and the acidic places. In this work, we present a new family of Porous Clay Heterostructures (PCH) formed from two high charge micas with 2 and 4 charges per unit cell respectively.

Textural properties, porosity and external surface of the PCH samples were determined by the  $N_2$  adsorption-desorption technique. X-Ray Diffraction (XRD) technique has been used to characterize the long-range order of the molecular sieves. Strength and acidity values are also reported. The PCH samples synthesized from high charge micas present type IV adsorption isotherms with a quasi-linear region at the partial pressures range between 0.05 and 0.25 characteristic of a

supermicropore to small mesoporous structure. Porous solids have surface areas of ca. 400 m<sup>2</sup>/g with pore volumes around 0.300 cm<sup>3</sup>/g. The acidity was determined using cyclohexylamine chemisorption. The samples were pretreated at 200 °C for 90 minute prior the cyclohexylamine adsorption. Temperature Programmed Desorption (TPD) experiments were carried out by heating the sample from 200 °C to 500 °C. The acidity of the PCH from high charge micas (0.50 mmol/g) are comparable of those exhibited by the previously described acidic-PCH synthesized from highly charge saponites. The full acid sites detected are placed in the medium and strong acidic regions, with two desorption peaks centred at 320 °C and 480 °C, respectively. The surface area values reported here, below the normal values described for PCH samples synthesized from smectites, may have its origin on the limited cation exchange capacity exhibited by the high charge micas, around the half of the theoretical exchange capacity associated to these samples. Consequently, an enhancement of stability is expected in those PCH from the extra thickness of the non-exchange mica layer in the stratified clay. However, despite the low surface area described above, acidity values associated to these samples are similar to those reported in the literature for PCH with surface areas as high as 800 m<sup>2</sup>/g. Furthermore, the strength of the acidic sites, all situated in the medium and strong acidity range, makes this new family of porous clay heterostructures as promising acidic materials for catalysis application.

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## DEHYDRATION MECHANISM AND STRUCTURAL TRANSFORMATION OF PALYGORSKITE

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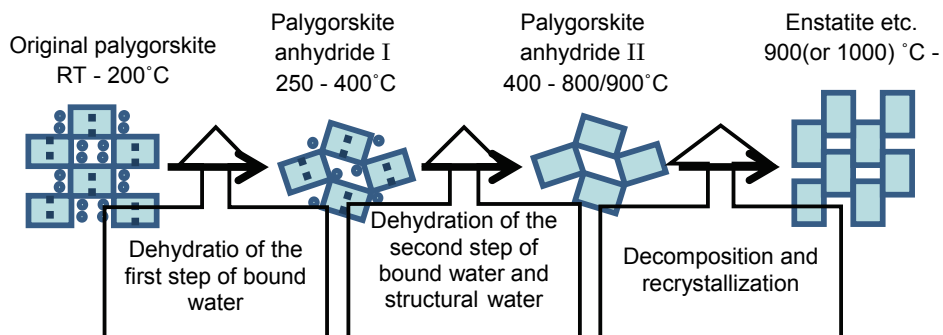
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Palygorskite is a hydrous magnesium silicate mineral characterized by its fibrous morphology and intra-crystalline channels, having the ideal structural formula  $(\text{Mg}_{5-y-z}\text{R}^{3+}_y\Box_z)(\text{Si}_{8-x}\text{R}^{3+}_x)\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4\Box 4\text{H}_2\text{O}$  for the half-unit cell. It has a structure similar to sepiolite, however, there is some vacant site in octahedral sheet caused by substitution of Mg by Al and etc. Palygorskite and sepiolite are known to contain three types of water molecules in different crystal chemical states; zeolitic water, bound water and structural water. The thermal dehydration of these minerals has been studied very extensively.

Dehydration of sepiolite is of most interest as the bound water is known to dehydrate in two steps accompanied by structural change of uniform folding of the crystals, followed by the dehydration of structural water at higher temperature. Kiyohiro and Otsuka (1989) confirmed that the two-step dehydration of bound water is caused by the following two factors: (1) the difference in the activation energy of dehydration between the water in the unfolded open channel and that in the folded one, and (2) the change in the rate determining process from the water separation process to the water diffusion one. In the case of palygorskite, two-step dehydration of bound water is not clear, because the dehydration of structural water occurs in the nearly same temperature region. Several mechanism models have been proposed to explain the dehydration of palygorskite. These models, however, have not given sufficient explanation to the dehydration behavior of palygorskite.

In this study, dehydration behavior of palygorskite was examined by thermogravimetry under controlled water vapor pressure and X-ray diffractometry. An attempt has been made to derive the dehydration mechanism model of palygorskite, which can explain the two-step dehydration of bound water and characteristics of the structure transformation. The experimental result revealed that the dehydration of structural water and the second step of the dehydration of bound water occur about the same time. The first step of the dehydration of bound water was greatly influenced by water vapor pressure, while the second step of bound water and the dehydration of structural water hardly responded to water vapor pressure. As a result, the two-step dehydration of bound water is caused by the same manner as the case of sepiolite mentioned above. The dehydration behavior of palygorskite may be shown schematically as in the following figure.



Kiyohiro T., Otsuka R. (1989). Dehydration mechanism of bound water in sepiolite. *Thermochim. Acta.*, 147, 127-138.



## INTERFACIAL STRUCTURE OF MUSCOVITE/AQUEOUS NaCl SOLUTION STUDIED BY X-RAY CTR SCATTERING AND MOLECULAR DYNAMICS SIMULATIONS

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Mineral/liquid interfaces are ubiquitous in the earth's crust and control the many important properties in geochemistry and geophysics such as the partitioning of elements, the swelling and dispersion of clay minerals, and the frictional strength of rocks at fault zones. Structures of mineral/liquid interfaces have a strong correlation with these properties and help the fundamental understanding of these properties.

Here we investigated the electron density profiles at the muscovite/NaCl solution interface using the surface x-ray scattering method. Surface of a mineral gives rise to a rod-shaped scattering perpendicular to the surface, which is called crystal truncation rod (CTR) scattering. The shape of the intensity around the Bragg reflection points of the mineral is proportional to the Fourier transform of the electron density distribution around the surface. Therefore the interfacial electron density distributions can be studied by the analysis of the CTR profile. The surface x-ray scattering experiments were carried out at the BL-4C of the Photon Factory, KEK, Japan. The CTR profile was modeled using atomistic structures that include a fixed bulk muscovite structure, relaxation of muscovite atomic positions near the surface, structured layers of ions and water molecules above the interfaces, and bulk water.

Molecular simulations have an atomic scale resolution and are useful to interpret the electron density profile obtained by the CTR scattering method as the atomic density distribution at the interfaces. We already derived the atomic distribution of the muscovite/KCl solution interface by the comparison of molecular dynamics (MD) simulations and the CTR profiles (Sakuma and Kawamura, 2009). Here we performed the MD simulations for an interfacial model of the muscovite/NaCl solution using the modified MXDORTO program. The interatomic potential models for muscovite, water and ions were originally developed and were successfully applied to clay minerals, water, and the interfaces.

The four distinguished peaks of the electron density were observed for NaCl solution near the muscovite surface. Our MD simulations indicate that these peaks correspond to the structured layers of hydrated Na<sup>+</sup> ions and water molecules. The Na<sup>+</sup> ions were adsorbed on the muscovite surface as inner sphere complexes and the layered structure of water was relaxed at further than 1.5 nm apart from the

muscovite surface. The obtained interfacial structure and the results of MD studies were used to understand the weak frictional strength of layered minerals saturated by NaCl solution at fault zones.

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## ADSORPTION ON KAOLINS MODIFIED

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This work is targeted to the study of the adsorption capacity of hexadecyltrimethylammonium bromide (HDTMA-Br) in kaolin mined (M) and washed (L), both modified thermally (T) and mechanically (O) and activated with acid (A) or alkali (K) and a natural zeolite (BR-4). The samples studied are silica sands mining and industrial kaolin (washed), obtained from the silica sands of a sedimentary deposit of Facies Weald Utrillas (Spain), and a natural zeolite, from the ridge-Golonche Chongón province of Guayas (Ecuador).

The chemical composition, obtained by XRF, is for sands: 74.78% of  $\text{SiO}_2$ , 19.15% of  $\text{Al}_2\text{O}_3$  and 2.27% of  $\text{K}_2\text{O}$ , for washed kaolin samples: 47.76% of  $\text{SiO}_2$  and 39.68% of  $\text{Al}_2\text{O}_3$  and for the Zeolite: 73.87% of  $\text{SiO}_2$ , 10.86% of  $\text{Al}_2\text{O}_3$ , 1.67% of  $\text{Fe}_2\text{O}_3$ , 2.34% of  $\text{CaO}$ , 1.08% of  $\text{K}_2\text{O}$  and 0.48% of  $\text{Na}_2\text{O}$ . The mineralogical composition obtained by XRD is 89% quartz, 7% kaolinite, 3% feldspar and 1% mica for the sample M, 94% kaolinite, 5% quartz and 1% mica for the sample L and 54% mordenite, 36% quartz, 7% of heulandite and 3% feldspar for the zeolite.

Modification of the kaoliniferous materials was carried out by heat treatment at 750 °C for 3 h (MT, LT), because the lowest crystallinity for kaolin is reached between 700 and 800 °C (Mejía de Gutierrez et al. 2008). The mechanical treatment was performed in an oscillating mill "Herzog HSM 100" operating at 50 Hz, 1.1 kW and 1420 rpm, 30 min was spent for sample M (MO) and 60 minutes for the sample L (LO). The acid activation was performed using HCl (6M) and alkaline activation with NaOH (5M), both with 3 hr of exposure at 60° C constant temperature. Changes in physico-chemical properties, mineralogy and morphology of the different treatments were studied by "San Cristóbal et al., 2009; 2010".

Adsorption isotherms tests were performed by absorption infrared spectroscopy (FTIR), showing the intensity of absorbance in the  $\text{CH}_2$  and  $\text{CH}_3$  bonds (2920 and 2850  $\text{cm}^{-1}$ ) range of vibration of HDTMA-Br molecules, setting the concentration range to 1 to 40 mM. Quantification of adsorption capacity of HDTMA-Br was measured by FTIR, using a straight pattern of known concentrations of the sorbent and the adsorbate. The results show that the LT sample has the largest adsorption capacity of HDTMA-Br.

## **PREPARATION OF HOMOIONIC EXCHANGED SMECTITES IN BENTONITES: INFLUENCE OF VALENCE OF CATIONS AND INFLUENCE OF IMPURITIES ON THE EXCHANGE PROCEDURE**

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The interlayers of natural smectites store a mixture of sodium and/or calcium and magnesium, respectively, and rarely potassium. Many chemical, mechanical and thermal properties of smectites and smectite-rich materials depend on the interlayer cations. Therefore, homoionic exchanged materials are prepared to investigate reaction mechanism as function of the interlayer cation or as function of the layer structure with uniform interlayer occupation. 54 publications from different journals from 1950 to 2009 were reviewed with respect to the applied homoionic exchange procedure. Only 6 papers reported on the result of homoionic exchange. Up to now there exists no general instruction to prepare homoionic exchanged smectites in dependency of layer charge, cation exchange capacity (CEC) and the obtained level of homoionic interlayers. The aim of the present study was to create a general instruction to prepare homoionic exchanged smectites and smectite-rich materials in dependency of the required cation and impurities of the used materials.

For the research three natural bentonites were applied, which differ in content of impurities especially calcite, dolomite, and gypsum and whose smectites differ in interlayer composition, CEC and layer charge. The homoionic exchange is achieved by repeated reactions of suspensions with readily soluble chlorides of the chosen cations (Na, Li, K, Mg, Ca, and Cu). The amount of the chloride solution was equal to 1x CEC, 5x CEC, 10x CEC and 20x CEC of each material. The solid-liquid ratio averaged 4.4%. The success of homoionic exchange was monitored by exchange of interlayer cations with Cu-Trien and subsequent analysis of the cations in the supernatant exchange solution by ICP-OES.

As expected from charge, size and hydration properties of the cations the homoionic exchange with bivalent cations (Mg, Ca, and Cu) was more effective compared to that with monovalent cations (Na, Li, and K). In addition the exchange of monovalent cations was strongly inhibited during exchange experiments with low salt concentrations (1-5x CEC) by present carbonates and sulfates that were dissolved during the exchange reactions. The released Ca or Mg replaced the monovalent cations in the interlayer, thus, the amount of Ca and Mg increased compared to the starting material.

The homoionic exchange is regarded successful if more than 95% of the interlayer consists of one interlayer cation like Li, Na, K, Mg, Ca, and Cu. To reach these occupancy rate, 20x CEC (three-times exchange) was necessary for monovalent cations and 5x CEC (three-times exchange) for bivalent cations. Purification improved the exchange behavior of the materials, thus, homoionic exchange was more successful especially for monovalent cations (reduced concentration of exchange solution e.g., 5x CEC for K).

To repeat preparation procedures and to compare several studies with each other, the following information: CEC, solid-liquid ratio, concentration of salt solution, type of salt, reaction time, repetitions, and success of exchange should be proved. It is important to calculate the used salt concentration in dependency of the measured CEC and to present the results of the exchange, because the success depends strongly on the mineralogical composition and pre-treatment of the starting material.

## DETERMINATION OF THE POINT OF ZERO CHARGE OF THE EDGES OF VARIOUS CLAYS

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Many modern composite nanomaterials contain clay platelets as functional compounds. This polymer layered silicate nanocomposites attracted great interest in recent years, because various properties of the material can be improved. The clay content determines properties like barrier activity, fire retardancy, electrical properties and mechanical reinforcement.

For many applications, a homogeneous dispersion of the clay within the polymer matrix is compulsive. Therefore aggregation of the clay platelets must be avoided. This can be achieved by modification of the clay surface. In most of the cases, only the basal planes are modified, because they amount most of the clay's surface [1]. The modification of the basal planes can be achieved via the electrostatic interaction of the negative charged surface with positive charged counterions, like for example polycations. Less effort has been spent on the modification of the clay's edges and on its investigation in general. But the influence of the edges on the aggregation behavior of the clay is not negligible.

Whereas the charge of the basal plains is always negative, the charge of the clay edges is dependent of the pH value. Below the point of zero charge, the charge of the edges is positive and aggregation occurs, because the positive edges are attracted to the negative basal plains. The obtained structure is referred to as "card-house" like structure [2].

In this work we tried to determine the point of zero charge of various types of clays. Therefore dioctahedral and trioctahedral clays of different composition and from different locations have been investigated by measuring the streaming potential. The clay was dissolved in water and then titrated with different cations in order to "neutralize" the strong negative charge of the basal planes and reach a streaming potential close to zero. This is an important step, as the charge of the edges contributes only a small part to the overall charge of the clay. Without the "neutralization" step, the charge of the edges can hardly be detected. For the neutralization, a polycation and Cu- and Co- complexions have been used.

In a second step, the pH of the solution is varied from a high level of about 10 to a low pH between 3 and 5. During this step, the streaming potential rises from a negative to a positive value. In this way, the point of zero charge can be determined.

As expected, the point of zero charge is different for the various types of clays, depending on the atoms contained in the octahedral layer of the clay. Although the charge of the edges only represents a small percentage of the total charge of the clay, their point of zero charge could successfully be detected.

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## STUDY OF ANOMALOUS BEHAVIOUR IN DFT IR SPECTRA AND CALCULATED BANDSTRUCTURE OBSERVED IN DIOCTAHEDRAL $\text{Fe}^{3+}$ , $\text{Ge}^{4+}$ AND $\text{Ga}^{3+}$ MICAS SUBSTITUTED SERIES

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Most of phyllosilicates such as micas have an excellent performance as insulators, so they have been widely used in industry. However, due to the cation substitutions some micas may change their electrical behaviour, becoming a conductor [3,4]. The conductivity in biotite mica and trioctahedral iron vermiculite and the influence of the composition in the conductivity were reported in biotite by Meunier et al.[3], and more recently in biotite and vermiculite by Ruscher et al. [4].

In this work we study, under DFT theory, the influence of the increasing Fe(III), Ga(III) content in the octahedral sheet, and Ge(IV) in tetrahedral sheet of dioctahedral micas, in the band-structure as a function of cations content, distinguishing, as a function of the band gap, the position of the Fermi level, and therefore the behaviour between isolators and conductors towards the use of SIESTA software package [5]. Also with SIESTA the dynamical matrix and Born effective charges were computed via a finite-difference approach in which each atom was displaced by  $\pm 0.05 \text{ \AA}$  in the three cartesian directions and the forces and polarization changes were computed to record the Infrared spectra of the hydroxyl groups.

The calculations show a good structural agreement in crystal parameters and atomic structure with the experimental values. The band-structure and density of state (DOS) plots models indicate a change of the electrical behaviour of the samples only with Fe (III) content while with Ga(III) and Ge(IV) it doesn't. The positions of the conduction and valence bands are also predicted to insulator samples showing a strong spatial localization due to not width dispersion curves found. We also reported the Infrared hydroxyl groups calculated spectra show a good agreement with experiment in mica with Fe(III) content. Nevertheless in samples with Ga(III) and Ge(IV) a discrepancy is found in hydroxyl stretching frequency because it is not in agreement with the inverse relationship of the OH bonded cation neighbours reduced mass as proposed by Vedder in 1964 [6].



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## NEW METHODS OF DATING HYDROCARBON GENERATION BASED ON K-Ar OF DIAGENETIC ILLITE

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Diagenetic illite can provide K-Ar dates that constrain the timing of hydrocarbon generation, because crystallization of illite occurs in the range of temperatures of the oil window. This information can be very difficult to extract because the diagenetic illite is most often contaminated with the detrital one, and it is impossible to separate them physically. Alternative approaches to this problem are possible and the aim of this project was to develop them and to test if these methods can be successfully applied to real basins.

The first of the developed methods is a computerized version of the Illite Age Analysis (MODELAGE), with polytype or illite/illite-smectite ratio as proxies for the ratio of detrital and diagenetic components. Using this approach, based on the genetic algorithms, it is possible to calculate the ages as well as the potassium ratio of diagenetic and detrital illites. It was found that if the potassium content is different in these end-member illites, this approach gives more reliable results than the original Illite Age Analysis.

The second approach also uses MODELAGE, but the illite crystal thickness distribution is extracted from X-ray diffraction patterns to study proportions between diagenetic and detrital illite. A computer program performing this operation via modeling of the XRD patterns of illite with polyvinylpyrrolidone (PVP) adsorbed on its surface was written and tested.

The third approach is based on chemical analyses of few grain size fractions with different proportions of diagenetic and detrital illite. This method employs the contents of elements, which concentrate in illitic minerals (K, B, Ar and Li). The set of equations is solved for the contents of the detrital and the diagenetic component. It was found that this approach can give important supplementary information which can constrain results of other methods.

## **TOPIC 2**

### *Mineralogy and Geology*



## *ORAL PRESENTATIONS*



## KEYNOTE

### LOW GRADE METAMORPHISM IN POLYDEFORMED ROCKS OF AVALONIA (ARISAIG GROUP, NOVA SCOTIA, CANADA)

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The Arisaig Group (Nova Scotia, Canada) provides the best exposure of shallow marine Silurian to Early Devonian rocks in the Appalachian Orogen. This sequence is approximately 1800–1900 m thick and made up of shallow marine to continental shale, mudstone with interbedded siltstone, and sandstones that are polydeformed and have undergone low grade metamorphism. This detailed study of the phyllosilicates (crystal-chemical parameters, textural, and chemical features) along a NE-SW composite cross section across a shallow plunging folds with cleavage development of varied penetrativity, and affected by a major dextral strike-slip fault (Hollow Fault) sheds light into the low-grade metamorphic conditions of these rocks, the clay mineral genesis, and its potential relation with the deformation processes (the lower Devonian Acadian Orogeny and the Carboniferous Appalachian Orogeny).

X-ray diffraction reveals that the sampled rocks contain ubiquitous quartz, K-white mica, chlorite and feldspars; illite-smectite and chlorite-smectite mixed layers are common but Na-K mica and kaolinite occur only in some samples. The crystal-chemical parameters of the white mica indicate the pressure and temperature of mineral growth and are widely used to discriminate between diagenetic, anchizone and low-grade metamorphic processes. Kübler Index (KI) values measured in the 10 Å peak of the <2 µm fraction are indicative of an increasing metamorphic grade from diagenesis to high anchizone in the samples closest to the fault (< 1km from the fault surface). The identification of illite-smectite mixed layers in samples with KI >0.50 °2θ and the highly heterogeneous b-cell dimension of the K-white micas are in agreement with the diagenetic conditions. In most of the samples, the peak at 14 Å corresponding to chlorite is small and even missing after ethylene glycol and dimethyl sulfoxide treatments, reflecting low chlorite quantities and poor “crystallinity”. The b parameter of chlorite suggests high-Fe contents (2.3-3.1 a.p.f.u.).

Backscattered scanning electron (BSE) images of selected samples show that these are quartz-rich rocks of fine-grained texture with phyllosilicate microdomains (predominantly white mica and chlorite) and iron sulphides and titanium oxides as common accessory minerals. The diagenetic samples preserve no evidence of fabrics that could be attributable to a tectonic origin but the samples near to the fault plane are characterized by an incipient slaty cleavage defined by subparallel packets of phyllosilicates that occasionally form chlorite-mica stacks with curved shapes. The chemical compositions of dioctahedral micas indicate an almost complete absence of illitic substitution ( $\Sigma_{\text{interlayer}} > 0.8$  a.p.f.u.) and variable phengitic content ( $\text{Fe} + \text{Mg} = 0.1\text{--}0.5$  a.p.f.u.). Trioctahedral chlorites correspond to the chamosite variety, which is consistent with the Fe content obtained from the X-ray diffraction data.

The mineral assemblage and textural features of the Arisaig Group lithologies are, in general, typical of very low-grade metamorphism, with illite-smectite mixed layers and kaolinite in the diagenetic samples and chlorite-white mica stacks, Na-K mica, and an incipient cleavage in the anchizonal ones. There is no evidence of a stratigraphic control of the metamorphic grade since the highest grade samples are distributed randomly throughout the sequence. The local influence of the deformation or the fluid circulation associated to the Hollow Fault may be responsible for the presence of the anchizonal samples. Lastly, the presence in most of the samples of minor quantities of chlorite-smectite mixed layers may be the result of a late fluid-mediated event associated to the Hollow Fault.



## STABLE ISOTOPE CONSTRAINTS ON THE ORIGIN OF KAOLIN DEPOSITS FROM VARISCAN GRANITOIDS AND FELSITES, AND FROM SEDIMENTARY BASINS OF GALICIA (NW SPAIN)

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Large kaolin deposits are described in Variscan granitoids and in some sedimentary basins of the northwestern Iberian massif in Galicia, Spain. A mineralogical, geochemical and isotopic study was carried out on a variety of these deposits formed from weathered granitoid and felsitic rocks at Vimianzo and Burela, from hydrothermal veins at Barilongo, and from Tertiary and Quaternary sediments at Lendo and Santa Tecla. The mineral composition of the deeply kaolinized rocks is dominated by kaolinite, mixed with halloysite at Burela, which is potentially biasing the  $\delta D$  data because of rapid isotopic exchange with ambient water, and minor amounts of quartz, K-feldspar, micas, locally gibbsite and traces of resistant minerals such as rutile, ilmenite, zircon and monazite.

Two size fractions ( $<45$  and  $<2 \mu m$ ) of some samples enriched in kaolin minerals were analyzed for their  $\delta^{18}O$  and  $\delta D$  values. There are systematic decreases in the  $\delta^{18}O$  and  $\delta D$  values when particle size increases. The  $<45 \mu m$  fraction range in  $\delta^{18}O$  from +16.9 to 19.3‰, but contains various impurities that lead to low measured  $\delta^{18}O$ , while the  $\delta D$  values range from -54 to -70‰.

There is no statistically significant overall correlation between the  $\delta^{18}O$  and  $\delta D$  values of the  $<2 \mu m$  fractions. All but two  $\delta^{18}O$  and  $\delta D$  values plot between the "kaolinite weathering line" (KWL) of Savin and Epstein (1970) and the "supergene/hypogene kaolinite line" (SHKL) of Sheppard et al. (1969). The two kaolinite samples with stable isotopic characteristics outside the two lines, one on the KWL and one above the SHKL are, interestingly, from the same Lendo Miocene sedimentary deposit, which suggests that both kaolinite concentrates with such various isotopic records are necessarily of different detrital origin.

Depending on a variety of assumptions involving plausible formation temperatures and/or the involvement of meteoric water with  $\delta^{18}O$  ranging from -5 to -1‰, the

formation temperature of the studied kaolinite deposits varies from about 18 to 48°C. In detailing the  $\delta^{18}\text{O}$  data of the  $<2\mu\text{m}$  kaolinite of each deposit, it can be suggested that most samples are of weathering origin, with data points close to or on the kaolinite line. There is no evidence in the oxygen and hydrogen isotopic records for an overprint at a significant higher temperature, but this cannot be ruled out unequivocally. This means in turn that migration of fluid of meteoric origin could have percolated the granitoids after surficial weathering at temperature up to 50°C and even slightly higher depending on the fluid isotopic signature. Such migrations could have modified the isotopic equilibrium of the weathering kaolinite precursors.

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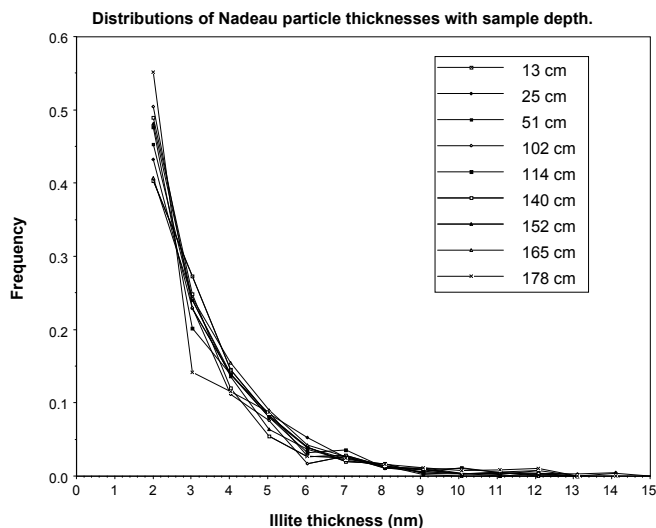
## ANATOMY OF A METABENTONITE

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Illite formation in a zoned, 2.5 meter-thick, K-bentonite bed, located in the Montana disturbed belt, USA, was studied previously by Cuadros and Altaner (1998), and more recently by McCarty et al. (2009). The latter authors found, based on Sybilla modeling of the mixed-layer clay X-ray diffraction (XRD) patterns, that the bed contains a mixture of coexisting R0 and R1 ordered illite-smectite (I/S) having 30% and 62% illite layers, respectively, with the proportion of the R0 phase increasing towards the center of the bed.

We studied the same samples as McCarty et al. (2009), but used techniques which included Atomic Force Microscopy (AFM) imaging, the Bertaut-Warren-Averbach XRD method for determining illite crystallite thickness distributions (MudMaster program), and polyvinylpyrrolidone (PVP) surface area determinations, to reveal that the mixed-layered clays are composed of stacks of small illite crystals, with an average number of three crystals per stack. The small illite crystals are termed “Nadeau particles”, and the stacks of particles that swell at particle interfaces, that diffract as I/S, are termed MacEwan crystallites. Dispersed Nadeau particles form asymptotically-shaped illite thickness distributions that are typical for the crystal growth mechanism of simultaneous nucleation and growth. The shapes of these distributions for particles that are equal to or greater than 2-nm thick (see figure below, with sample depths given from the base of the bed) are nearly constant



throughout the bed, with the samples differing mainly in the proportion of 1-nm-thick smectite particles.

We propose that the MacEwan crystallites result from the random stacking of Nadeau particles on the XRD slide, giving rise to R0 and R1 diffraction effects through interparticle diffraction, as was proposed previously for North Sea illites by McHardy et al. (1982), and for I/S in general by Nadeau et al. (1984). The Nadeau particles themselves form by the nucleation of smectite particles and their subsequent growth as illite particles.

## **KAOLINITISATION OF LOCALISED MUSCOVITE IN THE KGWAKGWE SHALE OF THE TRANSVAAL SUPERGROUP, BOTSWANA**

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Kaolinite is an important clay mineral; widely utilized in several industrial applications depending on its genesis. It could be primary, secondary or mixed; formed from the alteration of feldspathic and/or micaceous minerals in crystalline and sedimentary rocks. Its occurrence is generally common and well documented on all the continents in the world except Antarctica. However, its occurrence from micaceous minerals is not as adequately documented as that of feldspathic minerals. Several studies have been conducted on the geology, genesis and mineralogy of the different types of sediments constituting the Kgwakgwe Shale – a lower member of the Neo-Archaean Transvaal Supergroup (24° 59' 40" South – 25° 18' 30" East), found in the Kgwakgwe Basin (KB), in Botswana. The KB consists of the lower rhyolite of the Kanye Volcanic Formation (KVF) which is succeeded by the quartzite, shale and conglomerate of the Black Reef Quartzite Formation (BRQF). The varicolored manganiferous and ferruginous shale of the Kgwakgwe Shale (KS) overlies the BRQF; and is succeeded by the Chert clast breccia of the Kgwakgwe Chert Breccia (KCB). Kaolinite genesis in the KS hostrock, especially from feldspathic minerals, has been extensively studied. However, the determination of kaolinite originating from localised muscovite in the shale has not been appropriately reported on. This work thus investigated kaolinite genesis from localised muscovite associated with the KS.

X-ray diffractometry was used to identify mineral phases in whole and clay-size fraction of clay samples; scanning electron microscopy (SEM) aided in determining particle morphology of muscovite and kaolinite; X-ray energy dispersive spectrometer was employed to perform microchemical analysis of the samples; and  $^{40}\text{K}/^{40}\text{Ar}$  dating of the muscovite samples was conducted to determine its age. Quartz, muscovite, illite, kaolinite, hematite, goethite and Mn oxide minerals constituted the mineral assemblage in the KS. Within the KS, the kaolin consisted of quartz, kaolinite and illite; and the illitic/sericitic shale was comprised of quartz, illite and muscovite. The SEM photomicrographs depicted kaolinite particles being ragged-edged and flaky, swirl textured, coupled with some degree of rounding. The clay-size fraction of the kaolinite revealed irregular platelets, well developed and irregular flakes, and kaolinite booklets. Angular edges of pseudo hexagonal kaolinite platelets were evident in some samples, with crystal clusters lying in an ordered direction. The morphology of the muscovite particles was not well defined; but that of illite particles depicted good crystallinity and high porosity. Microchemical results depicted the

muscovite-rich samples to be having more K than the illite-rich samples; and no K was detected in the kaolin samples which contained only kaolinite and quartz.  $^{40}\text{K}/^{40}\text{Ar}$  dating for the age obtained for muscovite samples was  $1798 \pm 40$  MY; being slightly younger than the sediments of the Transvaal Supergroup (~2780 Ma – 2000 Ma). The geology of the Transvaal Supergroup and the results from  $^{40}\text{K}/^{40}\text{Ar}$  dating both infer illite recrystallisation forming muscovite as a result of low-grade metamorphism. The muscovite was later altered to kaolinite. The kaolinitisation of muscovite could possibly still be on-going. The findings of the study therefore portrayed the kaolinitisation of muscovite. The then existing geochemical and prevailing paleo-environmental conditions such as fluctuating pH, specific hydraulic behaviour, and the water chemistry at the different times of mineralisation (illitisation, sericitisation and kaolinitisation), and deposition thus greatly influenced the mineralogical trends which resulted to the alteration of muscovite to kaolinite within the KS.

## SEPIOLITE FROM ANATORIA TURKEY: IT'S MINING, MINERALOGY AND APPLICATIONS

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We imported sepiolite from Turkey followed by pulverization, shaping and using various industrial applications in Japan. The geological and mineralogical features of the Turkish sepiolite and the distinguishing applications are reviewed.

Geological Environment of the sepiolite deposit: The deposit is in the central Anatolia basin, Turkey, surrounded by basic intrusive rock, marble stone, magnesite deposit, and meerschaum (pure sepiolite lump) minings. The sepiolite rich layers with 0.2-5m thickness are found in the sedimentation of Neogene including dolomite (Fukushima and Shimosaka, 1987). Open-cut mined ores are dried, crushed, bagged and shipped to Japan.

Table 1. Characters of Sepiolite

|                      | Crystal Type | Fiber Size / $\mu\text{m}$ | CEC meq. /100g | Atomic Composition<br>[Tetrahedral] {Octahedral}<br>[ Si Al ] {Mg Al Fe } |
|----------------------|--------------|----------------------------|----------------|---|
| <b>Turkey</b>        | $\beta$      | <b>0.01 x 0.5</b>          | <b>4.5</b>     | <b>[12.0 0.0] {7.2 0.3 0.1}</b>   |
| <b>Spain</b>         | $\alpha$     | <b>0.1 x 5</b>             | <b>20</b>      | <b>[11.6 0.4] {7.5 0.0 0.1}</b>   |
| <b>China (Henan)</b> | $\alpha$     | <b>0.1 x 50</b>            | <b>—</b>       | <b>[11.8 0.2] {7.7 0.1 0.2}</b>   |

Mineralogical Features: The Characters are listed in Table 1 with Spanish and long fiber type Chinese one. Fine fibers with about 0.5 $\mu\text{m}$  length and 10nm thickness consist of the Turkish ores. Chemical composition is nearly identical sepiolite with a little isomorphous substitution, to which the low cation exchange capacity would be attributable. Although the definition of  $\alpha$  and  $\beta$  type structure is not clear, the Turkish one would be classified into the  $\beta$ -type because of the broad X-ray powder diffraction patterns and the results of TEM observation shown in Figure 1. Different lattice

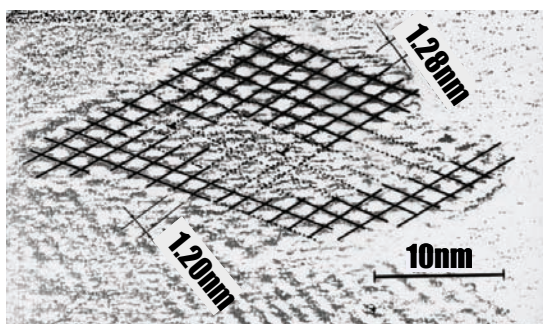


Figure 1. TEM image of a cross-section of the typical Turkish sepiolite

spacing for (110) planes at lower and upper part of Figure 1 and the irregular part between them suggested the disordered arrangement of various units suggested by Brindley (1984). The lattice defects, suggested by Shimoda (1982), were also observed by TEM study. Not only small crystallite diameter but also the disordered, which are typical features of  $\beta$ -type sepiolite, were observed for Turkish sepiolite.



Figure 2. Examples of Shaping Sepiolite

Industrial Applications; The powdered sepiolite is used for seat fabrics of vehicles or an accessory device toilet providing a deodorizing function. The powder is formed in different-shaped pieces shown as Figure 2, which was designed for various uses for deodorants, adsorbents, or moisture control.

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## CORRELATION OF LOWER PALEOZOIC K-BENTONITES: IMPLICATIONS FOR TECTONO-STRATIGRAPHIC CORRELATION IN EUROPE AND NORTH AMERICA

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Continuing studies of Ordovician and Silurian K-bentonites in Europe and North America show that many of them are distributed regionally and thus can serve as important marker horizons for stratigraphic correlation. Two examples of projects underway are from the Carnic Alps in Austria and the North American midcontinent. Lower Paleozoic K-bentonites occur in a region of the Carnic Alps that is characterized by a metamorphic overprint ranging from anchizone to epizone. As a consequence of this thermal history, the illite/smectite clay mineralogy that commonly characterizes such beds has been altered to illite and chlorite, similar to the clay minerals found in associated mudrocks. The volcanogenic origin of these beds is confirmed, however, by the presence of primary magmatic phenocrysts of biotite, apatite and zircon. In some samples the zircons show evidence of magmatic resorption. Lack of exposure at some sections makes correlation across the depositional basin problematic. Upper Ordovician beds are quite rare with one horizon noted in the Hirnantian. Three levels occur higher in the *perscultus* zone at the Cellon section, one of which may be correlated with the single horizon noted at the Oberbuchach section. Four horizons fall approximately within the *amorphognathoides* zone at the Oberbuchach section and eight in the Lower Wenlock, which appear to be traceable across the Cellon, Oberbuchach and Nölbling sections. The K-bentonite sampled from the Uggwa section may be of a similar age to those from the Llandovery of Nölbling Graben. Sixteen levels have been recorded from the *vesiculosus* zone and upwards within the Rhuddanian and eleven from the *triangulatus* zone (Aeronian). The abundant presence of these horizons in the Llandovery sequences of the Carnic Alps is similar to those in the British Isles, Sweden, Canada and North America and documents widespread volcanism related to the closing of the Iapetus Ocean and northward drifting of microplates derived from the northern margin of Gondwana. The Osmundsberg K-Bentonite has been recognized throughout NW Europe in the late Llandovery (Telychian) and it is probable that this level may also be identified from the samples taken at this stratigraphic level from the Cellon, Seewarte and Oberbuchach sections (*celloni* zone).

Although Gondwana was tectonically quiescent during the Silurian, Laurentia experienced at least two separate phases of collision. Evidence can be found in the basal Silurian strata of the Appalachian Basin in the form of widespread sheet sands and shale successions, K-bentonites, and zones of soft-sediment deformation. K-bentonites have been positively identified at multiple levels in the Llandovery-

Wenlock interval in eastern North America. While most of these beds are easily characterized by a dominant illite/smectite clay mineral content coupled with various volcanogenic phenocrysts, there are a few beds whose bentonitic character is less readily apparent. For example, a clay bed from the base of the Williamson Shale at Tryon Park in Rochester, New York and a clay bed at the base of the Estill Shale from Ohio Geological Survey core 2626 near Winchester, Ohio both appear to have volcanogenic phenocrysts and are tentatively considered to be K-bentonites. The dominant clay mineral is illite, but chlorite is also present. The sample shows a slight tendency to expand with ethylene glycol treatment, indicating the presence of some mixed-layer illite/smectite. But the sample is not as smectite-rich as many of the Silurian K-bentonites reported in the literature and it is possible that a detrital mud component is also present.

For the Silurian rocks of the Cincinnati Arch in Ohio, Kentucky, and Indiana seven depositional sequences are assigned on the basis of through-going unconformities that mirror those already recognized in the early Llandovery to early Ludlow of the northern Appalachian Basin. Revision of the conodont biostratigraphy for the Cincinnati Arch by previous authors has produced results that both agree and disagree with the other lines of data implemented in the sequence stratigraphic depositional model. Biostratigraphic correlations between southern Ohio and the Niagara Falls area are largely in agreement with correlations based on other lines of data, such as K-bentonite evidence, as are correlations between west-central and western Ohio, southeastern Indiana, and northern Kentucky. The integrated analysis suggests a relatively simple history of high-frequency relative sea level fluctuations superimposed on a tectonic signature of long-term basin subsidence and very slow forebulge migration.

## AMARGOSA VALLEY SEPIOLITE AND SAPONITE MINERALOGY AND MARKETS

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The Amargosa Valley, at the southwestern edge of the state of Nevada in the USA, has a unique geological environment that contains soluble silica and is rich in reactive magnesium while low in reactive aluminum. This environment formed two trioctahedral clay minerals: sepiolite and saponite. While saponite is a trioctahedral smectite clay with a platy crystal structure that extends in two directions, sepiolite forms lath structures that are fixed in two dimensions and extend in one dimension to about 1 $\mu$ m. The geological and chemical conditions for forming both of these clay minerals will be addressed.

The trioctahedral occupation of the octahedral layer of these clays gives them greater thermal stability than dioctahedral occupation clay minerals. As trioctahedral clay minerals, both clays disperse in saline water as well as fresh water, giving unique application characteristics. Sepiolite has an API specification for salt water drilling where it imparts non-newtonian shear thinning and particle suspension. Drilling applications are being pursued for saponite. Major commercial markets for these clay minerals include: absorbents, adhesives, animal feed, carriers of pesticides and fertilizers, ceramics, fillers & extenders, foundry, pet litter, iron ore pelletizing, refractories, water proofing and sealing. These markets are tied to the USA economy and population and will grow during recovery from the USA recession and the continued drilling to meet the increasing demand for more oil and gas on a world basis.

## VARIABILITY OF TRACE ELEMENTS IN SEPIOLITES FROM DIFFERENT SEDIMENTARY ENVIRONMENTS (MADRID BASIN, SPAIN)

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In this work the trace element geochemistry of sixteen samples of sepiolite-rich levels from five lithological sections in the Neogene Madrid Basin have been studied. The samples were collected from different representative deposits including alluvial fan facies (Vicalvaro, Cabañas de la Sagra), palustrine complex (Cerro de los Batallones) and mudflat environment (Esquivias, Magán). The analytical techniques used have been X ray diffraction (mineralogy) and optical microscopy for the mineralogical and textural characterization. The chemical analysis of trace elements has been performed by means of ICP-Mass spectrometry and Neutron Activation analysis. As an exception F was analyzed by colorimetry after pyrolysis treatment.

The results point out the abundant content of sepiolite in samples commonly higher than 95%, minor content of quartz, feldspar, calcite, palygorskite or stevensite have been locally observed. From textural point of view sepiolites occur in laminated, massive and brecciated facies, often with intraclasts in variable content, also of sepiolite composition. The geochemical results indicate that all the trace elements analyzed are depleted respecting the UCC standard (Upper Crust Composition), especially RE elements (<0.4). Taking into account the sedimentary environments the higher depletion has been observed in sepiolites from mudflat facies (V and U content are the exception). The cluster analysis corroborates the geochemical difference between mudflat sepiolites and those from palustrine and alluvial-related facies. The normalization of REE both with NASC and chondrite allow to differentiate clearly the sepiolites related to alluvial fan facies from all the remaining samples. On the other hand the La/Sc ratio against Th/Co ratio corroborates a source from felsic rocks. Likewise, the Th/U ratio suggests that sepiolites collected from palustrine and alluvial-related deposits underwent a higher leaching (>1) than those from mudflat facies. Among the remaining trace elements the high content in F (>4000 ppm) and the low content of Li (20-100 ppm) is remarkable, allowing to separate samples related to alluvial fan facies from those of mudflat and palustrine deposits.

The geochemical complexity observed in sepiolites should be a consequence of the different paleoenvironmental conditions where they form. Moreover the common evidences of subaerial exposure (brecciation) and the widespread presence of intraclasts in sepiolites suggest the existence of several generations of the fibrous

clay mineral. This fact is important because indicates mixing of geochemical signals in the samples, affecting especially to palustrine sepiolites. The obtained results allow differentiating sepiolites originated by precipitation from solution and those forming under diagenetic conditions. In the last case the geochemistry of authigenic sepiolite would be related to the Mg-clay/carbonate support involved and the composition and pH of the groundwater input.

## SYNTHESIS AND CHARACTERIZATION OF PHYLLOSILICATES IN MONTMORILLONITE – STEVENSITE COMPOSITIONAL SERIES

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The hydrothermal syntheses of smectites, interstratified clay minerals and related phases are the subject of great interest for basic researches in natural environments (diagenesis, hydrothermal alteration and the design of clay barriers for high level radioactive waste) and material sciences (catalysis support and new functional nanomaterials). In the present study, a series of hydrothermal experiments were performed to determine the phase relations on the montmorillonite – stevensite.

Quenched glasses with stoichiometric dehydrated composition of a Na-rich smectite on the join were treated hydrothermally at 250 - 500°C for durations of up to 150 days at 100 MPa. The products were characterized by XRD, FT-IR, TG-DTA, TEM and AFM.

The present time-temperature-phase change diagram showed that immiscibility occurs between dioctahedral smectite (montmorillonite-like smectite) and trioctahedral smectite (stevensite-like smectite) below 400°C. Above 400°C, interstratified clay minerals (Na-rectorite and/or regularly interstratified chlorite/smectite) were obtained with quartz and rarely mica in the intermediate chemical region of this join. Thus, smectite with intermediate chemical composition was considered to be metastable in this system. On the montmorillonite side of this join, montmorillonite, mixed-layer phases of smectites, and a regular interstratification of montmorillonite-beidellite, are possible phases obtained above 250°C. They reacted to form a mixture of dioctahedral rectorite ( a regularly interstratified dioctahedral mica/beidellitic smectite) and silica mineral. Then this assemblage changed to dioctahedral mica-like phase which can expand by ethylene glycol and quartz. On the stevensite side of this region, trioctahedral smectite, stevensite was found below 300°C, and transformed to stevensite and quartz with aging. Above 350°C, a unique regularly interstratified clay mineral composed of talc/talc/stevensite (TTS)<sup>1)</sup> was recognized. With increasing temperature and duration, regularly interstratified TTS disappeared, but the assemblage of randomly interstratified TTS and quartz appeared.

The obtained result supported the earlier works<sup>2-4)</sup> for beidellite – saponite pseudo-binary join, and reconfirmed the immiscibility between dioctahedral and trioctahedral smectites. The present study also confirmed that the alteration was strongly affected by the chemical composition of the binary system.

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## **MINERALOGY, GEOCHEMISTRY AND GENESIS OF YENIDOĞAN (SIVRIHISAR, TURKEY) SEPIOLITE AND RELATED MG-RICH MINERALS**

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Several layered sepiolite deposits occur in the Eskişehir Neogene lacustrine basin. The present occurrence found in the SE Eskişehir (Sivrihisar) is the largest layered sepiolite deposit known up to date. This occurrence was investigated in detail along several cross-cuts and consequently by means of XRD, SEM and chemical analysis. Sepiolite and related Mg-rich minerals occur in a ~80 m thick sequence of Lower Pliocene where alternating dolomite and dolomitic marl beds are represented as the principal rock assemblages. The lower half of this section begins with a nearly 2 m thick dolomite-magnesite layer and continues upwards in order: two separate strata with sepiolite, magnesite-bearing dolomite containing both saponite and sepiolite, sepiolite-bearing marl, and sepiolite-bearing saponite beds. The upper half of the sequence begins with a saponite bed and continues with alternating dolomite and scarce dolomitic marl layers in which saponite occur as the clay mineral constituent. At the uppermost part of the sequence, thick and massive dolomite beds are found.

Sepiolite occurs as rather continuous layers or lenses varying in composition from nearly 50 per cent dolomite-bearing sepiolite to nearly pure sepiolite. The thickness of the lower sepiolite strata is nearly 3 m thick whereas total thickness of the sepiolite-rich beds reaches up to 10 m at the upper strata.

The sepiolite and sepiolitic materials display detrital, massive or laminated megascopical textures. XRD studies revealed that sepiolite which is represented in the lower strata is well formed but poor ordered showing XRD pattern with a weak 110 reflection of 13.0 Å *d* value whereas sepiolite in the upper strata is well crystallized with a 12.1 Å *d* value and well resolved reminder reflections. In both kinds, fibrous morphology is apparent under the SEM. Saponite is poor ordered having diffused first basal reflections with unusual high *d* values ranging from 16 Å to 18 Å and from 17 Å to 18.7 Å under air-dried and glycol-solvated conditions respectively. Under the SEM, smectite displays flaky morphology where, in some cases, sepiolite fibers were developed on the smectite substrate.

Magnesium carbonates and silicates were formed by direct precipitation from solution in a Mg-rich playa lake environment. In addition, sepiolite was also formed during diagenesis and by transformation from saponite. Their formation were controlled by the relative concentrations of Mg, Ca, Si and Al ions and variations of pH values in lake water.



## *POSTER PRESENTATIONS*



## INTERLAYER AND OCTAHEDRAL SUBSTITUTIONS IN MESOZOIC GLAUCONITES AND OTHER AUTHIGENIC GREEN MARINE CLAYS DURING DIAGENESIS OBSERVED BY XRD, SEM, AND TEM

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Glaucconites and other authigenic green marine clays are useful facies indicators for sedimentary basins. However, the process and timing of glauconitization is still unknown. Glauconitic minerals are thought to evolve at the water-sediment interface under reducing conditions and are used as indicator for large-scale transgressions or regressions at a continental shelf. Authigenic illitic clays have been used for absolute age determinations, especially, when index fossils are absent. However, how accurate are the age determinations since diagenetic alteration processes from initial smectitic to more mixed layered illite-smectite phases are common? These processes will likely modify the authigenic green marine clays. This is expressed in Al-Fe-Mg substitutions in the octahedral sheet and K substitutions in the interlayer.

The goal of this present study is to identify diagenetic transformations and alteration processes in authigenic green marine clays. Therefore, authigenic Fe-rich and Fe-poor illite and illite-smectite phases from two localities in the Eastern Subhercynic Cretaceous Basin and near the Western Harznordrand thrust (Germany) were studied. The investigated sedimentary units of the Lower Cretaceous (Cenomanian-Turonian units from Langenstein) and Upper Jurassic (Kimmeridgian units from Oker) were selected because of the well known deposition conditions and burial history. These well understood geological settings are ideal to differentiate syndepositional and post-depositional diagenetic alterations.

Samples from Langenstein and Oker of diverse horizons were collected to allow differentiation of authigenic clay minerals from detrital minerals (natural background). The newly formed Fe-rich illite phases, the illite-smectite, and the (mostly) detrital Fe-poor illite phases were analyzed by XRD using random and oriented preparations. Interpretations were based on illite-smectite content, total K and Fe content (compared with NEWMOD® models), and polytype determinations (calculated with WILDFIRE®). Representative thin sections were prepared and studied by optical microscopy and SEM (including EDX). TEM analyses of particles <2 µm were also made to detect diagenetic substitution reactions in the octahedral sheet and the interlayer. Both, SEM-EDX and TEM-EDX data indicate a good correlation between octahedral Al, Fe and Mg as well as a linear correlation between the interlayer K and the octahedral cations. As K increases so does Fe, while Al and Mg decreases. These linear trends were observed both by SEM and TEM.

Chemical variations were observed for different morphologies of the minerals. Hairy or fibrous illitic minerals with moderate K and high Fe content, and 1M polytype (by TEM) were interpreted as authigenic minerals. Platy illites with high Al, high K and low Fe content, and 2M<sub>1</sub> polytype (by TEM) were interpreted as detrital minerals. Finally, all analytic and optical findings agree with XRD data resulting in comparable chemical compositions between calculated structural formulas by SEM and TEM and NEWMOD® models. Additionally, not all green minerals were glauconites; for the Langenstein samples two different green minerals were identified (glauconite and Fe-rich fluorapatite), which microscopically could not be differentiated.

As the final results of this study, we observed for both investigation areas of the Harz foreland different diagenetic influences of the associated clay minerals. This is expressed of Al-Fe-Mg substitution reactions in the octahedral sheet and a continuous K enrichment in the interlayer. These lead to a significant post-depositional alteration of the green marine clay minerals.

## **HYDROTHERMAL CLAYS AT THE FUTURO VEIN, MARTHA MINE SILVER EPITHERMAL DEPOSIT, DESEADO MASSIF, PATAGONIA, ARGENTINA**

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The Deseado Massif (DM) is a 60,000 km<sup>2</sup> geological province located in the southern Argentinean Patagonia. This region is an important Au-Ag producer characterized by middle to late Jurassic bimodal volcanic complex with numerous related epithermal deposits. This volcanism is composed of acid volcanic rocks (Chon Aike Formation) and intermediate to basic volcanics (Bajo Pobre Formation). These rocks are mainly calc-alkaline and peraluminous in nature [1].

The Martha Mine epithermal deposit is located in the south-western portion of the DM. This vein system is characterized by an episodic vein infilling dominated by silver and base metal-bearing sulphides with quartz and adularia gangue, hosted in rhyolitic ignimbrites. The main mineralized structures show a NW trend with E-W splays that builds up a sinistral “horse tail” structure. Regional mapping shows a spatial relation between these veins and a 12 Km diameter caldera eruptive centre [2]. Martha Mine hydrothermal alteration is represented by silicification, argilitización and sericitization.

The aim of this study is the characterization of dioctahedral clays formed as the consequence of hydrothermal processes affecting ignimbrites of the Chon Aike Formation at Futuro vein (a low grade E-W vein), at Martha Mine site. Fifteen samples have been collected from a surface cross-section; they were studied by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM) in order to identify the mineralogy, texture and composition of hydrothermal clays.

Fresh ignimbrite (host rock) consists of abundant crystaloclasts of quartz, K-feldspar, plagioclases (Ab up to An<sub>47</sub>), phengite, biotite and vitroclasts with spherulitic texture. Secondary clay minerals have been identified in the wall rocks of the Futuro vein replacing glassy clasts, feldspars and micas. The combination of XRD, SEM and TEM studies have shown the occurrence of dioctahedral 2:1 phyllosilicates (smectite and illite) in the altered rocks.

Three zones can be distinguished according the clay distribution: 1) in the less altered samples (7-8 meters away from the vein) the only clay observed was smectite. This is an Al-rich smectite (montmorillonite) with Ca>Na>K in the interlayer and a typical wavy flake morphology. 2) At 5-6 meters away from the vein, minor smectite and

discrete illite coexist. Smectite (montmorillonite) has  $\text{Na} \sim \text{K} > \text{Ca}$  in the interlayer. Smectite morphology is similar to that observed in zone 1 and illite shows anhedral sheet particles. 3) Between 5 to 0 meters away from the vein; the only observed phyllosilicate is the anhedral to subhedral laminar illite. Illite crystallinity increases toward the vein (from 1.20 to 0.60°2 $\theta$ ) indicating an increase in the crystal size; the crystallinity of this hydrothermal illite is similar to that of illites formed during burial diagenesis.

The data show a smectite to illite transition during the hydrothermal event without the occurrence of intermediate phases, such as illite-smectite interlayers. Such discontinuous series involving discrete phases must occur via a dissolution and crystallization sequence. Temperature of alteration provided the major control for the clay crystallization. Changes in the interlayer composition reflect that factors as the K<sup>+</sup>, Ca, Na availability, water rock ratio, and permeability also played an important role during clay formation.

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## KAOLINITE ILLITIZATION AT 300°C WITH INCREASING PRESSURE

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One of the important reactions producing illite as a consequence of burial diagenesis is the illitization of kaolinite, which has been investigated extensively in both natural systems and experimental conditions. Experimental illitization of kaolinite in aqueous solutions containing  $K^+$  has been the subject of study for a number of years since Velde (1965) synthesised muscovite from kaolinite and KOH solutions at 300 °C.<sup>1</sup> Most of the studies report results on the kinetics of kaolinite illitization (Chermak and Rimstidt, 1990; Huang, 1993; Bauer et al. 1998; Bauer and Berger, 1998).<sup>2,3,4</sup> Bentabol and coworkers (Bentabol et al. 2003a; Bentabol et al. 2003b; Bentabol et al. 2006) studied the influence of  $Na^+$  and  $Mg^{2+}$  ions on the kaolinite illitization while Bauer et al. (1998) studied the transformation in high molar KOH solutions at low temperatures.<sup>5,6,7,8</sup> All these studies analyse the influence of temperature, chemistry, pH and solid/liquid ratio on the illitization process. However, the reactions are conducted in autoclaves or hydrothermal reactors that generate an internal pressure corresponding to the water vapour pressure at each temperature. The use of this type of reactors, therefore, hinders carrying out the experiments at any other pressure value.

The aim of the present study is to understand the influence of pressure on to the progress of kaolinite illitization. The formation of illite via illitization of kaolinite takes place at an intermediate burial depth of 3-4 km, where pressure can reach values of some 100 MPa (~ 1000 bars) (Bjorlikke, 1980). Experiments with powdered kaolinite in KOH (2.85M) solution were carried out in cold-seal pressure vessels at 300°C and pressures of 500 bars to 3000 bars. The reaction products were analysed using long and short range order techniques: X-ray diffraction spectroscopy has been used to follow the formation of new crystalline phases and  $^{29}Si$  and  $^{27}Al$  MAS NMR spectroscopy have informed of the presence of small crystallites of new phases not detected with XRD. SEM and TEM have been used to analyse the morphology of the reaction products.

The XRD patterns showed a direct transformation of kaolinite into illite/muscovite (I/M) with increasing pressure. However the  $^{27}Al$  MAS-NMR spectra showed, in addition to the I/M resonances, the presence of signal at 60.9 ppm, that should correspond to an intermediate phase, invisible to XRD. A new series of experiments at 300°C and 1000 bars for 1,3, 6 hours was carried out to look for a direct evidence of such intermediate phase. Between 1 and 6 hours of treatment it was clearly

observed a well resolved series of reflections of a new crystalline phase called zeolite F. The  $^{27}\text{Al}$  signal at 60.9 ppm observed in the spectra must correspond, therefore, to zeolite F nuclei. In conclusion, Kaolinite transforms into I/M when submitted to hydrothermal treatment at increasing pressure, with the formation of an intermediate phase called zeolite F, although coherent diffraction domain size is very small to be detected by XRD.

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## MINERALOGY AND GEOCHEMISTRY OF BENTONITE ROCKS FROM THE SERRA DE DENTRO, PORTO SANTO ISLAND, MADEIRA ARCHIPELAGO

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Madeira archipelago represents the present location of the postulated >70-Ma-old Madeira hotspot that was responsible also for several seamounts to the northeast and comprises Madeira, Porto Santo and the three Desertas islands. The lower basaltic and the upper mugearitic to trachytic sequences are dominated by lapilli cone aprons in the Porto Santo island. Basaltic dykes network swarm up to 0.5m thickness cut the hyaloclastite trachitic sequences, where the heat derived from the basalt flow did burn at contact with the hyaloclastite rocks into a brick material. Whole rocks and clay fractions were studied by X-ray diffraction, Infrared-spectroscopy (IR) and chemical analyses. Bentonite rocks formed from the alteration of the hyaloclastite rocks under submarine conditions and low temperature are constituted by smectite (74%), Ca-Na feldspar (17.4 %), volcanic glass (3.6%) and hematite (0.6%). X-ray diffraction pattern of randomly specimens exhibit a broad asymmetric peak at d(20,13) indication of a turbostratic structure and the d(060) peak at 1.50-Å corresponding to a dioctahedral smectite. Oriented specimens of the <2µm clay fractions show a peak at 14-Å which expanded after ethylene glycol (EG) solvation at ~17-Å. The saddle/peak ratio measured in some samples was found high and the d(001) reflection broad, indicating some interstratification of 2EG, 1EG or OEG. The Hoffman-Kleman test shows that the localization of layer charge occurs in montmorillonitic layers. The IR spectra of Li saturated smectite show bending frequencies at 935 cm<sup>-1</sup>, 855cm<sup>-1</sup> and 812 cm<sup>-1</sup> associated with AlAlLiOH, MgAlLiOH and, MgFeLiOH. Crystal chemistry of di-smectite corresponds to a chemical formula (Si<sub>3.83'</sub>Al<sub>0.17</sub>)<sub>4</sub>(Al<sub>1.50</sub>Fe<sub>0.16</sub>Mg<sub>0.37</sub>)<sub>2.03</sub>O<sub>10</sub>(OH)<sub>2</sub>(Na<sub>0.12</sub>Ca<sub>0.21</sub>K<sub>0.07</sub>). Mobility of major and trace elements during alteration of hyaloclastite trachitic rocks into bentonite rocks was determined using Gresens equation. Mass balance calculations suggest that Nb, Zr, V and Ni are immobile and the water:rock ratio is about 11:1. The La/Yb, Nb/Ta and Zr/Hf ratios for the samples analyzed are very close to that of the hyaloclastite trachytic sampled. A positive Eu anomaly and a negative Ce anomaly were identified in samples analysed. The REE fractionation confirms the smectite formation from volcanic glass.

## EVALUATION OF THERMOMETRIC CAPACITY OF CLAY MINERALS: EXAMPLE OF THE GULF COAST'S CHLORITES (TEXAS)

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These 25 last years, several thermometers based on chlorites' chemistry were gauged. In fact, two methods were explored: the empirical calibration and the thermodynamic calculation of equilibrium conditions. In the first case, Cathelineau (1988) showed the direct correlation between tetrahedral Al occupancy and measured temperatures. This empirical calibration was then corrected with the XFe ( $XFe = Fe/(Fe+Mg)$ ) parameter by several authors, with the aim of extending their applicability. These thermometers can be easily calculated, but do not take into account the effects of the bulk-rock composition. On the contrary, the second method includes the effects of rock mineralogy's variations. Several geothermometers were proposed, in particular those of Walshe (1986), Vidal et al. (2001) and Inoué et al. (2009). But Inoué et al. (2009) explain that the majority of these models are gauged for high temperatures (metamorphic conditions), and not precise enough for diagenesis conditions. Moreover, they show the non-negligible influence of the FeIII/FeII ratio.

In this study, we propose an evaluation of the thermometric capacity of chlorites for diagenesis analyses purpose by comparing different temperatures obtained with the preceding thermometers using measured chlorites chemistry. The studied area is localised in the Gulf coast (USA). 15 drill hole plugs sampled at different depths were analysed with a FIB/EDX-TEM method. Estimated temperatures were attributed for each sample, on the base of the P-T measured *in situ*, in the bottom hole. The estimated temperatures were corrected to approximate the true maximum conditions.

The results show the limited impact of the XFe corrections on the empirical estimations of temperatures. Concerning the thermodynamic models, the results show the influence of FeIII occupancy on calculation, in agreement with Inoué et al. (2009). To circumvent that problem, a minimum ferric iron is calculated from the

stoichiometry. These comparisons permit to evaluate the relevance of the bottom-hole temperatures in the Gulf Coast, and the validity of the chlorites' thermometers in the low-T conditions.

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## **FIRST APPROACH TO THE CLAY MINERALOGY OF THE KAOLIN-RICH SEDIMENTARY DEPOSITS FROM THE WEALD FACIES IN THE IBERIAN RANGE (NE SPAIN)**

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The aim of this study is to characterize the clay mineral associations from the clayey sedimentary deposits of the Lower Cretaceous (Weald facies) in Maestrazgo basin (Teruel, NE Spain). These deposits, that are rich in kaolin minerals, are actively mined by the ceramic industry (sanitaryware). The studied rocks (claystones, siltstones and sandstones) constitute the Camarillas Formation (Barremian) and correspond to a fluvial environment. Most of these materials display red colors although there are also greenish and grey levels. The formation represents a fluvial system of multiple low sinuosity channels, evolving towards the top to a delta plain, with tidal influence (Díaz-Molina & Yébenes, 1987). A systematic sampling (45 samples) has been performed in two sections in the Maestrazgo basin: in an open pit nowadays mined close to Galve (Galve section) and in other outcrop at 50 km (Miravete section).

The X-ray diffraction analysis indicates claystones and siltstones have similar mineral composition in both sections. Claystones have ~50% quartz, ~40% phyllosilicates (kaolinite, micaceous phases and rare chlorite), and very low amounts (<5%) of feldspars (K feldspar and plagioclase), carbonates (calcite, dolomite, siderite) and hematite. The mineralogical composition of siltstones is similar to that of claystones although with lower contents in phyllosilicates (~30%). Sandstones of both sections have high quartz content (~75%), and minor feldspars (K feldspar and plagioclase, ~10%), phyllosilicates (<10%) and carbonates. Calcite content is larger in Galve section (~15%) than in Miravete (<5%). In addition, plagioclase and hematite are absent in Galve sandstones.

The analysis of fine fractions of claystones reflects that the major phyllosilicates are micaceous phases (mostly illite) and kaolinite, with minor chlorite. The kaolinite/micaceous phases ratio ranges between 0.3-0.7. In sandstones most of the fine fractions are formed by kaolinite (and minor dickite) with accessory micaceous phases and chlorite. The kaolinite/micaceous phases ratio ranges between 2-5. The kaolin minerals of sandstones have higher crystallinity ( $0.19^{\circ}2\theta$ , FWHM) than those of claystones ( $0.33^{\circ}2\theta$ ). In addition, the 7 Å peak in claystones enlarges with the ethylene glycol treatment indicating the presence of interstratified smectite layers in the kaolinite. No variations have been observed with the same treatment in sandstones.

Scanning electron microscopy study reflects striking textural differences between sandstones and claystones. Sandstones contain abundant booklets formed by subhedral to euhedral hexagonal plates of kaolin minerals; these booklets are absent in claystones. The kaolin plates are 5-20  $\mu\text{m}$  in diameter and the aggregate thickness along the c axis is up to 35  $\mu\text{m}$ . In these rocks, highly altered K feldspars have been also observed. In contrast, claystones are mainly formed by subhedral to anhedral flakes of kaolinite and illite with particle size  $<10 \mu\text{m}$ . These flakes have random orientation.

The differences in crystallinity, morphology and texture of clays from claystones and sandstones probably suggest that they have different origins. Kaolinite from claystones might be mostly inherited phases and their anhedral shapes would be a consequence of sedimentary processes. The delicate and fragile shapes of kaolin booklets might represent an authigenic origin as response to diagenetic processes.

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## CLASSIFICATION OF MONTMORILLONITES ACCORDING TO THEIR LAYER CHARGE: SIGNIFICANCE AND APPLICATIONS

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Montmorillonites are characterized as low- and high-charge according to the magnitude of the layer charge. However there is not an acceptable classification scheme. Typical low charge smectites are the formerly called Wyoming montmorillonites and high charge smectites are the Cheto montmorillonite (SAZ-1). However this characterization is arbitrary and cannot be used for other montmorillonites. Recently Emmerich et al. (2009) classified dioctahedral smectites according to the layer charge as low charge smectites with layer charge lower than 0.375 eq/fu, high charge smectites with layer charge higher than 0.425 eq/fu and smectites with medium charge those with layer charge between these limits. However this classification is not based on an acceptable reasoning. In this contribution we propose a classification scheme of montmorillonites according to their layer charge based on the characteristics of the XRD traces of K-saturated, ethylene glycol solvated smectites (Christidis & Eberl, 2003). These characteristics take into account the ability of K-smectites to form randomly interstratified units consisting of layers with variable swelling ability.

According to the proposed classification scheme, low charge montmorillonites consist mainly of fully swelling layers and are characterized by XRD traces with 001 d-spacing values greater than 16.6 Å, and well-defined and rational series of higher order basal reflections. Those montmorillonites have layer charge lower than 0.42 eq/fu. High charge montmorillonites are characterized by first order reflections between 15.5 Å and 13.5 Å, and a 003 reflection at 4.65-4.70 Å, which tails off with a shoulder at the low angle side. Those montmorillonites have layer charge higher than 0.48 eq/fu. Finally montmorillonites with layer charge between 0.425 and 0.475 eq/fu are characterized as montmorillonites with intermediate layer charge. These are characterized by 001 d-spacing values ranging between 16 and 16.6 Å that have irrational higher order basal reflections. Also, the 002 reflection for this type of montmorillonite is usually a shoulder. The layer charge boundaries of tetrahedrally charged smectites are slightly different because swelling of K-saturated layers is affected by charge localization. Low charge beidellites or nontronites have charge lower than 0.36 eq/fu, intermediate charge ones have layer charge between 0.365 and 0.415 eq/fu and high charge ones have layer charge greater than 0.42 eq/fu.

The proposed method has been successful to characterize a variety of smectites from various places in the world. Most smectites have been classified as intermediate charge ones. Saturation with a cation with low hydration enthalpy such as potassium is very sensitive and can probe slight changes in the layer charge of montmorillonite

after Li-fixation. This was not possible in the past and the decrease of layer charge was controlled mainly by the decrease of the CEC. Other applications include determination of slight modifications of layer charge of MX80 used for encapsulation of high level radioactive wastes, which was exposed to temperature, brackish groundwater and time. Moreover it has been used for determination of the layer charge of smectites used for the development of the fundamental particle concept (Pratikakis et al. 2010, this conference). In the latter case the layer charge values were confirmed both by chemical analyses of the  $-0.2\ \mu\text{m}$  clay fraction and from CEC measurements.

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## BIOMINERALIZATION OF SEPIOLITE BY SILICIFIED NANOTUBE TEMPLATES IN MIOCENE SEDIMENTS OF MADRID BASIN

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The formation of different minerals as carbonates (dolomite and magnesite), chert, barite and sepiolite, has been described in the lacustrine and fluvio-lacustrine Miocene sediments of the Madrid basin. These sediments have been related to microorganism activity (Leguey et al., 2010; Sanz et al., 2009). In a sedimentary sequence that has been sampled near Barajas (east of Madrid), within arkoses and lutites, several layers of carbonates and sepiolite can be recognized. These sediments contain dolomite aggregates resembling mineralized microorganisms with ovoid morphologies and spherical to tubular voids (termed biomorphs) and fibrous sepiolite-dolomite intergrowths has been frequently observed. Per mil amounts of  $nC<18$  fatty acid compounds were extracted in methanol from these samples and their origin is connected to the presence of algae and bacterium in the lacustrine environment.

The aim of this work is to analyze the geochemical and textural characteristics of the mineralized biomass found in the sediments. Hydration-desiccation cycles occur in the sediments and favor the biomass degradation and the dissolution-precipitation processes. In this environment, the sepiolite and/or dolomite or the opal are concentrated. Investigation tools such as scanning and transmission electron microscopy have allowed us, at micro and nanometer scale, to evidence how the mineralization of biomass is the driving process of mineral formation.

The invoked biomineralization process occurs in two steps. In the first step, the passive biomineralization (Si, Ca, Mg and Na) of vegetal residue is produced, and silica is found as nanotubes. In the second stage, the Mg, previously concentrated on exo-polysaccharides (EPS) generated by microorganisms (i.e., cyanobacteria), is liberated during the desiccation processes (Wright and Wacey, 2005). Reaction of Mg with the biogenic silica leads to the sepiolite crystals nucleation using the organic support. When the content of Mg or the organic support is scarce, biogenic silica is concentrated and later transformed into quartz. Diagenetic processes favor the salts loss and the growing of the sepiolite fibbers, which preserve the structure of microfibers and intergrowths of nanotubes.



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## GEOLOGY AND STRUCTURAL CONTROLS OF TWO KAOLIN OCCURRENCES FROM LIMPOPO PROVINCE, SOUTH AFRICA

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This study focuses on the geology and structural controls of two kaolin occurrences (Duthuni and Zebediela kaolins) in Limpopo Province, South Africa. Field mapping, inclusive of description of regional geologic setting, lithostratigraphy and structural controls of the kaolin outcrops were undertaken.

The geology of the Duthuni area is dominated by the Soutpansberg Group rocks. The kaolin occurs within the Sibasa Formation – a dominantly volcanic succession. Major faults within the area strike in the NW and WNW antithetic to the ENE general trend of the group. Kaolinisation is partly structurally controlled. The faults impose a fairly gentle relief (10 – 30°), reducing erosion rate and preserving formed kaolin matrix. The undifferentiated bedrock basalts serving as impermeable layers, further enhance deep weathering of the host tuffaceous materials.

The rocks of the Zebediela area on the other hand belong to End Archean / Early Proterozoic Transvaal Supergroup. The kaolin is hosted in a tectono – sedimentary – volcanic paleoenvironment constituting part of the Transvaal basin-fills of the Chuniespoort Group. Kaolinisation is ascribed to deposition of shallow to deep water argillaceous and arenaceous sediments of lacustrine environments; which were preceded by thermal subsidence following initial rifting of the sub-basin. Subsequent rifting due to emplacement of the Bushveld Complex accompanied by ENE – WSW folds and faults buckled the argillites to present geomorphological highs. The kaolinite was further refined by acid leaching due to action of meteoric water with faults serving as preferential pathways.

Field evidence suggests the Duthuni kaoloin is primary whereas the Zebediela kaolin is a reworked sedimentary deposit.

## COAL AND CLAY-MINERAL VERY LOW- TO LOW-TEMPERATURE INDICATORS, COMPARATIVE APPLICATION FROM DIAGENESIS TO GREEN- AND BLUESCHIST FACIES

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Vitrinite reflection (VR) together with bituminite reflection (BR) measurements and Kübler index values (KI) are compared and calibrated by different mineralogical, geochemical and isotopic data.

Data are taken from the Alps, e.g. the Upper and Lower Austroalpine of Switzerland and Austria. In eastern Switzerland the South, the Middle and the North Penninic units and the Helvetic realm in the Eastern and Central Alps was included in the study. In these tectonic units different sedimentary burial (0-2.0 kbar), oceanic (0-0.5 kbar) and orogenic metamorphic (0-6.0 kbar) histories with low, moderate, and high average heating rates at differing P-T-conditions are known.

Diastathermal metamorphism was compared in Chile (Vichuquén-Tilicura and Hualañé-Gualleco basin) with plutonic contact metamorphism from the Hualañé area, from the late Variscan intrusions in the Vosges mountains (France) and from the Adamello batholite aureole (Italy), and from small Alpine porphyry- dike granite intrusions in the Stara Planina (Bulgaria). Alpine orogenic studies were performed in the South Carpathians and specifically attention was focused on the high-metamorphic thermal gradient conditions during low-grade metamorphism in the very low- to low-grade metamorphic core complex of the Danubian window (Romania). Research on low-metamorphic thermal gradient conditions is based on studies from the Diablo range in the Franciscan complex in California, the Briançonnais zone in the French Alps and from high pressure sub-greenschist to blueschist areas of New Caledonia. Also sub-greenschist facies re-equilibration after high pressure sub-greenschist or blueschist events during subduction and subsequent orogenic continent-collision and volcanic arc-collision was included in the study (New Caledonia, Bündner schist-units of Switzerland, Vosges mountains of France).

In the diagenetic to epizonal volcano- to diastathermal settings of pre-orogenic burial or in the aureoles of post-kinematic plutons, temperature is the most important controlling parameter. Rock maturity at maximum temperature is accelerated relative to KI. This is also valid for normal-thermal conditions during a short orogenic heating period. Illitization (smectite-illite reaction progress) and maturity modelling allow to deduce a linear temperature dependency of VR/BR and less significant of KI from diagenesis to incipient metamorphism. Assuming iso-geothermal conditions, also time- and pressure-independent paleo-geothermometers yield accurate T°C

estimations. However, comparison of iso-geothermal gradients emphasize time-dependent differences for maximum temperature and VR versus KI (heating close to maximum conditions between 1 and 20 Ma). During heating periods >20 Ma, the time dependency of VR is reduced. During orogenic metamorphism under anchi-epizone/sub-greenschist facies conditions (2.0 to <4.0 kbar), organic maturity is almost entirely a product of temperature and time. This is well constrained by significant correlations of all low temperature indicators used.

In sub-greenschist to blueschist facies units (>6.0 kbar), VR/BR is retarded in comparison to KI. This relation is well documented in blueschist facies rocks and most pronounced in the Diablo Range (eclogite facies, >20.0 kbar). At higher pressures, where VR is retarded in respect to KI, modelling results in an underestimation of temperature. With new pressure-time-temperature dependent kinetic models field data and calculated data are compatible. If strain plays an important role also this model fails. The thermo-barometric use of KI versus VR/BR in orogenic settings is shown.

Finally field data is compared with experimental hydrothermal and piston cylinder high pressure (0.5 to 20 kbar) data on vitrinite and bituminite of different O-H and O-C composition. A new modelling technique presented is verified with a standard illitization model.

## GEOCHEMICAL “FINGERPRINTS” OF HISTORICAL BRICKS: A PILOT STUDY FROM AUSTRIA

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Clay and sediments rich in clay are used as typical raw materials for the brick industry.

Mineralogical and petrographical parameters as well as technological properties were analysed on several brick samples from the surroundings of Vienna. In addition elemental analysis were performed on total digestions of the powdered materials using inductively coupled plasma mass spectrometry (ICP-MS) as powerful technique for the determination of the trace element composition of the samples.

In the present work our intention is to characterise which parameters are the most significant for tracing the origin of historical brick stones. In archeometry it is a big task to determine the provenance and get information about the production technology in historical times.

Like in forensic studies we are using an interdisciplinary approach to detect markers like “fingerprints” which are significant for the materials. The natural elemental distribution, characterised by the geochemical and geological environment and the technological process during the brick making influences the chemical and mineralogical composition of the material. Additional, different inclusions in the bricks like by-products or recycling material can be typical for different production places. Further to the variables measured, the signs – possibly the symbols of the producer – are available.

Several multivariate statistical methods like factor analysis, cluster analysis and discriminant analysis were performed on the data set. The available variables are manifold. There are more variables available than objects to be classified. It is therefore necessary to reduce the dimensionality and the multicollinearity. This is done with factor analysis. The factors are then used in the classification process. There are about 5 to 7 different sources and/or production sites for the 36 bricks. Discriminant analysis is used in two ways. One way takes the results of the cluster analysis as classes which are tested with the same variable set. Second the symbols on the upper side of the brick stones are used as different classes and the measured

variables as explanatory variables to find out if the symbols could be used as hints about the different sources and production sites, which is obviously not the case.

As an example the ratios of Sr:U can be applied to distinguish the bricks into two groups which coincide with the two different geographical/geological regions we investigated in this pilot study.

The main objective of this study is to find the sources of clay used for brick stone industry. Additionally ways to identify the production places of the bricks are tested.

## WEATHERING OF GLAUCONITE: EVIDENCE FROM THE ABU TARTUR MINE, EGYPT

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The Abu Tartur mine is located in the Western Desert of Egypt, 50 km west of El Kharga City. The sediments are Upper Cretaceous (Campanian – Maastrichtian) phosphorites, black shales and glauconitic sandstones belonging to the widespread shallow-marine deposits of the Duwi Formation. The phosphate deposits are of great economic importance and have been mined since their discovery in 1967.

The main objective of the study was the mineralogical and geochemical characterization of one specific glauconite-bearing layer at surface. Additionally, these glauconitic sandstones were compared to a subsurface glauconitic sandstone sample from the mine to determine possible alteration (weathering) processes.

Sedimentological, petrographical and SEM investigations show that the glauconite grains are of an autochthonous origin.

Glaucinite grains from the outcrop layer vary in color and in their chemical composition. From the top to the bottom of the layer, grains show a systematic increase of Fe, K and a decrease of Al and S. Additionally the grains show an internal zonation in color which is caused by variation of Fe and K contents between the center and rim of the grains.

XRF, EMP and thin-section analyses show that the glauconite grains from the outcrop differ significantly in their chemical composition, morphology and color from the grains of the mine sample. Glaucinites from the mine are enriched in Fe and K.

XRD analyses of the clay fractions show that the grains consist of illite (glauconite)/smectite mixed-layers, with more illite layers (80 %) in the mine sample. The outcrop samples show a randomly interstratified (R0) mixed-layer with only 52% illite layers.

The charge distribution diagram muscovite-pyrophyllite-celadonite shows a clear trend from smectitic glaucony to illitic glaucony, the mine sample plots exactly in the glauconite field.

All these features indicate that the surface samples are strongly altered by weathering and that glauconite progressively transforms into iron-rich illite/smectite mixed layers and then into smectites. Weathering can thus completely reverse the glauconitization process.

For any chemical and mineralogical characterization of glauconites at surface, these weathering effects have to be taken into consideration.

## TOPOGRAPHY EFFECTS ON ALTERATION OF CLAY MINERALS

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Soil has different reaction in front of the using and management kind. The soil mineralogy properties knowing can be benefit to decide about the land use kind. Soodejan region that is one of Shahre Kord counties in Chahar Mahal Bakhtiari province, is one of the important region for agriculture in Iran was selected to study. This region is near the Zayandeh rud with 40 kilometers distances from south west of zayandeh rud dam that has 3000 hectares area. This region includes three kinds of landscapes such as mountain, hill and plateau. Also, there are flood plain, terraces, summit, back slope, foot slope and small parts of low land that located in the toe slope, in this region. The profile was dug on the all of the land forms. Eight soil properties were measured for this pedons. Ten representative pedons with different landscapes were selected for mineralogical and micromorphological study. They were classified as Calcixerepts, Haploxerepts, Haploxeralfs and Haploxerolls with xeric and mesic moisture and temperature regimes.

In the summit landforms the majority of the traces from the XRD analysis of the Mg-saturated clay sprayed with glycerol had well-defined peaks representing the 0.7 nm, 1.0 nm, 1.4 nm and 1.8 nm basal (001) layer spacings, that we defined as a smectite minerals. In contrast, the samples from back slope and shoulder landforms were characterized by poorly defined 1.4 nm peaks and 1.2 nm shoulders, indicating the presence of poorly formed and irregularly interstratified mixtures of expanded 2:1 layer silicate materials such as vermiculite.

The XRD analysis results showed that the Vermiculite mineral had the most extensive extent of the particles size distribution among the secondary phyllosilicates. Also there are the most of the mixed Illite and Smectite mineral in compare of the other minerals. Diffractograms that related to the others pedons on the end slope land form showed the Smectite mineral existence that this mineral amount increased by the increasing the depth. This matter is in the each typic sample. Also, we studied soil features by micromorphological techniques.

The main objectives of our study were to investigate the recognition of the clay mineral source and formation manner and their relationship with soil properties.



Because understanding relationship clay minerals with the soil physical and chemical properties on different landforms is the base to evaluate the soil behavior in agriculture, environment and management field in the future, also to study the relationship between the micromorphological and mineralogical properties of representative pedons in this study.

## STUDY OF Palygorskite Transformation Under Long Term Cultivation and Irrigation in a Arid Region (Khuzestan, Iran)

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Sugarcane (*Saccharum officinarum* L.) fields and rotational crops have been cultivated without potassium fertilization in Haft-Tapeh for 42 and more than 100 years, respectively. Sugarcane fields receive approximately 30 000 m<sup>3</sup> ha<sup>-1</sup> (or 300 cm) irrigation water which the rotational crops also received 10 000 m<sup>3</sup> ha<sup>-1</sup> annually. The objective of this research was to evaluate the palygorskite clay minerals of the two dominant cultivation systems in comparison with non-cultivated soils. Mineralogical analysis was done by XRD and TEM observations. It is increased CEC for cultivated soil. The CEC is 15.65, 29.55 and 19.45 cmol<sub>c</sub> kg<sup>-1</sup> for surface horizon of uncultivated, rotation cropping and sugarcane profiles, respectively. Although this increase is somewhat due to organic matter, some of this can be attributed to clay minerals transformation. In XRD pattern, despite of uncultivated soil, expandable minerals was seen a great deal in Ap horizon of cultivated soil and at least was formed in C horizon of cultivated soils. This trend is agreed with changes in CEC increasing. A part of this expandable mineral sourced from mica and some of them came from palygorskite. Although only weak palygorskite's peaks were observed by XRD, crystals is seen in TEM images in large amounts. The crystals of this clay are large and palygorskite fibers are more abundant in this soil. This trend is seen throughout the profile. The presence of a sharp tail near the illite peaks with 1.05-nm reflection, which remained unaffected by various treatments, can be attributed to palygorskite in XRD patterns. Also, in the TEM observation, although palygorskite fibers were abundant in uncultivated but a great deal of it was removed or destroyed in cultivated soils. This mineral was scarce in subsurface of cultivated lands. In contrast to the uncultivated soils, palygorskite is almost absent from rotation cropping soil; those present were thinner and smaller. This may be related to more time cultivation under rotation cropping. Smaller amounts of palygorskite in surface layer have been reported by other studies of cultivated soils. Palygorskite is less abundant in sugarcane than uncultivated soils, corresponding to trends observed in XRD patterns. In the surface horizons of the both cultivated soils, a few thick palygorskite fibers were observed. Movement of palygorskite particles thought the atmosphere is known to be intense in arid regions and it can add these palygorskite fibers to this soil surface.

## FLUID ROCK INTERACTION PROCESSES IN FAULT-ZONES: CLAY MINERAL AND GEOCHEMICAL EVIDENCE IN THE GUADIX-BAZA BASIN (BETIC CORDILLERA, SE SPAIN)

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The Galera fault is an active normal fault located in the NE of the Guadix-Baza Basin (central Betic Cordillera) with 23 km of long and N50°E strike of average. It has a 1.5 width fault zone with several parallel splays dipping between 40° and 60° to the NW, which cut Pliocene and Pliocene rocks (fundamentally lacustrine limestones and evaporites). This fault has associated a certain seismicity.

We examine the very low temperature clay-bearing alterations spatially associated to the Galera fault zone. The main goals of this study are: a) To accurately distinguish the clay-bearing assemblages related to the very low-temperature fluid circulation, and the sedimentary assemblages; and b) To determine the effect of deformation and fluid circulation on the texture, crystal structure and crystal chemistry of the clay minerals.

The comparison of the mineralogy and the major element oxide and trace element contents for the damaged rocks of the fault area and their respective protoliths along the Galera fault allows us to suggest two main zones probably related with the extent of the fluid-rock interaction processes with the depth increasing. Shallow areas located at the margins of the fault do not show significant mineralogical and geochemical differences between fault-damaged rocks and their respective protoliths. In both cases, mineral assemblages contain gypsum and dolomite and clay association is dominated by illite and minor amounts of palygorskite, whereas that isocon diagrams do not show significant gain or depletion in the chemical composition between these materials. Deep areas located at the core of the fault are characterized by the presence of significant mineralogical and geochemical differences between fault damaged rocks and their protoliths that can be the result of an alteration event during the fluid-rock interaction history of the Galera fault. In this area, fault rocks develop an alteration assemblage dominated by sepiolite, illite and small amounts of dioctahedral smectites. Large gains in Mg, Si and H<sub>2</sub>O with addition of trace elements such as Be and As is a typical pattern of changes produced by hydrothermal alteration. The most important mineral changes involved

in this process are the destruction of the original constituents (dissolution of feldspar, quartz and dolomite), with subsequent precipitation of authigenic assemblage. The gain of Mg corresponds with the formation of sepiolite. Given that sepiolite and smectite formation is restricted to the fault rocks, we conclude that the heat and fluid flows associated with clay mineral authigenesis were confined to the areas within the fault zone.

## MINERALOGY OF THE CLAY GOUGES DEVELOPED IN SHEAR ZONES OF THE HIGH TATRA MOUNTAINS, POLAND

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The Tatra Mountains are a part of Inner Carpathians which is located on the territory of Poland and Slovakia. The Tatras consist of two main geological units: the so called crystalline core, which is made of igneous and metamorphic rocks and the sedimentary cover composed of limestones, dolomites and siliciclastic rocks. The igneous part of the core crops out in the Eastern part of the Tatras (The High Tatras) mainly. The core is cut by a number of faults and shear zones with clay gouges developed.

The aim of this research was to determine the mineralogy of the clay gouges developed within the igneous part of the core in the context of their potential dating using radiometric (i.e. K-Ar, Ar-Ar or Rb-Sr) techniques. Samples were collected from seven different locations in the High Tatras. The bulk samples and the separated subfractions (<0.2  $\mu\text{m}$ , 0.2-2  $\mu\text{m}$ , <2  $\mu\text{m}$ , 2-10  $\mu\text{m}$ , 10-20  $\mu\text{m}$  and 20-400  $\mu\text{m}$ ) were analyzed using X-ray diffraction. The subfraction separation was preceded by: an acetic buffer treatment, Na<sup>+</sup> saturation followed by dialysis, and deionized water dispersion..

The analyzed samples contain quartz, Na-plagioclase, K-feldspar, dioctahedral (2M1 and 1M) micas, dismeectite, and chlorite. Quartz, feldspars, 2M1 dimica and chlorite was most likely inherited in the process of gouge formation from the tonalite protolith. Smectite, 1M dimica and potentially part of 2M1 mica and chlorite is likely to be formed at the expense of primary feldspars and biotite by hydrothermal alteration which accompanied the gouge formation. The analyzed clay material from most of the studied gouges contains significant amount of feldspars which are present in all (except for the finest <0.2 $\mu\text{m}$ ) fractions. The presence of feldspars inherited from the protolith disqualifies the samples as a potential material for extraction of radiometric age of the gouge formation. In the samples collected within two from the gouges studied the primary feldspars were completely altered into micas and those two examples can potentially be used for extraction of the of the gouge formation age using a combination of quantitative XRD and radiometric dating.

## ALLOPHANE AND PALAGONITE AS THE PRODUCT OF VOLCANIC GLASS ALTARETAION OF DIFFERENT AGES

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Volcanic cinders and ashes of different ages and compositions have been collected in the Kluchevskaya volcano group on Kamchatka and in Iceland. Experimental study of thermal properties and phase composition of water was performed (Motenko et al, 2007; 2008). There is no unfrozen water in the investigated modern volcanic cinders from Kamchatka in all temperature ranges (from -15 to 0°C). But for volcanic ashes unfrozen water content is fixed from 0,4 to 11% at -5°C that depends on age.

Unfrozen water content in the studied ashes was connected with transformation of volcanic glass and appearances of the clay minerals that presumably was connected with ages of grounds. For the substantiation of this fact the determination of mineral compositions of volcanic ashes and the examination of different water categories in samples were made.

Four samples of ashes have been chosen for researches: three of them (N<sup>o</sup>1-3) are collected on Kluchevskaya volcano group (Kamchatka), and one (N<sup>o</sup>4) – in the south of Iceland. Ash samples had different age: N<sup>o</sup>1 – about 35 years, N<sup>o</sup>2 – about 1500 years, N<sup>o</sup>3 – about 2000 years, N<sup>o</sup>4 - 15000-150000 years. Unfrozen water content in Kamchatka ashes (at -5°C) is accordingly 0, 2.5 and 11%; and in the Iceland ash is 3.5 %.

IR-spectroscopy study (IR-fourier spectrometer FSM-1201, Russia) was made for diagnostics of mineral compositions of ashes in the range of 400-4000 cm<sup>-1</sup> at room temperature, spectral resolution was 2.0 cm<sup>-1</sup>, absolute calibration error of wave number scale in not more than ±0.1 cm<sup>-1</sup>. Samples were ground with petrolatum. As the results there were found that the sample N<sup>o</sup> 1 was the waterless allophone, the samples N<sup>o</sup> 2, 3 – were allophanes with the various water contents and the sample N<sup>o</sup> 4 – palagonite (Peng Wenshi, 1982; Geptner, 1977).

Palagonite is hydrated glass which is the first alteration phase to form of smectites. Allophane is amorphous layered aluminosilicate and is the product of hydration of the beige-brown glass (Gerard, Stoops, 2005). Palagonite is genetically connected only with one type of basalt glass – sideromelane which is formed after magma interacted with water (Geptner, 1977). Allophane is formed at weathering both under conditions of tropical and subtropical climate and under condition of cryolithozone (Ershov, 1996).

The presence of the  $\text{H}_2\text{O}$  molecules in the structures of studied minerals was detected by the IR-absorption band at  $1630\text{ cm}^{-1}$  (bending vibrations) and by the broad band at  $3000\text{-}3600\text{ cm}^{-1}$  (O-H stretching vibrations). The IR-spectra showed that the increase of water contents in the mineral structures depends on the increase of the igneous ashes ages. The thermal behavior of the allophanes and the palagonite was studied by DTA and TGA techniques on a Q-1500 D derivatograph (Hungary) over the range from room temperature to  $1000^\circ\text{C}$ ; the heating rate was  $20\text{ K/min}$ . The masses of the samples were about  $200\text{ mg}$ . The samples № 2, 3, 4 lost the absorption (low) water at the interval from  $50\text{-}60^\circ\text{C}$  to  $110^\circ\text{C}$ . The endothermal effects in the temperature region from  $110^\circ\text{C}$  to  $750^\circ\text{C}$  were explained by the loss of the structure (high) water. The thermal study showed that the mass loss depends directly on the ages of the investigated samples. The content of absorbed and structure water were found as: sample № 1 -  $0\%$  и  $0\%$ , sample № 2 -  $1,0\%$  и  $2,8\%$ , sample № 3 -  $3,5\%$  и  $2,7\%$ , sample № 4 -  $6,3\%$  и  $5,3\%$ . The samples of ashes after heating to  $1000^\circ\text{C}$  were also investigated by IR-absorption method and the total absence of absorbed and structure water and the invariable mineral contents were detected.

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## A PLYGORSKITE-BEARING CLAY VEIN FROM THE FUTAMATA LANDSLIDE AREA IN NORTHEASTERN HOKKAIDO, JAPAN

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Palygorskite in Japan is a relatively rare mineral, and has previously been reported from epithermal ore deposits at the Miyatamata and Arakawa mines, Akita Prefecture, and the Tomii and Ogano mines, Tochigi Prefecture (Minato et al., 1969; Kato, 1973), contact zone of limestone at the Kamioka mine, Gifu Prefecture (Hattori et al., 1967) and Takizawa, Ibaraki Prefecture (Kato, 1973), dolostone at Kuzuu, Tochigi Prefecture (Minato, 1966) and Kanatake, Fukuoka Prefecture (Kato, 1973), and greywacke of the Tanba Group at Shizuhara, Kyoto City and Inugai, Kameoka City, Kyoto Prefecture (Masutomi and Fujiwara, 1976). Geology of the Futamata landslide area in northeastern Hokkaido, Japan, is composed mainly of the Paleocene-Eocene Rikubetsu Formation, the Miocene Futamata Andesite Formation, Pleistocene welded tuff and pumice flow deposits, and Pleistocene-Holocene talus and landslide deposits, and Holocene Alluvium. Bedrock of the Futamata Slide is conglomerate, sandstone, mudstone, shale, and coal of the Rikubetsu Formation. Mineral composition in fine-grained fraction of strongly weathered conglomerate from 6.2 m in depth of No.2 boring in the Futamata Slide area consists of major smectite with minor clinoptilolite, chlorite, illite, quartz, and plagioclase. Dark brownish grey weathered mudstone from 14.45 m in depth of No.2 boring includes large amounts of smectite and small amounts of chlorite and illite. Dark brownish grey fault clay cutting mudstone and coal of the Rikubetsu Formation is also composed of major smectite with lesser quartz and plagioclase. Therefore, authigenic mineral assemblage of conglomerate and mudstone from the earth's surface and boring cores is clinoptilolite and/or smectite. On the other hand, a light-tanish grey clay vein consists mainly of palygorskite with lesser smectite, quartz,  $\beta$ -cristobalite, and plagioclase. Palygorskite is newly found as a clay vein within jointed conglomerate of the Rikubetsu Formation. The clay vein is pale yellowish pink in color. It is in a left flank of the ancient Futamata Slide. In this presentation we report on the mode of occurrence, XRD, and SEM data of the palygorskite-bearing clay vein from the Futamata Slide area.

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## MIDDLE MIOCENE IN PANAMA, WET OR DRY?

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Miocene terrestrial mammal fossils recovered from the Cucaracha Formation of the Panama isthmus indicate that the Central American region was a peninsula connected to North America where free genetic flow took place. It is still puzzling, however, that mammals adapted to the dry North American savannas of the Miocene could flourish in what is supposed to have been a Miocene tropical rain forest. Previous studies have failed to demonstrate a clear correlation between paleobiological data (plant and mammalian fossils) and paleoclimate estimates based on both physical (depth to carbonate) and chemical index of alteration data from paleosols.

This study presents clay mineralogy characterization of the Middle Miocene Culebra and Cucaracha Formations to infer paleoclimatic conditions during the Miocene in Panama. The Culebra Formation consists of carbonaceous mudstone at the bottom and towards the top is interbedded with a coarsening-upward series of sandstone beds. The Cucaracha Formation is composed of reddish and yellowish to grayish claystone representing paleosols with some interbedded conglomerates and tuffaceous layers. Earlier provenance analysis from detrital zircons suggests homogeneous source areas (basic and intermediating rocks) during the Miocene. Diagenetic processes are assumed to be minimal, since the thickness of the entire sedimentary sequence is less than 1000 m and does not appear to have experienced deep burial.

We analyzed the relative proportions of clay minerals indicative of high (kaolinite, smectite) and low (chlorite, illite) weathering rates (Jackson Weathering Stages) in 20 samples collected from the Culebra and Cucaracha Formations. The samples were prepared following the guidelines of Moore and Reynolds, and X-ray powder diffraction was carried out sequentially on air-dried, glycolated and heated (550 °C) samples on a Scintag X-ray Unit with Si(Li) Cu- radiation target. Smectite was consistently present throughout the stratigraphic section, while kaolinite was recognized only at the top. Illite and Chlorite are not present anywhere in the section. Gypsum -presumably as a result of pyrite alteration- was identified as an accessory mineral in the Culebra Formation only. The abundance of smectite and kaolinite confirms that the climate in Panama was wet since Miocene times, suggesting that the mammals were adapted to a tropical climate. The absence of illite confirms that diagenetic processes were minimal.

## HOW TO CALCULATE MINERAL FORMULA FOR 2-MEMBERS DIOCTAHEDRAL MIXED LAYERS FROM EDX-ANALYSIS BY TRANSMISSION ELECTRON MICROSCOPY: EXAMPLE – FRIEDLAND CLAY

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Transmission electron microscopy (TEM) is a very sensitive tool to recognize alteration processes of montmorillonite or other clay mineral phases. Alteration processes of montmorillonite occur in geological processes (e.g. illitization by diagenesis) or technical processes (pyrophyllitization, kaolinitization or illitization in barriers e.g. in repositories for radioactive waste like published in Herbert et al., 2008).

The particle-wise analysis by EDX-TEM is mirroring alteration in chemistry that means in composition of interlayer space, octahedral and tetrahedral layers of investigated particles.

The total charge of half unit cell is the basis for calculation of mineral formula considering Koester (1977). Srodon et al. (1992) offer a further tool. They have established a set of equations allowing to quantify the ratio of illite and smectite in mixed layers (IS-ml). The principal of that is relationship of “fixed” cations in interlayer with expandability (%S<sub>MAX</sub>) of particle (equ. 1). The end members are postulated by interlayer charge for smectite with 0.4 and for illite with 0.89 per O<sub>10</sub>(OH)<sub>2</sub> (equ. 2). Based on IS-ml data published these authors it is to calculate an equation to identify and calculate chemical formula of IS-ml phases (equ. 3) combined with Koester (1977).

$$\%S_{MAX} = (95.6 - 105.75 * FIX) \quad (1)$$

$$\text{Interlayer charge} = [0.89 * (100 - \%S) + 0.4 * \%S] / 100 \quad (2)$$

$$\%S_{MAX} = 100.38 * (IVAl)^2 - 213 * (IVAl) + 109.4 \quad (3)$$

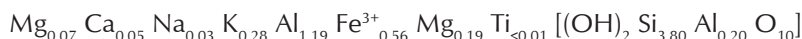
Experiences of last ten years of TEM-EDX-analysis have shown that it is to distinguish between IS-ml in senso of Srodon et al. (1992), but also IS-ml phases which are characterized by K- and charge-deficiency. This group is called by authors as dioctahedral vermiculite – smectite mixed layer phases (diVS-ml).

The clay deposit of Friedland clay (Germany) is originally composed by IS-ml phases with 30% of illitic and 70 % of montmorillonitic layers. The alteration of this clay is mirroring in an excellent manner the mentioned charge deficiency with duration of

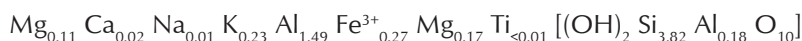
clay contact with water, which was not in equilibrium with original clay pore solution (room humidity, surface water, glacial water).

Alteration like in a closed reaction system (comparable with development in a barrier):

IS-ml of Friedland clay (%S=70%) (centre of deposit, contact in geological time only with pore solution):



IS-ml of Friedland clay (%S=70%) (margin of deposit, ~10,000 years in contact with glacial water, closed system):



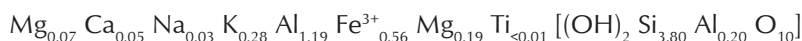
diVS-ml of Friedland clay (%S=70%) (margin of deposit, ~10,000 years in contact with glacial water, closed system):



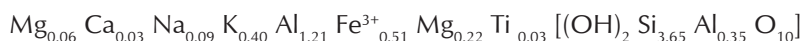
Especially in closed reaction systems diVS-ml alter their chemical composition faster than IS-ml (here: octahedral Fe and Mg is substituted by Al). In dynamic reaction systems the process of illitization is dominating.

Alteration like in a dynamic reaction system (partially comparable with dry & wet cycles):

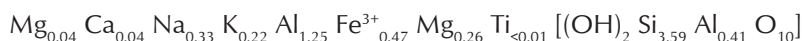
IS-ml of Friedland clay (%S=70%) (centre of deposit, contact in geological time only with pore solution):



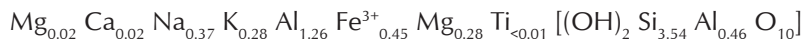
IS-ml of Friedland clay (%S=50%) (clay percolated by 1n NaCl-solution for 30 days):



IS-ml of Friedland clay (%S=40%) (clay from open cast mine in contact with surface water since about 10 years):



diVS-ml of Friedland clay (%S=40%) (clay from open cast mine in contact with surface water since about 10 years):



Also an increasing broadening of (001)-interference in ethylene-glycol solvated samples in XRD-measurements is to consider as indication of alteration of IS-ml phases.

## METHODS TO CHARACTERIZE HISTORICAL BRICKS FROM VIENNA

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Vienna has an at least 2000 years old tradition in making and use of bricks.

The first bricks were probably produced by the Romans in order to have enough construction material to fortify their military camps Petronell and Vindobona. We assume, that the first brick-kilns were situated at the banks of the Alserbach, where excellent raw material for bricks was available [1]. During medieval times huge amounts of building material were needed to build and preserve the town wall [2]. In particular, the urban expansion in the 19<sup>th</sup> century is a highlight in historical brick use.

Although the historical background is well known, the knowledge about material properties like mineralogical composition, geochemistry, compression strength and so on is very weak. About 1950 Ernst Schirnböck started to collect historical bricks from Vienna and the surrounding area systematically. Finally the Viennese Brick Museum was founded in 1978 [3]. Since that time the museum's collection increased from around 1.000 bricks to more than 25.000 today. This collection clearly represents the Viennese brick history of the past 2.000 years. Many examples are clearly identified, but a huge amount of bricks are totally unidentified. Nothing is known about the time of production, the production process and the origin of the raw material. The scientific need of the archeologists is to get more knowledge about material properties to deduce the origin and other important parameters of many collected bricks.

About 40 bricks from the Viennese Brick Museums' collection were selected for proper research. The objects were selected to get detailed information and data of brick production around Vienna. The main focus was set on products of the 19<sup>th</sup> century. The following pretreatment and preparation steps were performed prior analyses: A small plate was obtained by means of two parallel cuts with a diamond saw in the middle of the longitudinal axis of the brick. This plate was used to produce a petrological thin section and to perform mineralogical and geochemical analyses. One part of the cut brick was polished and covered with a matt paint to protect the surface. This treatment gives a good view of the bricks inside and the used material. It can also be examined with a microscope.

The following analyses were performed on the different bricks to obtain as much as possible parameters for classification

- Analysis of thin sections with polarized light microscopy

- Bulk mineral analysis with XRD to identify the mineralogical composition
- Simultaneous thermal analysis (STA) to get information about the thermal behavior of the material
- Fourier transform infrared spectroscopy (FTIR)
- Trace elements and rare earth elements with ICP MS. The different raw materials show their geochemical composition like a „fingerprint“
- density and porosity are important parameters to gain more information about the burning process
- Mechanical properties

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## PROGRESSIVE STAGES OF HYDROTHERMAL ALTERATION OF PLAGIOCLASE TO HALLOYSITE FROM LIMNOS ISLAND, GREECE

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Volcanic rocks, principally trachyandesites, occurring over an area of about 1 km<sup>2</sup> in the southwest part of Limnos Island, Greece are altered mainly to halloysite. The goal of this study was to determine the alteration processes acted on andesine present in these volcanic rocks and to describe in detail the mechanism of the halloysite development. For this purpose samples were collected from this location and analyzed by polarizing microscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical analyses.

The mode of occurrence of the altered rocks, coupled with the morphology of the halloysite, strongly suggest a hydrothermal origin. The above suggestion is confirmed by the chemical composition of the altered rocks. Extensive transformation of the parent rocks apparently occurred by the circulation of hydrothermal fluids through faults and fractures, which led to alteration of plagioclase to halloysite. The alteration of plagioclase to halloysite tubes, laths and interconnected laths occurred in seven discrete stages. Dehydrated, not well formed, halloysite nanoparticles (10-60nm in length), grew on the surface of plagioclase. Some of these tubes got detached and small holes were found on the surface of plagioclase. Tubular halloysite of about 50-100nm (nanotubes), formed within cubic holes parallel to the cleavage. With progressive alteration, these holes increased and combined to form a “stairs” like shape. Tubular halloysite was curved and characterized by the formation of a hollow interior. Further alteration led to accumulation of halloysite tubes, laths, as well as interconnected tubes on plagioclase surface. Still further alteration showed only traces of plagioclase as almost the entire crystals altered to halloysite tubes and laths. In the most altered rocks plagioclase crystals completely disappeared and only their shape could be found. Interconnected laths and tubes dominate the crystal habit of halloysite in the most altered rocks.

## INFLUENCE OF PALEOENVIRONMENTAL CONDITIONS IN THE FORMATION OF SEPIOLITE AND Palygorskite IN THE BATALLONES DEPOSIT (MADRID BASIN, SPAIN)

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The Batallones sepiolite deposit is located near the villages of Torrejón de Velasco and Valdemoro (Madrid province, Spain)). From a geomorphological point of view the Cerro de los Batallones is a butte where the hard lithologies forming the cap-rock consist of silicified limestones. Nowadays the area is actively mined in quarries for sepiolite (up to 9 m thick). Both mapping and sedimentological analysis allow to distinguishing three main lithological units: I) mudstones, dolomitic mudstones and Mg-bentonites II) Sepiolite and opal CT. III) Limestones, marls and siliciclastic sediments. Mudstones from unit I are interpreted as mudflat deposits associated to a Mg-rich lake margin. The sepiolites and opals of Unit II are interpreted to represent thick polyphasic sepiolite paleosoils developed in a similar alkaline lake margin environment undergoing periods of prolonged sub-aerial exposure and groundwater inputs. Deposited in disconformity the Unit III comprises associated siliciclastic and carbonate deposits forming sequences that are interpreted to represent deposition in a fresh water palustrine to shallow lacustrine environment. In this work 78 samples from Unit II and top of Unit I were collected from five lithological sections. The selected outcrops and quarry fronts were analysed in terms of lithofacies, supplemented by thin-section petrography, SEM-EDX analysis and clay and whole-sample mineralogical determinations (XRD). The scope is to establish the paleoenvironmental conditions of fibrous clay minerals formation and their evolution.

The Unit II (sepiolite deposit) includes three shallowing upward sequences with paleosoils developing at top. In sequences II-1 and II-2 sepiolite is predominant with replacive opal CT locally abundant and minor calcite. The sequence II-3 is characterized by the occurrence of palygorsite besides sepiolite and the noteworthy increase of carbonates (calcite) locally forming calcretes. Mineralogical and textural evidences indicate that initially sepiolite formation was related to intrasedimentary unstabilization of Mg-smectite at top of Unit I. A later neoformation from solutions or Si-Mg gels has been also inferred. The petrographic identification of several phases of sepiolite growth corroborates the complexity of its origin in the palustrine environment. The salinity depletion in addition to the silica input from groundwaters (increasing the Si/Mg ratio), should be responsible for the formation of sepiolite instead of Mg-smectite. Moreover, the recognition of dolomite-rich seepage mounds and



travertine deposits with clay inserts containing Mg-smectite and sepiolite enhanced the role played by groundwaters in the Mg-clays authigenesis. The occurrence of palygorskite at top of Unit II (sequence II-3) suggests a noteworthy change in the sedimentary environment. So, the origin of palygorskite should be interpreted as due to transformation (dissolution-precipitation) of inherited clay minerals (mainly Al-smectite) after the input of fine detrital sediments. Therefore, from a geochemical point of view, two paths controlling the mineralogenetic reactions in the palustrine environment are inferred. Indeed, in sequences II-1 and II-2 the abundant sepiolite and opal CT means predominant silica input whilst in sequence II-3 the input of Al-rich clay particles and calcium bicarbonate waters should be responsible for the calcretes development and palygorskite formation.

## FUNDAMENTAL PARTICLE CHARGE AND ITS SIGNIFICANCE

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The novel concept of fundamental particle charge is introduced in this contribution. The surface charge density of 2:1 clay minerals expressed in C/m<sup>2</sup> is given by (Lagaly, 2006):

$$\sigma_0 = 1.602 \times 10^{-19} (x+y) / \alpha b$$

where  $\sigma_0$  is the surface charge density,  $1.602 \times 10^{-19}$  Coulomb (C) is the elementary charge of one electron,  $\alpha$  and  $b$  the  $\alpha$  and  $b$  dimensions of the unit cell and  $(x+y)$  the charge per formula unit (i.e. per half unit cell).

Fundamental particles are individual or free particles that yield single-crystal electron diffraction patterns from the  $ab$  plane (Nadeau et al. 1984). According to the concept of fundamental particles smectites consist of single 10 Å thick layers with variable basal area. The layer charge as it is defined is a fundamental property of the unit cell and is not representative of the fundamental particles; therefore a new concept should be introduced, which will be representative of the charge of each fundamental particle. This concept has been named the *fundamental particle charge* ( $F_{pc}$ ) and is described below.

A charge of  $1.602 \times 10^{-19} (x+y)$  C corresponds to each  $\alpha b$  area. Each basal area ( $A$ ) of the fundamental particle contains  $A/\alpha b$ ,  $\alpha b$  areas so the fundamental particle carries  $[(A/\alpha b) + (A/\alpha b)] \times 1.602 \times 10^{-19} (x+y)$  C. Consequently, the fundamental particle charge ( $F_{pc}$ ) will be

$$F_{pc} = 2 \times A \times \sigma_0$$

Assuming that the sample consists of fundamental particles which have comparable area, the  $F_{pc}$  will be equal to the ratio of the total charge of a specific mass of the sample in Coulomb, to the number of the fundamental particles in this mass. The  $F_{pc}$  is the sum of the charges per unit cell (in Coulomb) of all the unit cells that exist in the fundamental particle.

It follows that compared to the layer charge the fundamental particle charge provides additional information because it combines the data of the surface charge density and the size of the fundamental particle (area of a basal surface). So far it has been applied in smectites, but it can be extended to other clay minerals as well. This will be done in the future.

The fundamental particle charge is a new concept in smectites and so far it has been useful in understanding particle charge-related smectite-water properties, such as free swelling, flow resistance (viscosity),  $\zeta$ -potential and the bonding properties of smectites. Moreover it will shed light on the hydrophilic/hydrophobic nature of the smectite surface. Applications of the fundamental particle charge model are presented.

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## TETRAHEDRAL ARSENIC (As<sup>+5</sup>) IN ANTIGORITE: GEOLOGICAL ORIGIN AND IMPLICATIONS FOR GROUNDWATER QUALITY

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In the fractured bedrock aquifer of northern Vermont, USA, arsenic concentrations in ground water range from <1 to 327 ppb (<13 to 4360 nm/L) and the spatial relationship of elevated As with ultramafic rock bodies suggests that arsenic is derived from the ultramafics. The ultramafic rocks are comprised mainly of serpentinites and talc-magnesite rocks with average As concentration of 94 ppm (range = 1 to 1105 mg/kg As), which is at least an order of magnitude greater than crustal average. Evidence from sequential chemical extraction, X-ray diffraction (XRD), inductively coupled plasma-mass spectrometry (ICP-MS), ICP-emission spectrometry and Fourier transform infrared (FTIR) analysis of serpentinites indicates that arsenic is located in the tetrahedral sheet of antigorite. In particular, SCE indicates that release of arsenic from serpentinites is proportional dissolution of antigorite, and FTIR analyses document a peak at 880 cm<sup>-1</sup> that is positively correlated with As content in the antigorites and is absent in antigorites that lack As. This peak is associated with the arsenate anion in arsenate minerals and is consistent with substitution of AsO<sub>4</sub><sup>-3</sup> (arsenate) for SiO<sub>4</sub><sup>-4</sup> in the tetrahedral sheet. The recognition of arsenic in antigorites from Vermont is consistent with X-ray absorption data documenting the occurrence of tetrahedral As(V) in antigorites elsewhere (Hattori et al., 2005) and with requirements for ionic charge and radius – As(V) is 0.34 Å in tetrahedral coordination whereas Al(III) is 0.39 Å. SCE analyses of talc-magnesite (rocks that occur as later-stage alterations of serpentinite) indicate that arsenic is also contained within magnesite (MgCO<sub>3</sub>) in this aquifer system, likely as arsenate anions substituted for carbonate anions. Weathering of both antigorite and magnesite leads to release of arsenic and formation of iron hydroxides that at least partially sequester arsenic in shallow, oxidized portions of the aquifer system but likely release arsenic under conditions of elevated bicarbonate and pH that accompany progressive weathering. Reducing conditions at depth may also lead to desorption and increased availability of arsenic.

Hydrochemistry of monitoring wells drilled into fractured ultramafic rock in a ground water recharge area with no anthropogenic As source reveals elevated As and a magnesium bicarbonate hydrochemical facies that reflects dissolution of antigorite and magnesite, confirming that As in ground water is related to ultramafic rock dissolution. Arsenic mobility in ground water appears to be enhanced by slightly alkaline pH values (mean = 7.5; range = 7.0 to 8.3) and anion chemistry that is dominated by relatively high bicarbonate concentrations (155 to 179 ppm) that lead to desorption of As from iron hydroxides. Regarding the origin of arsenic in these

rocks, As is positively correlated with Sb and light rare earth elements in whole-rock, indicating that As was introduced to the ultramafic rocks during metasomatic reactions in the presence of fluids derived from the subducting slab during late Cambrian or early Ordovician time prior to the Taconian Orogeny. Subsequent metamorphism related to the Taconian and Acadian orogenies may have caused some redistribution of As within the ultramafic rock.

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## COMPOSITIONAL VARIATIONS OF INTERSTRATIFIED CHLORITE/SMECTITE OCCURRING AS A VEIN-MINERAL FROM THE TODOROKI EPITHERMAL Au-Ag DEPOSITS, HOKKAIDO, JAPAN

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Interstratified chlorite/smectite frequently occurs as a vein-mineral in epithermal Au-Ag quartz veins. The occurrence characteristics and mineralogical properties of interstratified chlorite/smectite are important in understanding its formational condition in hydrothermal environments and its usefulness as an exploration indicator for Au-Ag mineralization. This study investigates the mixed-layering and chemical composition of chlorite-smectite series minerals including interstratified chlorite/smectite from two Au-Ag quartz-veins, the Chu-etsu vein and the Shu-etsu vein of the Todoroki deposits, Hokkaido, Japan, by XRD, optical microscopy, SEM, ATEM, and EPMA.

The chlorite/smectite minerals occurring as the main vein-mineral of the two ore-veins can be divided into four different types (I-IV) of mixed-layering of chlorite and smectite. That is, the I type is similar to a normal chlorite occasionally with minor amounts of smectite; the II type with small amounts of smectite, 10-20% (S%) is mixed-layering ( $g=1$ ) of chlorite-chlorite layers and corrensite layers; the IV type with about 50 S% is corrensite; and the III type with 20-45 S% is a mixture of the I and IV types, suggesting a segregation structure. It is shown that the changes in the chemical compositions by EPMA and ATEM analyses are approximately continuous from the I type to IV type concordant with increase in S%, however the mixed-layer structure based on the XRD line profile analysis is not continuous in the 0 to 50 S%.

The occurrence characteristics of the minerals show that the I-III types characteristically occur in the Shu-etsu vein, whereas the IV type commonly occurs in the Au-Ag ores of the Chu-etsu vein, suggesting that the difference in mixed layer structure of the minerals may be constrained by the hydrothermal environment of the vein formation. On the basis of the chemistry of co-existing minerals and fluid inclusion thermometry of quartz, the I-III types of the minerals may have been formed at relatively high temperatures in a range of 150-240 degrees Celsius, whereas the IV type may have been formed at relatively low temperatures in the same temperature range. In addition, the  $S_2$ -activity of hydrothermal environments related to the ore formation of the Shu-etsu vein may be higher than that of the Chu-etsu vein, implying different redox environments for the I-III and the IV types of the minerals. A comparison of the chlorite-smectite minerals occurring in two Au-Ag quartz veins shows that the hydrothermal environments of the epithermal Au-Ag mineralization can provide a suitable formational environment for the mixed-layering of chlorite and smectite.

## **TOPIC 3**

### *Soils and Sediments*





## *ORAL PRESENTATIONS*



## KEYNOTE

### STUDY ON CRYSTAL GROWTH AND CONTROL TO IMPROVE SOIL FERTILITY IN WEST AFRICA

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In the tropical dry lands, for the production of crops, harvests will be increased by effectively utilizing several characteristics of the soil. An effective improvement method of the soil will be chosen by a geological survey and analyses of clay minerals in the soil, in each region. In this study, three methods are proposed to improve soil fertility.

#### 1. The formation of the urea-kaolinite complex in the soil

The urea is intercalated in the interlayer of the kaolinite by the methods of mixing and heating. Nitrogen was included in the fine grain fraction separated in dry condition from the soil of West Africa and observed by X-ray photoelectron spectroscopy. In addition, the elution of the nitrogen from this fraction was confirmed by the dissolution experiments. In nature, it is predicted that intercalation reaction occurs between a kaolinite and urea.

#### 2. Struvite extracted from the feces of the livestock

The feces of livestock sampled in West Africa were dissolved in pure water with an ultrasonic washer and shaker. Most of the impurities were filtered out as the solution passes through the membrane (100nm). The separation of many crystals resulted in what was observed to be a dried filtrate (Fig. 1). These minerals were identified as struvite (-K). In so many farmlands, the feces of the livestock are not used effectively.

#### 3. Surface modification of the apatite

Low crystallinity of apatite crushed with a mortar was identified after a long time by X-ray diffraction analysis. The change of the binding state on the surface of the apatite particle was proved by XPS and infrared spectroscopic analysis. The slightly soluble apatite's uppermost surface was altered to a readily soluble material by this mechano-chemical method.

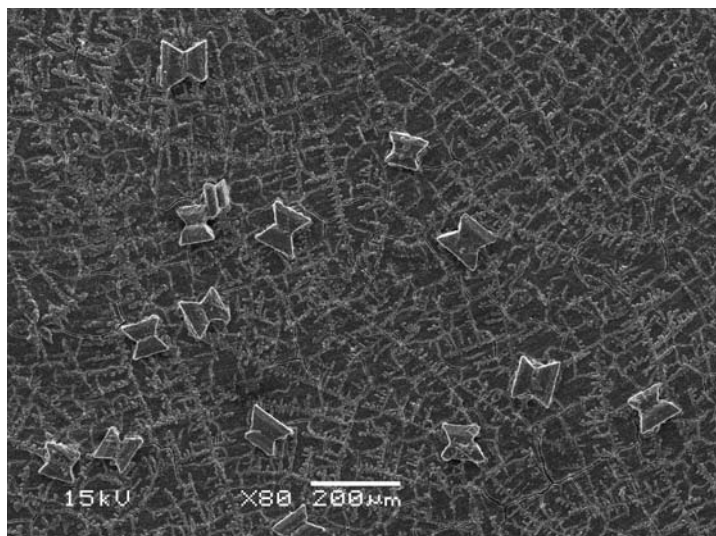


Fig. 1 Struvite extracted from the feces of the livestock.  
The dendritic structure is composed of sylvite.

## EFFECTIVE CATION EXCHANGE CAPACITY (ECEC) AND CATION EXCHANGE CAPACITY (CEC) OF A FULLER'S EARTH FROM GEORGIA

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Effective cation exchange capacity (ECEC) and cation exchange capacity CEC of 48 Twiggs Clay samples from three mines (Pilcher, Bell and South Bynes) were measured with the single extraction silver thiourea (AgTU) procedure described in 1980 by Pleysier and Juo (1). AgTU CEC is directly related to the quantity of the silver complex adsorbed and ECEC is the sum of the displaced and dissolved cations (Ca, Mg, Na, K, Al, Mn, Fe and Si). The Twiggs Clay, a late Eocene marine clay, is represented by two highly absorbent, opaline, and smectitic lenses near Wrens, Georgia. They contain varying proportions of smectite, kaolinite, illite/mica, quartz and disordered silica.

ECEC ranges from 16 to 62 meq/100g; however, the majority of the samples are between 25 and 45 meq/100g. Only two samples exceeded 60 meq/100g. Differences among mine locations are evident. Pilcher values are significantly lower than the other two.

CEC ranges from 15 to 60 meq/100g and is typically slightly lower than the ECEC. Five samples from the South Bynes location have CEC values 13 to 16 meq/100g lower than the ECEC. Samples from the Bell and South Bynes mines have base saturation percentages between 60 and 90%. The average for the Pilcher samples is 37%.

Exchanged cations in Pilcher samples are dominated by Al, which averages 58% of the ECEC, but Al is essentially absent from South Bynes. Ca is the dominant cation in Bell and South Bynes samples, averaging 55% and 61% of ECEC, respectively. There is little variation in the proportion of Fe, K, Na, and Mg. Exchanged Mn and Si are more variable. Mn is usually high near fractures. In South Bynes samples Si may account for more than 20% of the ECEC.

The AgTU CEC not satisfied by the dominant exchangeable bases (varying from zero to over 30 meq/100g) is termed "unfulfilled" AgTu CEC. The near equivalence of AgTU CEC to the sum of bases plus Al extracted is evidence that the Al is exchanged. The strong negative correlation of Al and Ca suggests that Al occupies sites formerly occupied by Ca. Si in the ECEC totals appears to come from the dissolution of disordered silica and clay minerals. Major variations in ECEC and AgTU CEC can be attributed to changes in the smectite content and permeability of the materials.

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## STRUCTURE OF NANOCRYSTALLINE PHYLLOMANGANATES PRODUCED BY FRESHWATER FUNGI

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Chemically reactive nanosized manganese dioxides are produced by a variety of living organisms including bacteria, fungi, and plants. The biotic oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$  is approximately two orders of magnitude faster than the heterogeneous oxidation catalyzed by mineral surfaces, thus supporting the currently held view that the biogenic route to Mn oxide formation prevails in nature. Vernadite, a nanosized phyllosulfate consisting of randomly-stacked layers of edge-sharing  $(\text{Mn}^{4+}\text{O}_6)^{8-}$  octahedra (Giovannoli 1980), is the main biogenic Mn oxide, possibly with tectomanganates, such as todorokite. Phyllosulfates such as birnessite owe their surface reactivity to the presence of vacant layer sites and/or to  $\text{Mn}^{3+}$  for  $\text{Mn}^{4+}$  substitutions that confer to the layer a charge deficit up to three times higher than that of smectite. Vernadite have in addition high amounts of border sites because of its infinitesimally small particle size. The ratio of external to internal Mn sites increases indeed when the crystal size decreases, and biogenic vernadite with a layer dimension of 60-70 Å (Lanson et al. 2008) has approximately 20% of its Mn atoms exposed at the crystal border compared to ~0.4% for a birnessite layer ~300 Å (Lanson et al. 2000). Thus, organic pollutants can be degraded and trace metals taken up by vernadite in natural systems.

The production and sorption capacity of fungal vernadite are well documented, but progress in the interpretation and modeling of sorption data is limited by the lack of a comprehensive structure model. In the present study, chemical analyses, XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectroscopy, and powder X-ray diffraction (XRD) were combined to determine the nature and amounts of structural defects in vernadite produced by three fungal strains. The fungi-mediated oxidation of aqueous  $\text{Mn}^{2+}$  produces layered Mn oxides analog to vernadite, a natural nanostructured and turbostratic variety of birnessite. The crystallites have domain dimensions of ~10 nm in the layer plane (equivalent to ~35  $\text{MnO}_6$  octahedra), and ~1.5-2.2 nm perpendicularly (equivalent to ~2-3 layers), on average. The layers have hexagonal symmetry and from 20 to 30% vacant octahedral sites. This proportion likely includes border sites, given the

extremely small lateral size of the layers. The layer charge deficit, resulting from the missing layer  $\text{Mn}^{4+}$  cations, is balanced mainly by interlayer  $\text{Mn}^{3+}$  cations in triple-corner sharing position above and/or below vacant layer octahedra. The high surface area, defective crystal structure, and mixed Mn valence confer to these bio-minerals an extremely high chemical reactivity. They serve in the environment as sorption substrate for trace elements and possess catalytic redox properties.

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## REASSESSING ATMOSPHERIC PALEO- $p\text{CO}_2$ WITH MONTE CARLO SIMULATIONS AND CARBON ISOTOPE PROXIES IN HYDROXIDE SOIL MINERALS: A CASE FOR LOWERING PALEO-ATMOSPHERIC $\text{CO}_2$ ESTIMATES BY FACTOR OF 10

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Disagreement between field-measured soil respiration rates and model-determined soil respiration rates derived from carbon isotope concentrations in modern gibbsite indicates that the formulation of analytical solutions for Fickian diffusion does not accurately describe the process by which soil carbon is incorporated into the gibbsite structure. Results from numerical Monte Carlo simulations to determine soil  $\text{CO}_2$  stable carbon isotope compositions as a function of soil respiration rate and atmospheric carbon dioxide partial pressure further indicates the assumption pedogenic mineral carbon isotope compositions record mean annual conditions is incorrect. Acceptable numerical solutions are only obtained when the soil respiration rate used is approximately one-tenth the annual average measured in the field. Based on sensitivity testing of all model parameters (e.g., bulk density, tortuosity, moisture content, isotopic composition of vegetation, and atmosphere, soil  $\text{CO}_2$  production rates, and atmospheric  $p\text{CO}_2$ ), the difference in results can only be accounted by several orders of magnitude variation in the soil  $\text{CO}_2$  efflux rate. Efflux rate is known to vary over a very large range in modern soils depending on the temperature and amount of moisture in the soil. This is consistent with the idea that the setting of the stable carbon isotope composition in pedogenic hydroxide minerals is established during episodic events of low respiration when soil conditions are favorable for mineral formation (i.e., periods of lower moisture levels where mineral growth is accelerated by super saturating solutions). This observation necessitates a paradigm shift in our current understanding of atmospheric paleo- $p\text{CO}_2$  proxies found in paleosols. Estimation of soil respiration rates and the assumption that the carbon is occluded in pedogenic gibbsite under all conditions are in need of updating. Atmospheric paleo- $p\text{CO}_2$  estimates from paleosol hydroxide minerals should be diminished by a factor of 10 because the natural process of soil respiration at the time of mineral formation is expected to be 10 times lower than the average annual rate.

## EXPERIMENTAL STUDY OF THE EFFECT OF SALINE ACIDIC CONDITIONS ON ILLITE DISSOLUTION

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Dissolution of phyllosilicates is one of the acid neutralizing processes that occurs in soils and is particularly important in extreme acidic conditions. Illite is a dominant clay mineral in many soils of Australia, Europe, and North America and in soils from desert areas. The determination of dissolution rates of minerals provides an estimate of their acid neutralizing capacity in soil. This study reports the first attempt to determine the dissolution rates of illite in saline –acid sulfate solutions. The results of these experiments will be applicable to a wide range of environmental conditions where the natural weathering process of illite has fastened through the acidity generated by sulfide mineral oxidation.

Dissolution experiments were conducted using Silver Hill illite at a pH ranging from 1 to 4 and at 25°C. The clay fraction ( $< 2 \mu\text{m}$ ) was separated by sedimentation procedure and Na-saturated clay was used in the experiments. X-ray diffraction analyses of the clay fraction showed the presence of minor amounts ( $< 1\%$ ) of kaolinite and quartz. Transmission electron microscopic characterisation of the illite sample prior to dissolution showed particle aggregates, with individual particles in 200–500 nm size range; the BET surface area was  $42 \text{ m}^2 \text{ g}^{-1}$ .

Dissolution experiments were conducted in stirred flow-through reactors. Input solutions at a specific pH were prepared by adding AR-grade  $\text{H}_2\text{SO}_4$  to E-pure water, and NaCl was used to maintain a constant ionic strength of 0.25. Output solutions were analysed for Al and Si using colorimetric analytical methods, and solution pH was also measured immediately after sample collection. Aqueous ion activities were calculated using Visual MINTEQ; the estimated  $\log K_{\text{eq}}$  value for the illite dissolution reaction was 10.51.

The dissolution reaction was very fast during the first 60–70 hours of the experiment with a rapid and incongruent release of tetrahedral, octahedral and interlayer cations. A preferential release of Al over Si was observed initially over the whole pH range, with the highest Al release at pH 2 and 3 (Al/Si ratio  $> 4$ ). Under steady state conditions at pH 1 and 4, congruent dissolution of illite occurred with Al/Si ratios in the leachate similar to that in the original illite sample. For these experiments, the dissolution rates were calculated on the basis of Al and Si release rates. The dissolution rates for the pH 2 and 3 experiments were calculated on the basis of Si

release rate alone because of a continued preferential Al release even after 2200 hours. A possible reason for the non-stoichiometry in dissolution of illite at pH 2 and 3 is the formation of a Si rich layer that forms because of the depletion of Al resulting from a very rapid release during first 60–70 hours of the experiments.

The dissolution rates measured from Si release rates in the present study were  $-1.78 \times 10^{-13}$ ,  $6.12 \times 10^{-14}$ ,  $-3.77 \times 10^{-14}$  and  $-1.81 \times 10^{-14}$  mol m<sup>-2</sup> s<sup>-1</sup> at pH 1, 2, 3 and 4, respectively. These results suggest that like other phyllosilicates, the dissolution rate of illite decreased with the increasing pH in acidic range. The dissolution rates for illite calculated in the present study are found to be intermediate to the dissolution rates for kaolinite and montmorillonite in acid sulfate solutions.

## FIXATION OF $K^+$ , $NH_4^+$ AND $Cs^+$ BY DIOCTAHEDRAL VERMICULITE

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Dioctahedral vermiculite is a very common constituent in soils of cold, temperate and subtropical climates. It occurs in soils and fresh sediments but, according to the author's knowledge, practically has not been reported from sedimentary rocks. The evolution of divermiculite during diagenesis remains obscure. In general, divermiculite exhibits strong potential for selective sorption and fixation of cations with low hydration energy (i.e.  $K^+$ ,  $NH_4^+$ ,  $Cs^+$ , and  $Rb^+$ ). The fixation is caused by interlayer dehydration and layer collapse. According to the data available it is very likely that vermiculite interlayer collapse takes place in natural environments (i.e. soils and marine environments) by the selective sorption of potassium and/or ammonium ions and the dehydration of the interlayer space. The occurrence of the collapse could explain the lack of divermiculite in sedimentary rocks and could be the potential mechanism for so called "soil illitization". The aim of this study was to find out if the dioctahedral vermiculite collapses irreversibly to 10 Å phase (mica-like) when saturated with  $K^+$ ,  $NH_4^+$ ,  $Cs^+$ . Due to the fact that no divermiculite standard reference material was available, two natural samples of soil clays rich in dioctahedral vermiculite were selected for this study. In a first set of experiments the clays were saturated with  $K^+$ ,  $NH_4^+$ , and  $Cs^+$  using chlorine solutions and immediately (without air- or freeze-drying) were saturated with  $Na^+$  and  $Sr^{2+}$ . Only a very small fraction of vermiculite interlayers collapsed in this experiment, the amount of the collapsed interlayers was higher for  $Cs^+$  saturated vermiculites than for K-saturated ones.  $NH_4^+$  saturation practically did not produce any collapse and the vermiculites were completely rehydrated by  $Na^+$  and  $Sr^{2+}$  saturation. It was also found that  $Na^+$  saturation protocol (i.e. acetic buffer treatment at 90°C + 3 x 1M NaCl treatment at room temperature) used in this study was more effective in rehydration (reopening) of the vermiculite interlayers than the traditionally used  $Sr^{2+}$  saturation (i.e. 4 x 0.5M  $SrCl_2$  treatment). In a second set of experiments the studied samples were saturated with  $K^+$ , air-dried and treated using the  $Na^+$  saturation protocol. The amount of collapsed interlayers obtained in this experiment was significantly higher. In the third set of experiments the vermiculite samples were treated using  $K^+$  containing solutions for an extensive period of time. The treatment resulted in more significant collapse of the interlayers than the collapse reached in the first set of experiments. The amount of collapsed interlayers obtained by the extensive K-treatment (without drying) was lower than the amount reached by K-saturation followed by air drying. The results of the experiments conducted clearly indicate that vermiculite collapse is likely to occur in soils during weathering and in sediments during early diagenesis. The collapse results in formation of stable, mica-like phase.

## *POSTER PRESENTATIONS*



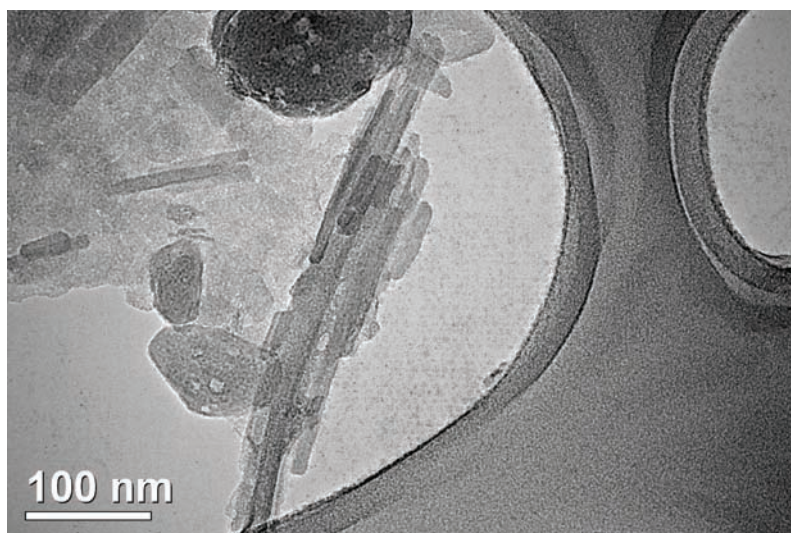
## SOIL PLYGORSKITE FORMATION AND ITS ASSOCIATED MINERALS IN TWO CONTRASTING CLIMATIC REGIMES

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Palygorskite is a fibrous modulated 2:1 silicate clay mineral commonly found in arid environments. Under high precipitation, soil palygorskite converts to smectite and other silicate minerals and is usually unstable when annual precipitation is greater than 300 mm. We have investigated the occurrence of palygorskite and associated minerals in soil environments in contrasting climatic regimes: the Mojave Desert in southwestern USA (150-250 mm mean annual rainfall,) and the northern and southern transects of the Great Dyke, Zimbabwe, with mean annual rainfall of 850 and 550 mm, respectively. The Great Dyke is located on serpentinized ultramafic parent rocks rich in Mg and Fe. Minerals were characterized by X-ray diffraction, transmission electron microscopy, and Fourier transform infrared spectroscopy. In the Mojave Desert, palygorskite occurred in strongly cemented petrocalcic horizons and was more abundant in the <0.2  $\mu\text{m}$  fine clay fraction. Smectite, talc, kaolinite and



Fibrous palygorskite in soils of the southern transect, Great Dyke, Zimbabwe. The blunt ends of the fibers suggests an authigenic mineral in comparison to a transported one

vermiculite were associated with palygorskite in the Great Dyke. Same minerals and chlorite have been found in the Mohave Desert. But only in the southern part of the Great Dyke did palygorskite occur in soil, despite similarly high concentrations of Mg and high pH ( $>7$ ) at both transects. The content of palygorskite increased with soil depth in correlation with the increase in secondary carbonate minerals. Our results demonstrate that palygorskite can form in soil and remain stable, even in areas that receive mean annual rainfall of more than 500 mm. These results suggest that alkaline reaction, a high concentration of alkaline soluble salts, and the high availability of Mg could each be important factors impacting palygorskite formation. We conclude that palygorskite in these environments is of pedogenic origin.



## DISSOLUTION OF KAOLINITE, ILLITE AND MONTMORILLONITE IN ACID-SALINE SOLUTIONS

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The development of sulfidic sediments resulting from rising ground water levels and their exposure due to natural and human induced drying events poses a major threat to the soil and water systems. In these environments, high salinity combined with extreme acidity produces unique biogeochemical environment. Chemical weathering of phyllosilicates is the only process that can neutralize the acidity over long periods of time in such environments. The dissolution of phyllosilicate minerals have been investigated in the past few decades with an emphasis on determining the effects of pH and temperature. The present study was conducted to evaluate the dissolution behaviour of phyllosilicates in saline acidic environments.

Dissolution experiments were conducted using three reference clay minerals i.e., Georgia kaolinite, Silver Hill illite and Wyoming montmorillonite, at pH 1–4 and at ionic strengths of 0.01 and 0.25. The clay fraction (<2  $\mu\text{m}$ ) of the three minerals was separated by sedimentation-resuspension procedure and Na-saturated clays were used in the experiments. The dissolution experiments were conducted in stirred flow-through reactors using a flow rate ranging between 0.02 and 0.05  $\text{mL min}^{-1}$ . Input solutions at a specific pH were prepared by diluting AR-grade  $\text{H}_2\text{SO}_4$  with E-pure water, and NaCl solution was used to maintain the required ionic strength.

The output solutions were collected daily and solution pH was measured immediately after sample collection. The total concentrations of Al and Si were determined calorimetrically by a UV visible spectrophotometer. The saturation state of the solution with respect to mineral dissolution was calculated in terms of Gibbs free energy of reaction,  $\Delta G_r$ . The dissolution rates of the minerals were calculated from Al and Si release rate at the steady state.

The dissolution rate decreased with time until a nearly constant rate was reached after several hundreds of hours. The steady state was between 1500 and 2200 hours. A stoichiometric dissolution of kaolinite was observed and similar dissolution rates were found over the whole acidic pH range and at both ionic strengths. A preferential release of Al over Si for kaolinite and illite was observed during the first 60–70 hours of experiments. A stoichiometric dissolution of illite was found in experiments conducted at the low ionic strength (0.01) for the studied pH range. However, at the high ionic strength (0.25), a stoichiometric release of elements occurred at pH 1

and 4 whereas more Al was released than Si at pH 2 and 3. A small inhibiting effect of ionic strength was observed on illite dissolution rate. In case of montmorillonite, a preferential release of Al over Si was observed at the high ionic strength. The dissolution of montmorillonite was inhibited at high ionic strength over the studied pH range. A similar effect of ionic strength has been reported for studies conducted on other minerals including albite and feldspar.

Our results show that there is no significant effect of ionic strength on kaolinite dissolution; however, it has a slight to significant inhibition effect on the dissolution rates of 2:1 phyllosilicate minerals. The fastest dissolution rate was observed for montmorillonite followed by illite and kaolinite over the whole acidic pH range.

## CLAY MINERALS EVOLUTION IN A SOIL CLIMOBIOSEQUENCE OVER MICA-SCHIST FROM SIERRA NEVADA MOUNTAINS (SPAIN)

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Clays and clay minerals are recognised as one of the most reactive mineralogical fractions in the Earth's Critical Zone and soils, and they may report with great precision about environmental conditions, including climate and vegetation. In this work, four soil profiles (M1, M2, M3 and M4) have been sampled along an altitudinal gradient from 1250 m over sea level (profile M1) to 3101 m (profile M4) in Sierra Nevada Mountains (Southeaster Spain). The soil parent material was a graphitaceous mica-schist from the Nevadofilabride Unit, showing a high to moderate degree of metamorphism (greenschist facies). Vegetation is distributed according to altitude in bioclimatical zones, from oak wood (*Quercus rotundifolia*, M4) to alpine grassland (*Festuca sp*, M1).

Soil profiles were shallows and stoniness, sited over mica-schist outcrops (Entisols). Morphologically they show less evolution with altitude. From an analytical perspective, we can highlight their relative high organic carbon percentage (except for the highest soil, M4), an equilibrated C/N ratio and a slightly acid pH.

Mineralogical composition was studied by x-ray diffraction (XRD) with a Siemens D5000 diffractometer using Cu-K $\alpha$  radiation at 35 kV. Disoriented crystalline powder (fine earth fraction, < 2 mm) and oriented aggregates (clay fraction, < 2  $\mu$ m) were prepared. Decomposition of air-dried and ethylene-glycol (EG) patterns of clay fraction was performed with the DecompRX software, using the MULCALC software to a precise identification (nature and proportion of the different layer types) and whole pattern simulation of the previously decomposed peaks (the quality of the fit was estimated with the unweighted R parameter, Howard & Preston, 1989).

Total mineralogy for fine earth was rich in phyllosilicates and quartz, showing a general trend to decrease phyllosilicate contents with altitude. Clay fraction of all samples was dominated by potassium micas ( $d_{001} \approx 0.10$  nm), paragonite ( $d_{001} = 0.96$  nm) and kaolinite ( $d_{001} \approx 0.72$  nm), with moderate contents of chlorite ( $d_{002} = 0.705$  nm) and low presence of smectite ( $d_{001} = 1.70$  nm, EG).

Decomposition and simulation revealed a significant heterogeneity of samples in the 6 – 10  $^{\circ}2\theta$  range, including peaks for paragonite, muscovite, illite (both, poor

and well crystallized) and illite-smectite mixed-layers (with variable proportion of expandable layers).

From an evolutionary perspective, paragonite and chlorite were inherited from the mica-schist; kaolinite was mainly neoformed, while smectites are probably linked with inherited potassium micas through transformation processes. In general, the dominance of poor or non-expandable micaceous phases (poor crystallized illite and I/S mixed-layer with higher proportion of illite) *versus* expandable phases (smectites and I/S mixed-layer with a higher proportion of smectite) were more related with the vegetation type and organic carbon content of the horizons than with the altitude of the profile.

## WEATHERING OF A SMECTITE CLAY FROM A PERSPECTIVE ON ASSIMILATION OF SOME TRACE METALS BY A PLANT GROWN UNDER A LABORATORY CONDITION

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The substrate was Ca-smectite material, and the plant that was *Populus eugenei*. Small cuttings from a stem of a previous poplar plant were planted to the substrate that was wetted periodically with deionized water, a condition from which new stems and leaves grew. No difference in the X-ray diffraction characteristics was observed between the clay particles from the rhizosphere or the root zone and the clay particles which were not subject to the root activity. The basal d-001 spacings for the both clays were: 15.1Å for the oriented untreated samples, 17Å for the glycolated ones, and 9.7Å for the ones heated to 470 °C. The two groups the clay particles had nearly similar major chemical compositions, but varied only in a subtle way some trace element compositions. It may be that either the fraction of particles involved in rendering metals available to the plant roots was quite small, or the particles involved in supplying metals to the plant roots were thoroughly destroyed leaving no trace of the original crystallographic composure. Yet the plant metal chemistry with fractionations among different metals that became incorporated in different organs (roots, stems, and leaves) was different from that of the clay particles that were the sources of the metals for the plants. The specific concentrations of the following elements were higher in the leaves than that in the roots: K (20,744 ppm vs. 5534 ppm), Na 340 ppm vs. 155 ppm), Ca 18,556 ppm vs. 8998 ppm), Sr (175 ppm vs. 136 ppm), Mg (4,745 ppm vs 2,189 ppm), and Fe (246 ppm vs. 410 ppm), but of Rb nearly the same (11.7 ppm vs 11.5 ppm) and of both Al (1,202 ppm vs. 1410) and REEs (13.6 ppm vs. 39.3) lower in the leaves. Evapotranspiration by plants may explain the relatively high concentrations for Na, K, Rb, Ca, Sr, Mg, and Fe, but not the lower concentrations of Al and REEs in the leaves, or nearly the same concentrations of Rb. This apparent incongruous metal accumulation trends may be linked to metal complexation or chelation effects or to a factor of enzymatic influence in response to physiologically controlled plant metabolism. The case in point lies with the K/Rb ratios, the leaves were with 1,776, the roots with 479, and the clay particles with 390, pointing to a high need of K in the leaf region. It has been reported that K has some influence in stomatal opening, in protein synthesis, and in the activation of some enzymes. K need for the plants is a strong force that extends far beyond the root zone. This distant force makes a strong impact on the intensity and the nature of the chemical breakdown of the natural source material for the metal. Both Fe and Mg concentrations were higher in the leaves, although the leaves

and the roots had nearly the same Fe/Mg ratios of about 0.10, in contrast to the clay particles with a ratio of 0.29. Mg is a known catalyst for leaf metabolic activity. An impact of plant leaf metabolic activity was also evident in the REE fractionation data: clays outside the root zone had 275 ppm; the root zone clays had 203 ppm; the roots (39.3 ppm) were heavy REE-enriched with a positive Eu anomaly relative to the clays; and the leaves (13.6 ppm) were heavy REE-depleted with a slight negative Eu anomaly relative to the roots. The Eu anomalies could have arisen from preferential inclusion or exclusion of this metal as an enzyme co-factor. Leaf metabolic activity is a big force that should enter in nearly all models of weathering of minerals.

## GEOLOGICAL, AND ENGINEERING OF EXPANSIVE SOILS OF WEST MAWHOOB AREA, DAKHLA OASIS, WESTERN DESERT, EGYPT

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Geological, engineering and detailed mineralogical investigations were carried out on the expansive soils of Mawhoob Shale Member of Dakhla Shale (Late Maastrichtian) at West ElMawhoob area, Dakhala Oasis, Western desert, Egypt.

The west Mawhoob expansive soils are considered one of very problematic soils that having a high expansiveness nature. Where many buildings in this area include homes, schools, and offices, have been damaged by the movements of the superficial expansive clays, because the foundation design has not taken into consideration the expansive properties of the soil.

The exposed sedimentary succession in the west Dakhla Depression ranges in age from the Middle Campanian to Late Paleocene. These rock units are Quseir Formation, Duwi Formation Dakhla Formation and Tarwan Chalk Formation The Mawhoob Shale Member is the lower unit of the Dakhla Formation. It marks the basal part of the scarp face and the floor of the studied area

The studied expansive soil are composed mainly of poorly graded, moderately sorted clayey soils that were deposited in a shallow marine environment. Four types of clay minerals were identified throughout the studied sequence, namely kaolinite, smectite, illite, and. smectite-illite mixed-layer.

Geotechnically, the free swelling of this soil range between 150 and 165, the swelling percent ranged from 28% to 37% of initial volume. The swelling pressure varies from 9.1kg/cm<sup>2</sup> to 11.7kg/cm<sup>2</sup>. The major stress  $\sigma_1$  ranged between 8.4kg/cm<sup>2</sup> and 7.5kg/cm<sup>2</sup>. The residual major stress ( $\tau_r$ ) varies from 5.25kg/cm<sup>2</sup> to 6.25kg/cm<sup>2</sup>. The effective cohesion (c) of the studied samples fluctuates between 0.49kg/cm<sup>2</sup> and 0.68kg/cm<sup>2</sup>. Using the Mohr 's circles the determined values of the angle of internal friction ( $\phi$ ) of the studied samples vary from 25° in to 32°.

The studied soils are classified as medium to high expansive soils according to the most of the classifications suggested by numerous authors. Following the grades of consolidation suggessted by Maslov (1987), the studied soil was lied in the field of medium compressibility (0.005-0.01 cm<sup>2</sup>/ kg).

The scanning electron micrographs of the studied soil indicate its flocculation and aggregation fabric. This type of fabric affects engineering properties where aggregation generally increases the soil permeability. When particles are flocculated,

liquids move relatively easily and permeability is increased. Dispersion, on the other hand, reduces permeability. Particles tend to plug small pores and impede water flow. Flocculation also increases major stress and reduces compressibility.

There are strong mutual relations between geological and engineering properties of this soil where the swelling pressure shows positive correlation with clay content. The clay mineral species play an important role in the engineering characteristics of this soil. The major stress ( $\sigma_1$ ) and cohesion strength ( $c$ ) correlate positively with kaolinite content of this soil. On the other hand, the major stress ( $\sigma_1$ ) and residual strength ( $\tau_r$ ) correlate negatively with smectite content of this soil. Swelling pressure shows a reverse relation with kaolinite content but proportionates directly with smectite content of this soil. Major stress, cohesion and residual strength correlate positively with calcium carbonate content, whereas, swelling pressure correlates negatively with calcium carbonate content of this soil. Initial water content affect negatively major stress and cohesion of the studied soil and positively on swelling pressure. Cation exchange capacity and dry density correlate negatively with swelling pressure, whereas depth and dry density correlate positively with major stress, cohesion and residual strength.



## REACTIVITY OF CA-BENTONITE IN THE PRESENCE OF LIME: A NMR AND TEM STUDY

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Lime stabilization is a widespread technique in the field of earthworks as it can improve both the workability and mechanical properties of wet clayey soils. The improvements brought by lime treatment are attributed to two major stabilization mechanisms, being (1) the immediate reactions of cation exchange and flocculation-agglomeration, and (2) the long term pozzolanic strength development. When quicklime (calcium oxide) is added to a clay soil a dehydration reaction forming calcium hydroxyde takes place that pumps water from the soil. In addition, a cation-exchange reaction between  $\text{Ca}^{2+}$  ions brought by lime and existing interlayer cations of the clay minerals results in the flocculation of clay mineral particles and subsequently in a decrease of the soil plasticity properties. Another process, called “long-term stabilization” and involving pozzolanic reaction, is considered as responsible for the improvement of the strength properties of clay. It correspond to the interaction of lime with silicon-containing material of the soil in the presence of water, forming a hydrated gel corresponding to calcium silicate hydrates (C-S-H) and/or calcium aluminate hydrates (C-A-H). However, the mechanical properties of treated clayey soils were found to depend on its mineralogical composition. In particular, bentonite behavior strongly differs from the kaolinite one, with difference resistance under shear stress and/or compression that is far greater in the case of bentonite. To better explain this specific behavior, Ca-bentonite was treated with 5-10% of lime over a week to several months. Nuclear magnetic resonance (NMR) spectroscopy and transmission electron microscopy (TEM) were used to investigate the modification of the montmorillonite and as well as the accessory minerals upon lime treatment, as well as the nature and location of the newly formed phases.

## A LONG-TERM NATURAL ANALOGUE FOR RADIOACTIVE WASTE REPOSITORIES? MINERALOGY AND CHEMISTRY OF A VOLKONSKOITE (CR-RICH SMECTITE) IN TRAVERTINE DEPOSITS FROM CENTRAL JORDAN

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In Quaternary travertine deposits of central Jordan emerald and green clays were noticed filling cavities and fractures, believed to be volkonskoite. Foord et al. (1987) defines volkonskoite as a dioctahedral member of the smectite group dominated by Cr in the octahedral sheet, meaning more than one of the two octahedral sites should be occupied by Cr. Smectites with lesser Cr (e.g.  $\text{Cr}_2\text{O}_3$  typically less than 15%) would be properly termed chromium montmorillonite. The travertine deposits precipitated from warm hyperalkaline groundwater (pH = 12.5) at the interface between bituminous marl and marble making it a potential long-term natural analogue of carbonation and remobilization of alumino-silicates in cement barriers for radioactive waste repositories.

Previous study by Khoury et al. (1984) in a similar location failed to prove that the newly discovered clay locality in central Jordan was volkonskoite. The green clayey material from central Jordan was characterized mineralogically and chemically by XRD, TEM, and XRF.

From XRD, dioctahedral Cr-smectites and calcite were mainly identified. Quartz, opaline phases, and sulphates (gypsum and ettringite) were minor constituents.

From XRF data of bulk rock upto 7.5 % Cr, with very high V (9500ppm), Zn (1600ppm) and U (419ppm) concentrations were measured. The high Cr, U, V and Zn concentrations were derived from the spontaneously combusted bituminous marls. The TEM-EDX data indicated that the smectites were dioctahedral and octahedrally charged with two clusters of smectites, a Cr-rich montmorillonite and a volkonskoite based of Foord et al. (1987)

A) Cr-rich montmorillonite:  $\text{Ca}_{0.3}(\text{Cr}^{+3}_{0.6}, \text{Mg}_{0.8}, \text{Al}_{0.7})(\text{Si}_{3.9}\text{Al}_{0.1})\text{O}_{10}(\text{OH})_2$

B) Volkonskoite:  $\text{Ca}_{0.2}(\text{Cr}^{+3}_{1.1}, \text{Mg}_{0.4}, \text{Al}_{0.6})(\text{Si}_{3.9}\text{Al}_{0.1})\text{O}_{10}(\text{OH})_2$

All samples contain low concentrations of K. The Fe was generally very low in concentration but varied significantly in some samples. That was interpreted as contamination of Fe oxides associated with the smectites.

In conclusion authigenic volkonskoite and Cr rich montmorillonite were identified. Both smectite phases were formed at pH values similar to the ones expected at radioactive waste repositories. Whether these minerals represent a solid solution or distinct minerals is still open for further discussion.

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## PALYGORSKITE DISTRIBUTION AND GENESIS IN CENTRAL IRANIAN SOILS

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Palygorskite is a fibrous clay mineral widely reported in soils and sediments of arid and semi-arid regions. Very few comprehensive studies investigated the distribution and origin of palygorskite in soils developed on Tertiary sediments in central Iran. The objectives of this study were (1) to determine the distribution and origin of palygorskite in soils associated with Tertiary sediments, and (2) to identify the major soil properties that influence palygorskite distribution in soils studied. Eighteen soil profiles developed on Paleocene, Eocene, Oligocene, Miocene and Pliocene sediments were described, sampled and studied by X-ray diffraction analysis, transmission and scanning electron microscopy, and inductively coupled plasma mass spectrometry. Physicochemical characteristics of soils and sediments including particle size distribution, pH, EC, organic carbon, gypsum and carbonates, and soluble Si, Ca and Mg were also determined. The principal component analysis was used to establish the relationships between palygorskite and physicochemical characteristics of the soils studied. Results showed that palygorskite is absent in sediments of Paleocene, Eocene and Oligocene ages. In contrast, sediments of Miocene and Pliocene ages are rich in palygorskite. Clay fraction of all the soils in the study area is dominated by palygorskite. The highest amount of palygorskite was found in horizons in which both carbonates and gypsum accumulated. A low quantity of palygorskite was found in salic and calcic horizons. Palygorskite seems to be of eolian origin in the surface horizon of some soils as it was captured in the dust traps in the region during a 2-year study. Using principal component analysis, the Mg/Ca ratio, pH,  $H_4SiO_4$  and gypsum contents were identified as the most important factors affecting the distribution and genesis of palygorskite in the soils studied. This may suggest the neoformation of palygorskite by precipitation from solution where the evaporation fluxes are very high. In conclusion, palygorskite in soils developed on Tertiary sediments in central Iran seems to be of both inherited and pedogenic origin.

## MICROMORPHOLOGY INVESTIGATION OF SEPIOLITE BEARING PETROCALCIC HORIZONS FORMED FROM LACUSTRINE SEDIMENTS ON THE SOUTHERN HIGH PLAINS OF TEXAS AND NEW MEXICO

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Petrographic analyses and Scanning Electron Microscopy (SEM) were used in the investigation of depositional and pedogenic processes of petrocalcic horizons formed from lacustrine sediments on the Southern High Plains (SHP) of Texas and New Mexico. This investigation was carried out within the ancestral Brazos River drainage system. Sepiolite formation on the SHP of Texas and New Mexico has been found to be commonly associated with alkaline lacustrine environments in conjunction with dolomite and calcite. The presence of sepiolite in soils has long been thought to have been attributed to inheritance from alternative parent material via secondary (eolian, alluvial) depositional processes due to sepiolite being unstable in pedogenic environments. The petrocalcic horizons that formed from the lacustrine sediments are multicyclic with varying degrees of laminae and pisolitic characteristics. Macromorphology and micromorphology of the petrocalcic horizons show extensive influence of pedogenic processes. Typical sepiolite morphology displays lath-like or fibrous needle shaped particles and on the SHP often interbedded with calcite and dolomites. Petrographic analysis and SEM's show unique spheroids comprised of sepiolite. The sepiolite spheroids occur within multiple laminae throughout the petrocalcic horizons. Micritic calcite has precipitated on to the surface of the sepiolite spheroids. The sepiolite spheroids formed as Mg-rich waters reacted with the silica-rich volcanic ash.

## **DYNAMIC DEW POINT METHOD FOR MEASURING MOISTURE SORPTION ISOTHERMS**

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Moisture sorption isotherms for clays and clay-rich soils have been recognized as effective proxies for characterizing a much wider array of properties and processes, including vapor flow and transport, swelling potential, wetting-drying hysteresis, the use of bentonites as barrier and buffer materials for waste disposal, and the quality of bonding between cements and aggregates. Numerous examples of water vapor isotherms obtained for clays using a variety of testing equipment may be found throughout the literature.

A comprehensive series of laboratory tests was conducted to assess the performance of a new dynamic equilibrium method for measuring water vapor sorption isotherms of clays and clayey soils. Samples are placed into a small environmental chamber and continuously wetted or dried by circulating either a vapor saturated or desiccated air stream around the sample. Sample water activity is directly measured at select snapshots during the sorption process using a chilled-mirror dew point sensor and infrared thermometer integrated into the testing chamber. Sample mass is simultaneously tracked using a magnetic force balance and used to construct the sorption isotherm from the corresponding water activity at that moment in time. Unlike conventional techniques for measuring sorption isotherms, there is no dependence on equilibration of the sample to preset conditions in the testing chamber. For samples with relatively fast vapor diffusion rates, moisture penetration into the sample is rapid and the dynamically generated isotherm would be expected to be close to that generated by conventional equilibrium methods. For samples with slow diffusion rates, however, the dynamically generated isotherm may not represent equilibrium conditions.

The objective of this study was to assess the performance of the dynamic measurement approach using a series of kaolinite/bentonite mixtures to represent a wide range of clay sorption behavior. Emphasis was placed on quantifying temperature stability, measurement reproducibility, establishing a recommended testing protocol, and on comparing dynamically generated isotherms with independent measurements obtained using a conventional equilibrium method. Water vapor adsorption-desorption loops at water activity ranging from 0.03 to 0.95 and containing as many as 140 discrete measurements were obtained using the dynamic method in 12 to 24 hours. Far less intensive isotherms obtained using the equilibrium method required approximately 600 hours (25 days). Measurement reproducibility using the dynamic method was within 6% of the full-scale range. Clay water content at activities less

than 0.60 compared excellently with values measured using the equilibrium method and were within 10% to 15% of the full-scale range at higher activities. Surface properties derived from the dynamically generated isotherms compared well with values obtained from analysis of the equilibrium isotherms. The percent difference in calculated specific surface area ranged from a minimum of 4.6 % to a maximum of 22.3 %.

## IMPORTANCE OF POROSITY IN THE ROCK WEATHERING PROCESSES. SOME EXAMPLES

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Weathering profiles outcropping beneath old piedmont platforms (the Raña landscapes) and the earliest terraces of the main rivers in Central and Western Spain depict: i) a sedimentary cover of pebbles and gravels of quartzites and quartzs, all embedded into a clayey matrix, and ii) the hercynian basement beneath which is weathered up to tenths of meters in depth. Mechanisms of weathering occurred on these pebbles and gravels, and within the slates of the hercynian basement, are studied here. To do so, mineralogical and water techniques have been used.

At the soil surface oxy-hydroxides form a thin and reddish cortex of weathering around pebbles and gravels. At the lower part of the sedimentary cover pebbles and gravels are embedded into the clayey matrix, with an ochre and/or whitish cortex of some cm thick around. Whereas at the top of the profiles xerolysis can occur during dry periods, ferrolysis and dissolution of silica joining the quartz grains are the main mechanisms at the lower parts of the cover.

Beneath this cover, weathering of slates gives rise to slabs which colour grades from grey, of the apparently not weathered slates, to yellowish, orange and a reddish and clayey mass at the top of the weathered basement. Two parts are also distinguished here: i) lower part, where alteration leads to a progressive reduction of the inherited minerals (e.g. feldspars, chlorites, illites), and generation of new ones (smectites), and ii) upper part, beginning at ca. 3-4 meters beneath the contact to the sedimentary cover, where smectites decrease, illites stay more-or-less distorted, and Fe oxy-hydroxides and phyllosilicates of the kaolinite group increase. Weathering produces a reduction in ca. 30% of the bulk density of the sample, leading to a fine porosity where diffusion is the main mechanism of weathering, and where kaolinites and the somewhat de-hydrated phases of the Fe oxy-hydroxides preferably develop. Bleached zones occur along planes of fissures and discontinuities due to the leaching of the Fe oxy-hydroxides.



## INFLUENCE OF SOIL IRON MINERALS ON THE FORMATION OF TRIHALOMETHANE

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Huber et al. (2009) describe a new abiotic source of trichloromethanes (THM) from the terrestrial environment induced by the oxidation of organic matter by iron (III) and hydrogen peroxide in the presence of chloride. These findings were based upon laboratory studies using catechol as model compound for phenolic moieties of soil humic substances with a system of iron(III)-H<sub>2</sub>O<sub>2</sub>-KCl to gain mechanistical

insight of involved reactions on the one hand. On the other hand, tests with organic-rich soils to verify the development of THMs under natural conditions were performed. From previous studies (Huber, 2008, 2009; Pracht, 2000; Schöler and Keppler, 2003) it is known that iron is essential in the proposed degradation pathway of model soil humic compounds via 1,2,4,5,- tetrahydroxbenzene to THM. The phase in which iron is present might be one factor of controlling reaction kinetics by Fenton-like chemistry in the presence of H<sub>2</sub>O<sub>2</sub>. However, previous research did not specifically address the impact of the form in which iron is supplied to induce THM or organohalogen formation. In this study we investigated the dependence of THM formation on iron mineral phase in order to optimise the conditions of THM formation of natural soils in laboratory experiments. Minerals were obtained from commercial sources or synthesized/modified in the laboratory and confirmed with XRD analysis. THM liberation was analyzed after 2 and 24h using GC/ECD. The optimized conditions of Fe(II)-Sulfate were applied to corresponding systems with different iron (hydr)-oxides, pyrite as well as a Fe-saturated smectite and Cu- and Mn-salts. Contrasting to Huber et al. the pH of the reactant solution was not fixed at 2,4 but instead the system was allowed to reach the natural acid milieu according to the corresponding Fe-phase. As a result only Fe(III) bearing minerals yielded detectable THM concentrations after 24h reaction time. Highest yields for trichloromethane were achieved for 2-line ferrihydrite, Fe(III) saturated smectite as well as Fe(III) sulfate solutions. Thus, a low crystallinity of the iron species seems to favour its contribution to the reaction. Smectite showed interesting reactivity with a variety of additional peaks for volatile organic compounds which are up to now not identified. Parallel experiments with Mn- and Cu-salts did not confirm their catalytic activity for THM formation. While the potential organic precursors in soils are vast, the numbers of possible iron phases present in natural soils and soil solutions are rather limited. These results may present a first step in identifying soils that are prone to naturally production of THM in the presence of halides and H<sub>2</sub>O<sub>2</sub> based on mineralogy and organic matter content. Reactions with Fe-saturated smectite may deserve further study.

## **K-Ar AGE VALUES OF BULK SOIL SAMPLES AND CLAY FRACTIONS: EFFECTS OF ACID EXTRACTION AND IMPLICATIONS FOR THE ORIGIN OF MICACEOUS CLAY IN SAVANNAH RIVER SITE SOILS**

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The impact of varying degrees of acid extraction on age values of clay fractions and bulk soils was determined using K-Ar dating of materials from five near-surface soil samples from the Savannah River Site, SRS, before and after extraction. Bulk soil and clay fractions of each sample were subjected to acid extraction for three hours under moderate conditions using 6-10%  $\text{HNO}_3$  (aq) at 80°C or more severe conditions using 50%  $\text{HNO}_3$  (aq) at 100°C. K and the Ar isotopic composition of the original materials and the extraction residues were measured by known methods.

Before acid extraction, clay fractions showed lower apparent ages than the bulk soils. Age values for clay fractions ranged from 248 to 360 Ma and averaged 305 Ma while age values for bulk soils ranged from 337 to 815 Ma and averaged 545 Ma. The age values of clay fractions near 300 million years are consistent with the idea that the K in the soil clay is in remnants of detrital muscovite that was in the parent Tertiary sediments. Hassanipak [1] reported an apparent age range of 191 to 412 Ma with an average of 286 Ma in muscovite rich samples from the Georgia kaolin belt and Elser [2] reported an apparent age range of 114 to 388 Ma with an average of 277 Ma in select muscovite separates from the Georgia Kaolin belt sediments. The ratio of K to Ar in the micaceous interlayers of the clay fractions suggests an ultimate origin for such interlayers in mica from the Paleozoic and Precambrian rocks of the Appalachian Mountain belt. Hydroxy interlayered vermiculite has been shown to be responsible for most of the exchange capacity of the SRS clays [3], and the 300 Ma apparent ages of the clay fraction indicates that the nonexchangeable K within the soils has been in closed systems throughout the sedimentary and pedogenic processes responsible for the present day soils.

Acid extraction under moderate conditions caused no significant changes in the age values for the clay fractions. For the bulk soils, moderate extraction conditions yielded higher age values than materials not subjected to acid extraction presumably because the acid removed exchangeable K. Moderate conditions resulted in slightly higher age values than strong conditions in bulk soil samples. These results suggest that strong extraction conditions of bulk soils may release nonexchangeable K (and thus  $^{40}\text{Ar}$ ) from the primary mica sites by altering the mica structure. Because the

exchangeable K is removed from expandable mica layers at moderate levels of acid extraction, the moderate extraction conditions used are sufficient for K-Ar methods.

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## TOPIC 4

*Environment & Energy*



# *ORAL PRESENTATIONS*





## KEYNOTE

### EARTH ENGINEERING TECHNOLOGY LEARNT FROM LOW TEMPERATURE PRESENT-DAY-SERPENTINIZATION

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For our sustainable development, engineering technology in 21st century should be in safety, low-cost and environmentally friendly for human living together with the Earth. In such technology, not rare earth and platinum group elements but rather ubiquitous elements such as Si, Al, Mg, Fe should be used. Natural process is a physical, chemical and biological process existing in nature without the intent of human beings. Therefore, products and technology learnt from natural processes are available with low-cost and safety. In the natural processes, of course, ubiquitous elements play a key and major role. Not only civil and geological engineers but also engineering chemists and biologists are interested in natural processes for sustainable engineering technology. Especially, chemical processes at extremely alkaline environments have been attracted their attention for sustainable management of waste disposal used huge amount of concrete, recycling of alkaline materials such as cement, slag and fly ash, and so on. However, an understanding of the processes at such a hyperalkaline condition is not enough for safety assessment of the waste disposals and the recycling. In addition to this, many engineering chemists and biologists are also interested in the hyperalkaline processes for safety CO<sub>2</sub> geological storage, application of Fisher-Tropsch type reaction to natural system, and so on. Therefore, there are many contents to make lessons and be learnt from natural processes at hyperalkaline conditions. Fortunately, we can have the lessons at some ophiolites where occur low temperature present-day serpentinization.

Serpentinization has unambiguously been recognized as important geophysical and geochemical processes in mantle wedge and oceanic lithosphere. Serpentinized peridotite generally forms at reaction temperatures of 100–500°C as indicated by chemical, mineralogical and isotopic data. On the other hand, temperatures of present-day serpentinization observed at ophiolites and Lost City vents are considerably lower (40–75°C). This is in strong contrast to other known serpentinization systems. Thus, the temperature variability expressed by vent fluids from ultramafic-hosted hydrothermal systems on or slightly removed from mid-ocean ridge, is not altogether surprising. The low temperature hydrothermal field is characterized by a combination of extreme conditions never before seen in the marine environment. These conditions include venting of hyperalkaline and metal-poor hydrothermal

fluids with high concentrations of dissolved  $H_2$ ,  $CH_4$ . Huge amount of  $CO_2$  gas is fixed into carbonate minerals observed in chimneys at the hyperalkaline vents and fissure filling of ultramafic rocks at the ophiolites.

In this context, the previous studies on low temperature present-day serpentinization will be reviewed from the engineering points of view (hazardous anion migration,  $CO_2$  geological storage, hydrogen and methane generation, abiogenic hydrocarbon production) in this presentation with introduction of our studies (lessons) at Oman ophiolite.

## GRAPHENE-LIKE MATERIALS SUPPORTED ON CLAYS: EASY PREPARATION AND APPLICATIONS

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Nanostructured materials attract much scientific and industrial interest due to their remarkable physical and chemical properties, as for instance superior mechanical, electrical, optical or magnetic performance, afforded by confining the dimensions of such materials and because of the combination of bulk and surface properties to the overall behavior. Among them, carbon nanostructures is a topic of growing relevance due to their potential application in many different fields including energy storage, catalysis, separation, sensor devices, etc. A key point for these applications is the control of textural properties and the possibility of further functionalization of the created nano- and macro-structures. Clay minerals of different topologies, from layered silicates to porous sepiolite or pillared clays, have been used as porous substrates to produce nanostructured carbonaceous materials using a large number of molecular and polymeric organic precursors [1]. Although the carbon-clay materials may have interest *per se*, most of the carbon-clay precursors are used as source of nanostructured carbons provided with electronic conductivity for applications as electrode materials for secondary battery and supercapacitors [2]. Nevertheless, few reports on the use of carbon-clay derivatives as functional materials have been reported though the presence of the clay may provide additional advantages.

In this context, the present contribution will introduce various examples to show the interest in diverse applications, such as energy storage or ion-detection in aqueous media, of conducting nanostructured carbon-clay materials prepared from different type of clay minerals (smectites, sepiolite and palygorskite) and a natural, cheap and abundant source of carbon such as sucrose [3-5]. The preparation of these conducting carbon/clay materials consists in a two step process involving formation of a caramel-clay nanocomposite under microwave irradiation and a further controlled thermal heating till reach the formation of supported graphene-like materials [3]. These resulting materials may have interest in a large number of applications including their use as electrode in different electrochemical devices as well as in catalysis and specially electrocatalysis. In this way, carbon-sepiolite nanocomposites can act as electrode of rechargeable Li-batteries without requirement of any other conducting additive [5]. These supported graphene-like materials can be also associated to biopolymers with ionic sites, such as alginate or  $\iota$ -carragenate, and act as active phase of carbon paste electrodes (CPEs) for detection of ions without requirement of any other conducting additive as well. Moreover, when the involved clay is sepiolite

further functionalization by treatment with organosilanes makes possible to develop multifunctional materials. For instance, the incorporation of ionizable functional groups, i.e. sulphonic or protonated amines, procures additional ion-exchange properties and the presence of thiol groups makes possible the association to heavy metal ions, additional properties that can be of interest to use the conducting functionalized materials in specific sensors for detection of monovalent and heavy metal ions [4,5].

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## LAYERED DOUBLE HYDROXIDE / HUMIC ACID NANOCOMPOSITES AS PESTICIDES AND HEAVY METALS ADSORBANTS

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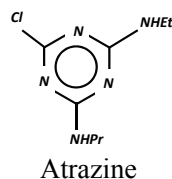
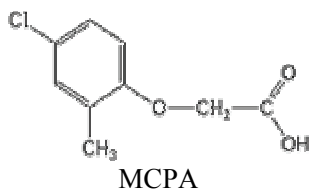
The fate of pesticides in the environment is strongly related to the soil sorption processes that control not only their transfer but also their bioavailability. Contributions of the various organic and inorganic soil constituents to this process are difficult to evaluate, especially because both these fractions are often intimately associated. The various organic and inorganic soil constituents can contribute independently or together to the sorption of pesticides but also to heavy metals. Numerous studies have documented the key role of organic matter, particularly the humic substances as the major component of OM, in the sorption of nonpolar compounds such as AT (10, 11), the main mechanism being hydrophobic partitioning.

In this context, we were interested in studying the interactions between anionic clays and humic substances. The adsorption of humic acids (HA) onto Mg<sub>R</sub>Al-Cl layered double hydroxides (LDH) with R ranging from 2, 3 and 4 was studied by adsorption isotherms. LDH-HA nanocomposites with 5%, 10% and 15% humic acid loading were prepared and synthetic organo clays were fully characterized in terms of chemical, structural, surface and morphology properties.

Adsorption isotherms of humic acid are L-type reflecting a high affinity adsorbate / adsorbent. The mechanism appears to be complex since the ratio Mg/Al had not a regular influence on the capacity of adsorption. Results indicate that the experimental data fit the Langmuir adsorption Isotherm. The LDH appear to be excellent adsorbents for humic acids substances. The removal of humic acid mostly occurred through surface anion exchange reaction without any significant intercalation. Adsorption of HA at LDH platelet surfaces progressively reverse the electrochemical zeta potential of the anionic clay particles, modifying their surface charges. LDH retains part of their anion exchange properties. Moreover, adsorbed humic substances display free acid sites such as carboxylic and phenolic groups allowing complexation of heavy

metals. Consequently, these LDH-HA nanocomposites display both anion and cation exchange properties, of great interests for organic and mineral pollutant retention.

The various LDH-HA complexes were tested with respect to organic pollutants (pesticides) and inorganic ones (heavy metals). Three pesticides were tested: MCPA, mesotrione and atrazine. Modification of LDH materials by humic acid decreased their adsorption capacities towards MCPA and mesotrione. The reverse phenomenon was observed for atrazine and heavy metals ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ).



## SOIL CLAY MODIFICATION WITH SPERMINE AND ITS EFFECT ON THE BEHAVIOR OF THE HERBICIDE FLUOMETURON

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Research on organoclays as sorbents of pesticides has shown the usefulness of these materials both as soil amendments and as pesticide supports, to prolong the efficacy of soil-applied pesticides and to reduce the large transport losses that usually affect pesticides applied in an immediately available form. Organoclays can also be formed “in situ” by direct modification of smectite-rich soil clays through treatment with appropriate organic cations. Thus, Lee et al. (1989) and Rodríguez-Cruz et al. (2007) demonstrated that the addition of alkylammonium cations to soils can enhance the retention of organic pollutants and reduce the leaching through the soil profile. From an environmental point of view, the use of natural organic cations has recently been proposed to minimize their impact once incorporated into natural system (Cruz-Guzmán et al., 2004).

In previous laboratory experiments, we found that spermine-exchanged Wyoming montmorillonite (SW-SPERM) had a high affinity for phenylurea herbicides, such as fluometuron, and that addition of this organoclay to sandy loam and clay soils greatly increased the retention capacity of the soils for such herbicides. Accordingly, SW-SPERM was proposed as a soil amendment to reduce herbicide leaching through the soils and mitigate the risk of ground water contamination.

In this work, laboratory experiments were conducted to investigate the effect of the addition to soil of the natural organic cation, spermine, on sorption, persistence and leaching of the herbicide fluometuron. Our hypothesis was that spermine cations should react with soil smectites, increasing the soil retention capacity and retarding herbicide leaching, that is, an “in situ” slow release herbicide formulation could be formed in soils. For this purpose, three soils with different clay contents and mineralogy were selected. As expected, the increase in fluometuron sorption upon spermine addition was greatest for soil 1, a clay soil rich in smectites, whereas the effect was negligible for soil 3, a soil with a similar clay texture but lacking smectites. Soil 2, a sandy loam soil with moderate smectite content, had an intermediate behavior. Leaching and persistence experiments revealed that coapplication of fluometuron and spermine to the smectite-rich clay soil (soil 1) retarded the leaching of the herbicide, and, interestingly, also prolonged the soil persistence of fluometuron, compared to the application of the herbicide without spermine. In contrast, the presence of spermine had no effect on the leaching pattern of fluometuron in the clay soil lacking smectites (soil 3). Bioassay experiments are in progress to evaluate the weed control efficacy of the coapplication of spermine and fluometuron. The potential usefulness

of spermine treatment for the *in situ* modification of soil clay smectites, with the purpose of enhancing herbicide retention in soils with low retention capacities, is discussed.

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## SYNTHESIS OF ORGANO-CLAYS WITH A NON-IONIC SURFACTANT

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The transformation of clay minerals into organo-clays by the intercalation of surfactant is of great environmental and industrial importance (Gournis et al., 2006). Indeed, the chemical treated clays can trap hydrophobic contaminants and other non-polar organic compounds (NOCs) which are not retained by traditional geochemical clay barriers used in the case of waste landfills (Deng et al., 2003; Guégan et al., 2009). However, the intercalation of surfactant in the interlayer space of the clays implies several and various interactional processes depending on the nature of the surfactant (ionic or non-ionic) that are important and relevant to study and understand.

The aim of this study is to synthesize and to characterize organo-clays by an intercalation of a non-ionic surfactant ( $C_{10}E_3$ ) in a natural (from Wyoming) and a synthetic montmorillonites (Le Forestier et al., 2010). This last non-ionic surfactant differs from previous studies, and displays a lamellar phase consisting to a stack of surfactant molecules aggregated into a 2-D structure (membrane) and layers of water. The nano-composites materials ( $C_{10}E_3$ -clays) were characterized by a set of complementary techniques (adsorption isotherm, ATD-ATG, NMR, DRX, infrared spectroscopy). The synthesized organo-clays show the intercalation of a bilayer of  $C_{10}E_3$ , resulting to the aggregation of non-ionic surfactant membrane in the lyotropic phase on the clay mineral surface which widely expands the interlayer space. The adsorption of  $C_{10}E_3$  differs from cationic surfactants, usually used for the synthesis of organo-clays, and does not depend on any electrostatic interaction and rather is due to weaker interaction processes such as ion-dipole or H-bonds interaction; of which the NMR study allow us to highlight and to quantify.

The resulting organo-clays, produced by a non-ionic surfactant, are stable, display a hydrophobic chemical surface and allow others cations to be exchanged, which is of great importance for the realization of new composites or geochemical barriers in waste landfills since these organo-clays are relevant to attract and retain both NOCs and cationic trace metals.

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## BEHAVIOURS OF CLAY MINERALS IN THE EXTRACTION OF ALBERTA OIL SANDS: AQUEOUS VERSUS NON-AQUEOUS EXTRACTION PROCESSES

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Oil production from the Alberta oil sands, the largest oil sands deposit in the world, is anticipated to increase from the current 1 million barrels per day to 5 million barrels per day by 2030. Currently, the production is based on an aqueous extraction process, which is plagued with many shortcomings most of which can be traced to the effects of clay minerals. The clay minerals in the oil sands alter water chemistry, degrade bitumen recovery and froth quality, and slow down the settling rates of the fine tailings in the aqueous extraction process. As part of an effort to develop a non-aqueous extraction process, the behaviour of clay minerals has been characterized in both a simulated aqueous extraction and a non-aqueous extraction process in this study. X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analyses were used as the main characterization techniques. The XRD results showed the preferential enrichment of kaolinitic clays in the extracted bitumen products. The 2:1 layer clay minerals, on the other hand, were observed to segregate to the other product streams. The HRTEM observations highlighted the role of smectitic clay layers in both aqueous and non-aqueous extraction processes. Clay minerals showed some differences in their behaviour in the absence of water during non-aqueous extraction. For instance, aggregates of clays and organic matter were unaffected in non-aqueous extraction. In general, the results indicated that the amount and nature of clay minerals in different oil sands ores need to be considered in order to optimize both aqueous and non-aqueous extraction processes.

## A METHODOLOGICAL APPROACH TO FOLLOW TRACE ELEMENT MOBILIZATION IN SOILS AFFECTED BY SPILLS. APPLICATION TO THE GUADIMAR SOILS (SW SPAIN)

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The mine accident occurred in 1998 in Aznalcóllar (Iberian Pyrite Belt, SW Spain) as a consequence of the tailing dam failure released about 2 hm<sup>3</sup> of pyrite sludge and 4 hm<sup>3</sup> of acidic water, flooding more than 4000 ha of Agrio and Guadimar riverbanks. The pyrite sludge revealed high contents of As (1000-5500 mg/kg), Pb (3600-12,000 mg/kg), Zn (4400-16,000 mg/kg), Cu (700-2200 mg/kg), Cd (15-50 mg/kg) and Sb (200-1000 mg/kg). Clean-up operations were carried out by removing the sludge and contaminated soils and adding lime, red-soils and organic matter amendments. In this study we present the evolution during a decade of the residual contamination based on the normalization of toxic trace elements to a characteristic one of the pyrite sludge. This methodological approach can be also used to study the sources of such elements.

Ten hectares, which remained highly contaminated after the cleaning operations, were randomly sampled every two years (1999, 2001, 2003, 2005 and 2007, 45 samples). The general characterization of soils consisted in the determination of pH, carbonate, total organic carbon, grain size distribution, mineralogy (bulk and clay fraction) and chemical analyses of major and trace elements. For data analyses, element concentrations were normalized through the formulae:  $NF = (C_x/C_{ref})_{soil} / (C_x/C_{ref})_{sludge}$ , where NF is the normalization factor,  $C_x$  is the concentration of element x and  $C_{ref}$  is the concentration of reference element, in soil and sludge, respectively.

According to the general characterization, the area studied can be divided in two zones: i) the northern part, with minor or absent calcite, showed weak acid pH (5.1-7.1, mean values); ii) the southern, with 3-12 % calcite, is more alkaline (pH = 6.9-7.5). The soil evolution from 1999 to following campaigns showed an increase in pH (particularly in the northern part), a 30% decrease in phyllosilicate content and a loss of clay particles. These results suggest that although remediation actions satisfactorily corrected soil acidity the cleaning works also caused spoilage of soils. On the other hand, pyrite content was depleted from 1999 to 2003 with subsequent absence in following campaigns, as a consequence of oxidative dissolution.

Chemical analyses of trace elements revealed a high heterogeneity of contamination, even in the same sampling hectare. Evolution of very mobile elements (Cd and Zn) displayed a general decreasing trend, particularly in the north part, where pH is more acidic, clay minerals content is lower and smectite is absent. The results for more

immobile elements (As, Cu and Pb) are not clear owing to the soil heterogeneity. In order to reduce this variability the concentration of these elements was normalized to Sb. This element was selected because: i) it is very immobile and conservative in this environment; ii) it is a characteristic element of the sludge and its natural concentration in soil is not significant; iii) the ratio  $C_x/C_{sb}$  in the sludge was constant ( $x = \text{As, Cu or Pb}$ ).

The NF value for As and Pb was around 1 in 1999, which involves that pyrite sludge was the only significant source of these elements in soils. The evolution of NF showed that average concentration of As are being depleted with time, which suggests that it is leaching to subsoil or even to aquatic media. On the contrary, Pb is very stable and its concentration kept constant during the study period. The results obtained for Cu are not clear, but the index values for this element ( $NF > 1,5$ ) suggests that there were other sources for this element, others than the pyrite sludge and the background of soils, such as acidic waters coming from the accident or even caused by flooding events before the accident.

In conclusion, Cd, Zn and As have been leaching for a decade after the mine accident, while Pb is very stable. The evolution of Cu is not clear, but the results showed that there were several sources for this element. The use of Sb as normaliser element has reduced the soil variability caused by remediation actions and by the sampling itself. On the other hand, the NF can be proposed for assessment of contaminated sites provoked by mining or industrial spills.

## AMMONIUM CHLORIDE TRANSPORT THROUGH DIFFERENT NATURAL CLAY BARRIERS

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Landfill leachate is generated by excess rainwater percolating through the waste layers in a landfill when soluble components are dissolved out of a solid material by percolating water (Salem and others, 2008). Leachate from urban landfills may contain a wide range of contaminants but  $\text{NH}_4^+$  and  $\text{Cl}^-$  concentrations remains the same value with the age and represent the dominant inorganic components in the aqueous phase (Pivato and Raga, 2006). Then, based on average composition of leachates from old landfills, a synthetic composition was formulated to be used in transport experiments through clays:  $\text{NH}_4\text{Cl}$  0.25 M,  $\text{NaOAc}$  0.15M and  $\text{NaHCO}_3$  0.1M, pH 7.8.

Several Spanish ceramic clays were characterized for hydraulic and several geochemical properties (mineralogy, cation exchange capacity and specific surface area). Although all the clays fulfilled the hydraulic conductivity (HC) requirements ( $< 1 \cdot 10^{-9}$  m/s at the optimum density/moisture conditions: aprox. 2 kg/dm<sup>3</sup> : 15 % moisture), significant differences were observed for the advective transport behaviour of anions and cations. The experiments were performed with the synthetic leachate thorough the compacted clays at similar HC. Mixtures of sand/bentonite were also used in order to test the feasibility of improving the barrier performance properties of natural raw clayey materials.

As a general rule, when clays contained smectite ( $< 20$  %) both anions and cations were retained during the transport of 5-6 pore volumes. However,  $\text{NH}_4^+$  is selectively adsorbed and retained. This was not the case for clays, either kaolinitic or illitic, when smectite was absent (Cuevas et al., 2008). In these clays Chloride and ammonium front is detected after 1-2 pore volumes without selective retention of cations. Anion exclusion and cation exchange can explain this effect when a high specific surface smectite mineral is present. Even when a commercial bentonite is added in minor quantities (2%) to reconstituted arkoses composed of 10 % fines ( $< 50 \mu\text{m}$ ) and 90 % sand ( $< 2 \text{ mm}$ ), HC and ion retention became critically improved. Furthermore, 5 % additions of bentonite to sand are enough to set the HC values to the established requirements. As a consequence, geochemical properties of smectite are unique for the design of clay barriers.

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## BASAL SPACINGS OF SMECTITE IN COMPACTED BENTONITE

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In many countries employing nuclear power, deep geological disposal is an option for the long-term confinement of heat-emitting high-level nuclear waste. The construction of deep repositories will involve the excavation of a network of tunnels in a suitable host rock a few hundred meters below surface. The canisters containing nuclear waste will be placed in either horizontal drifts or vertical boreholes. Around the canisters, a sealing material, also called engineered barrier, will be placed. Most repository concepts opt for compacted expansive clays, particularly bentonite, to construct this barrier, because of their low permeability, high swelling capacity and retardation properties. The bentonite will be used with its hygroscopic water content, what means that initially the barrier will be unsaturated, *i.e.* the pores of the barrier will be filled with air and water. The barrier will interact with the groundwater and eventually will become saturated. In order to analyse the hydration mechanism of compacted bentonite, which is a key process to be understood for assessing the performance of engineered barriers, the interlayer distance of the smectite has been measured in samples of compacted bentonite with different degrees of water saturation. Although there is extensive literature on the influence of relative humidity and exchangeable cations on the basal spacing of pure, powdered smectites, there is not much information on the variation of this parameter for natural bentonites compacted at different water degrees of saturation.

This work analyses the basal spacings measured in samples with different water contents of bentonite compacted at various dry densities. The materials used were two natural bentonites composed mainly of montmorillonite, one of them with a predominance of divalent cations in the exchange complex (FEBEX bentonite), and the other one with predominance of exchangeable sodium (MX-80 bentonite). They were prepared in two different ways. To prepare some of the samples, the powdered bentonite was mixed with water and subsequently compacted to different dry densities between 1.0 and 1.8 g/cm<sup>3</sup> and let to stabilise for different periods of time. Other samples were manufactured by compacting the powdered clay with its hygroscopic water content and they were later saturated to different degrees of water saturation either with liquid water or with water in the vapour phase. The two kinds of samples were finally X-rayed to determine the smectite basal spacing. For that, a sufficiently flat surface of the samples was X-rayed at room temperature without any previous treatment. The position of the peaks was adjusted by using the quartz in the samples as an internal pattern.

For a wide range of water contents, between 14 and 29 percent, the basal spacings measured were around 15 Å, indicating the predominance of a 2-layer hydrate in



the interlayer. For higher water contents, the basal spacing gradually increased, the highest values measured being around 20 Å for water contents of 37 percent and dry densities of 1.35 g/cm<sup>3</sup>, what corresponds to almost fully saturated bentonite. On the other hand, the lowest basal spacings, slightly below 13 Å and corresponding to predominantly mono-hydrated smectites, were measured for water contents of about 8 percent. The transition between the 2-layer and the 1-layer hydrate state took place gradually in the range of water contents between 14 and 8 percent. Evidently, samples with water contents close to 0 had basal spacings around 9.5 Å. These observations seem to be rather independent on the kind of bentonite, dry density, way of saturation, and even temperature, since some of the samples were submitted to temperatures higher than 60°C prior to X-raying.

## ADSORPTION AND INTERCALATION OF CIPROFLOXACIN BY MONTMORILLONITE AND RECTORITE IN AQUEOUS SOLUTION

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Swelling clay minerals play important roles on the fate and transport of certain antibiotics detected in the environment, which creates potential impacts on ecosystems without a proper watch. This research determined the adsorption and intercalation properties of ciprofloxacin (CIP), a second-generation antibiotic, on montmorillonite (SAZ-1; CEC = 123 meq/100g) and rectorite (41 meq/100g) in aqueous solutions with initial CIP amounts up to 0.98 and 1.47 CEC. Adsorption experiments showed that most of the initial CIP were adsorbed within a reaction time of 24 h and the rate constants of CIP adsorption on montmorillonite were 37 times greater than those on rectorite under the various conditions studied. The maximum CIP adsorption capacities for montmorillonite and rectorite were evaluated as 1.00 mmol/g and 0.38 mmol/g, corresponding to 0.81 and 0.92 CEC, respectively. FTIR spectra revealed that two ends of the CIP molecule adopted electrostatic attraction and hydrogen bonding with the clay surfaces through its specific protonated amine group and carboxylic acid. Maximal amounts of replacement of exchangeable cations by CIP were 0.77 CEC of the montmorillonite and 0.87 CEC of the rectorite but the maxima of layer expansion occurred at replacements of 0.66 CEC and 0.83 CEC, respectively, as determined by XRD. The adsorption by montmorillonite showed a positive linear correlation between the total amount of the charges of desorbed exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and the quantity of the adsorbed CIP with a small parallel shift from the 1:1 line toward slightly greater CIP adsorptions whereas the rectorite adsorption exhibited a 1:1 relationship but a somewhat reduced slope at CIP adsorption levels greater than 0.85 CEC. Both adsorbed CIP and CIP-intercalated clays showed greater thermal stability as relatively high CIP decomposition temperatures and large dehydroxylation temperatures of the clay phases were recorded. The data imply that both montmorillonite and rectorite are highly effective sorbents and removers of CIP and their adsorption processes are principally dominated by a cation exchange/intercalation mechanism with different minor contributions from a surface adsorption/complexation mechanism probably due to differences in the distributions of layer charges and non-exchangeable cations between the montmorillonite and rectorite.

## *POSTER PRESENTATIONS*



## ADSORPTION OF THE HERBICIDE CLOPYRALID BY CHITOSAN-INTERCALATED MONTMOTILLONITE

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The environmental problems caused by increased pesticide use in the last decades have become a matter of growing concern. The mobility of pesticides affects soil and water quality, food chain and ultimately humans. This has led to increased research to minimize the adverse environmental effects of pesticide use. Since the last decade, nanocomposites and bionanocomposites have become materials of increasing interest due to their structural or functional behavior. One of the polymers used to prepare bionanocomposites is Chitosan (CH), poly- $\beta$  (1,4)-2-amino-2-deoxy-D-glucose, a natural cationic polymer found in the exoskeletons of crustaceans and insects and fungal cell wall and microorganisms.

Previous work has shown that CH can be intercalated in montmorillonite and that the resulting montmorillonite-CH bionanocomposite can act as an anionic exchanger, showing a higher selectivity toward monovalent anions (Darder *et al.*, 2003). The aim of this work was to evaluate the ability of montmorillonite-CH bionanocomposites to adsorb the anionic pesticide Clopyralid (3,6-dichloropyridine-2-carboxylic acid), which could find application in the prevention and remediation of soil and water affected by the presence of anionic pesticides.

Low Molecular Weight CH (Sigma-Aldrich) was intercalated in SWy-2 Wyoming montmorillonite (The Clay Minerals Society) under different conditions, and the resulting montmorillonite-CH (SW-CH) complexes were assayed as adsorbents of Clopyralid at different pH levels, contact times, and initial pesticide concentrations. Desorption of the pesticide from SW-CH samples was also characterized using different extracting solutions.

In contrast to the negligible adsorption of Clopyralid by the unmodified SWy-2 montmorillonite, the SW-CH bionanocomposites were good adsorbents for the herbicide, although adsorption occurred only at pH levels where both the anionic form of the herbicide ( $pK_a = 2.1$ ) and the cationic form of CH ( $pK_a = 6.3$ ) predominated (i.e., pH 3-5). Adsorption of Clopyralid by SW-CH was rapid and mostly linear up to herbicide concentrations as high as 100 mg/l. High salt concentrations (0.1 M NaCl) promoted desorption of the adsorbed pesticide from SW-CH, thus indicating adsorption of Clopyralid occurred through an ion exchange mechanism on positively charged CH sites at the montmorillonite surface.

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## ALGERIAN BENTONITE AS ADSORBENT FOR THE REMOVAL OF HEAVY METAL IONS FROM THE AQUEOUS SYSTEM: APPLICATION IN WASTEWATER TREATMENT

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A sample of bentonite from Mostaganem (N.W. Algeria) was characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated bentonite was used as adsorbent for four heavy metal ions from aqueous solutions by mean of batch experiments. The effect of shaking time, pH of aqueous solution, metal concentration and adsorbent amount was studied. The effective pH range was from 4 to 6 for these metals. It was found that Algerian bentonite had significant removing potential for  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  ions from aqueous solutions.

## COMPARATIVE ASSESSMENT OF THE ADSORPTION OF PAHS ON CLAYS AND INDUSTRIAL WASTES

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The need to prevent and restore the pollution of aquatic ecosystems has motivated new lines of investigation to look for suitable materials for use as adsorbents. Polycyclic aromatic hydrocarbons (PAHs) represent a group of pollutants of anthropogenic origin, widely present in many soil-air-water ecosystems. Most of them are highly hydrophobic and low solubility compounds, but those with a low molecular weight (2 – 4 aromatic rings) often involve a high water pollution risk. Hence, the aim of the present paper is a comparative assessment of two cationic and one anionic clay minerals with several materials of diverse nature and origin as adsorbents of low-molecular weight PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene).

The clay minerals selected were: 1) a bentonite clay from Zamora area (NW Spain), 2) an organoclay: phyllosilicate modified with the organic cation hexadecyl trimethyl ammonium (SA-HDTMA) and 3) a layered double hydroxide modified with the organic anion dodecylsulfate (HT-DDS). Also, two mineral industrial wastes (gypsum and wollastonite) and an organic industrial waste (OIW) were used as adsorbents.

Adsorption-desorption experiments were carried out to study and compare the capability of the above mentioned adsorbents to uptake the selected PAHs from aqueous solution. Duplicate adsorbent samples and PAHs solutions were shaken at room temperature, for 24 h, and the supernatants were centrifuged and separated to determine the concentration of PAHs. The amount of PAHs uptaken by the samples was monitored by the batch equilibration technique using high performance liquid chromatography with fluorescence detector (HPLC-FL). The results indicated a very low amount of PAHs adsorbed on the inorganic adsorbents (bentonite, gypsum and wollastonite) compared with that on organic adsorbents (SA-HTDMA, HT-DDS and OIW). The organic phase in the interlayer increased the affinity of the clays for PAHs, as well as the organic nature of OIW.

Adsorption isotherms, carried out varying PAHs concentration (from 1 to 50 ppb) with the three organic adsorbents, along with Freundlich parameters, were of C-type according to the classification of Giles et al. (1960). It is interesting to note that isotherms and  $K_f$  values suggested greater affinity of the PAHs for SA-HDTMA and HT-DDS than for OIW. Furthermore, SA-HDTMA and HT-DDS showed no significant differences in PAH adsorption capacity. Moreover, the affinity of the adsorbents is greater in all the cases for high-molecular weight PAHs, even reaching up to 100% of



fluoranthene and pyrene adsorption on both organoclays (HT-DDS and SA-HDTMA). In these cases, it has not been possible to apply the Freundlich model.

Finally, desorption curves showed very high hysteresis in most cases, reflecting an elevated irreversibility of the adsorption process. This can be interesting from the point of view of the applicability of these materials as adsorbents of PAHs for their immobilization in polluted soils

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## ADSORPTION – INTERCALATION OF NAPHTALENE DERIVATES BY LAYERED DOUBLE HYDROXIDES

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Layered Double hydroxides (LDHs) are found application as sorbents and catalysts. Their use is especially effective as sorbents of organic compounds from liquid phase. The development of effective methods of adjusting of processes of activating and modification of mineral sorbents with the purpose of increase the degree of cleaning of sewages has an important theoretical and applied value.

This work is devoted to research on structural and adsorption properties LDHs, with the aim to adjusting the processes of their activation and modification.

interlayer distance in LDHs depends mainly on nature of anions and molecules of solvates in internal space of LDH, and also on the degree of isomorphous substitution.

Adsorption of organic compounds on LDHs, depending on the structure of organic molecule, can undergoing both the process of physical sorption and ionic exchange. In first rough activity and selectivity of process of the sorption is determined on the specific surface and size of pores, in the second - by the concentration of active centers on the surface of sorbent and their availability for the molecules of substrate. At the anion-exchange interlayer distance in LDHs can change widely that is does not observed at physical sorption however, to our opinion, this process can take a place too.

The purpose of our work was to research the processes of physical sorption and anionic exchange on LDHs of variable composition, and also to study of changes in the structure, basicity and sizes of interlayer space because of sorption processes.

LDHs of variable composition were obtained with different amount of  $Mg/(Mg+Al)$ : 0,72; 0,81; 0,86 mol/mol.

We have used amile alcohol, phenol, naphthalene and  $\beta$ -naphthole as sorbates. A specific surface was determined the BET method.

Measurements of sizes of interlayer space were conducted by X-ray analysis.

Research of sorption of amile alcohol showed that alcohols reacted with LDHs by the reaction of anionic exchange, with establishment of equilibrium. Time of equilibrium establishment depends on rate of process of intercalation of alcohols in the interlayered space with the simultaneous moving apart of layers and reorientation of

hydrocarbon radicals. At increase of length of hydrocarbon radical, with achievement of number of atoms of carbon, equal 5, there is an increase of interlayered distance.

Sorption of naphthalene is a process of physical sorption, and  $\beta$ -naphthol, as well as phenol, participate in an anionic exchange. A phenol and  $\beta$ -naphthol are prepotent acids, and the process of sorption takes a place considerably quickly, than for alcohols.

The aromatic rings of the adsorbed naphthalene are disposed parallel to the inorganic layers, regardless of concentration of active centers. The size of interlayered distance in our LDHs is about 7 Å. This size of comports with the «thickness» of aromatic ring, making 3,5 Å, while a diameter of molecule of benzol is 7,1 Å.

And for a phenol and  $\beta$ -naphthol trivial-parallel location is observed only in the initial stage of ionic exchange. An effective area of  $\beta$ -naphthol is 9,89 Å<sup>2</sup>, that considerably less size of one active site ( $\sim 16$  Å<sup>2</sup>), that it is possible to suppose absence of blocking of sites organic molecules. An equilibrium, attended with the increase of interlayered distance and increase of number of active site accessible for the next molecules of  $\beta$ -naphthol, is set in future. This process is accompanied the increase of specific surface of LDH.

## MECHANISMS OF CO<sub>2</sub> INTERACTION WITH EXPANSIVE CLAY

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Clays represent abundant geomaterials with well-developed microporous structure. The objective of this project is to evaluate the GHG (greenhouse gas) sequestration potential of clayey materials and to investigate what factors affect the sorption capacity, rates, and permanence of CO<sub>2</sub> storage in these solids. For these studies, we used the source clay samples from The Clay Minerals Society repository as well as the field samples collected in the Lovell-Greybull area of Wyoming, USA.

Preliminary study showed that expansive clays have the CO<sub>2</sub> sorption capacity comparable to or even greater than the sorption capacity of coal. Availability of the CO<sub>2</sub> sequestration options depends on various external factors, specific surface area, trapping mechanisms, and the kinetics of sorption. The interlayer surface area of clays is several times larger than the values for the external surface area reported in the literature. However, the penetration of CO<sub>2</sub> molecules into the interlayer region has not been sufficiently well investigated.

We collected and systematically analyzed the XRD, DRIFTS (infrared reflectance spectra), and TGA-MS (thermal gravimetric analysis) data to compare the effects of various factors on CO<sub>2</sub> trapping. To interpret the experimental data, we performed computer simulations of CO<sub>2</sub> interaction with free cations (normal modes of CO<sub>2</sub> and Na<sup>+</sup>CO<sub>2</sub> were calculated using B3LYP / aug-cc-pVDZ and MP2 / aug-cc-pVDZ methods) and with clay structures containing interlayer cations (molecular dynamics simulations with Clayff potentials for clay and a modified CO<sub>2</sub> potential).

Our preliminary conclusion is that CO<sub>2</sub> molecules may indeed intercalate into interlayer region of swelling clay and remain there via coordination to the interlayer cations.

## REMOVAL OF PESTICIDES FROM WATER BY USE OF ORGANOHYDROTALCITE

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The development of new adsorbents to be use in the decontamination of water is a research subject of current interest which has arisen from a rise the use of plaguicides to increase agricultural production and provide an adequate food supply for the increasing world population. Hydrotalcite type compounds have specific properties to be used as anionic and non polar pesticide adsorbents. The great interest in this type of compounds as adsorbent materials is mainly related to their layered structure, the ease with which they are synthesized and the possibility of modifying their surfaces to increase their affinity for specific adsorbates

The hydrotalcite materials are also known as layered double hydroxides (LDHs) since their structure is described as a layered hydroxide of  $CdI_2$ -type. The hydrotalcite compound consists of brucite-layers,  $Mg(OH)_2$ , with partial isomorphous substitution of  $Mg^{2+}$  for  $Al^{3+}$ . The positive charge thus generated in the hydroxide sheets is compensated with hydrated carbonate anions in the interlayer region. These anions in hydrotalcite can be ion-exchanged with others present in aqueous solutions.

Its composition corresponds to the general formula:  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}X^{m-}_{x/m} \cdot nH_2O$ . The intercalation of hydrophobic molecules in the interlayer changes its nature from hydrophilic to hydrophobic and makes these materials capable to adsorb molecular or non-polar contaminants.

This work reports the adsorption of two types of non polar plaguicides: Alachlor and Metolachlor on Organohydrotalcite with Sebacate anion (SEB),  $[Mg_6Al_2(OH)_{16}]SEB \cdot nH_2O$  (OHT). Adsorbents and adsorption products were characterized by X-ray diffraction, FT-IR spectroscopies and thermal analysis. The amounts of pesticides removed from water were determined by UV-Vis spectrophotometry.

The results indicate that the adsorption capacity of OHT depends on the structure and size of the adsorbed molecule and is not affected by the pH solution. The isotherms are L type which indicates there is a high affinity between solute and adsorbent. For Alachlor a higher level of adsorption on OHT was observed than for Metolachlor ( $C_s \approx 0,41 \text{ mmol/g}$  vs  $C_s \approx 0,27 \text{ mmol/g}$ ). The capacity of OHT to adsorb Alachlor is higher than for Metolachlor. The adsorption of pesticides on OHT is

confirmed by the changes of the interlayer space from  $d \approx 15 \text{ \AA}$  to  $d \approx 20 \text{ \AA}$  as well as by the presence of pesticides bands in the FT-IR spectra.

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## UPTAKE OF ORANGE-10 BY CALCINED Mg/Al LAYERED DOUBLE HYDROXIDES

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The rapid growth of the world economy has caused environmental disorder with a huge pollution problem. The demand for water has increased tremendously in agricultural, industrial and domestic sectors. And this has resulted in the generation of large amounts of wastewater with a high number of contaminants. Many industries such as textiles, paper and plastic use dyestuffs in order to colour their products and they also consume substantial volumes of water. Colour is the first contaminant to be recognized in wastewater. Due to their good solubility, synthetic dyes are common water pollutants and they are frequently found in industrial wastewater. Two per cent of generated dyes are discharged directly in aqueous effluent. Consequently, restriction on the organic content of industrial effluents is necessary so that dyes are removed from wastewater before being discharged. However, this type of contaminated water is very difficult to treat given that dyes are resistant to aerobic digestion and are stable to light heat and oxidizing agents. Due to their low biodegradability, dyes are generally removed from aqueous solutions by a sorption process using activated carbon. The high cost of this process led to numerous studies on alternative removal methods using less expensive natural materials and waste by-products.

Among the different sorbents, layered double hydroxides (LDHs) are promising waste carriers due to their high anionic exchange capacities and high layer charge densities, both of these characteristics favour strong interaction with anion pollutants. The LDH consists of brucite-layers,  $\text{Mg}(\text{OH})_2$ , with partial isomorphous substitution of  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$ . The positive charge thus generated in the hydroxide sheets is compensated with hydrated carbonate anions in the interlayer region. These anions in hydrotalcite can be ion-exchanged with others present in aqueous solutions. Its composition corresponds to the general formula:  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{X}^{m-}_{x/m}\cdot n\text{H}_2\text{O}$ . The carbonate anions have shown strong affinity for the layers of hydrotalcite compounds, which cannot be easily exchanged by other anions, limiting their use as sorbents for anionic pollutants. However, the capacity of their calcined products to regenerate the LDH structure upon rehydration with the suitable anions present in solution may be used to remove the anions species.

The objective of this work is to study the uptake of the acid dye orange-10 on calcined Mg/Al hydrotalcite with different crystallinity and the kinetic of the adsorption process. The adsorbents and the adsorption products were characterized by XRD, FT-IR spectrophotometry, Thermal Analysis and Electronic Microscopy.

Different factors have been studied: the influence of pH values, dye-adsorbent contact time, various temperatures of the experiments and the crystallinity of the pristine HT. Three calcined samples with different grade of crystallinity have been prepared. The results have shown a decrease in adsorption with the decrease of HT crystallinity. The higher values of adsorption have been obtained at pH=4 in agreement with the adsorption of other anionic species. The kinetic data showed that the uptake of the orange-10 was a rather fast process and that was equilibrated after 6h for HT500B for 400mg/L solution of dye, whereas for HT500 was 24h. The adsorption isotherms are described by Langmuir model due to the homogeneity of the surface and the isotherms were L-type. The values of  $C_m=1,447$  mmol/g for LDH more crystalline against to 0,885 mmol/g and less for poor crystalline adsorbents.

To obtained additional information for later application the direct synthesis with orange 10 like interlayer anion have been carried out. The intercalation of the organic ion was clearly evidenced by the net increase in the basal spacing from 7,69 Å for HT-CO<sub>3</sub> to 16,8 Å for the organic derivative.

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## KEY PROCESSES AFFECTING THE PORE WATER CHEMISTRY IN BENTONITES: COMPARISON BETWEEN THE MX-80 AND FEBEX CLAYEY MATERIALS

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A knowledge of the pore water chemistry in the bentonite barrier is one of the main issues for performance assessment of nuclear repositories, since the pore water composition strongly influences the release and transport of radionuclides. However, quantification of the water chemistry in compacted bentonite under repository conditions is difficult. This study reviews the advances on the study of the pore water chemistry of expansive clays. A comprehensive understanding on the key parameters affecting the pore water composition, the groundwater-bentonite interactions, and the geochemical processes in the near field of an engineered barrier system (EBS) is overviewed, taking into account the influence of microstructural features of the bentonite. This review is focussed on two different bentonites, the MX-80 bentonite, a Na-smectite; and the FEBEX bentonite (a Ca-Mg-Na smectite), due to their different physico-chemical and swelling behaviour in the bentonite-water system. Both bentonites are the main reference materials in different countries as a backfill and sealing material in high-level radioactive waste disposal (HLW) concepts.

The characterization of the mineralogical and geochemical properties of bentonite, the properties of smectite surfaces exposed to migrating solutes and radionuclides and the water-rock interaction processes are required for understanding the complex interactions between water, bentonite and solutes. The major mineral phase of the MX-80 and FEBEX bentonites (75 and 92 wt. %, respectively) is a montmorillonite (dioctahedric aluminic smectite with a 2:1 structure). In spite of its high smectite content, the bentonite contains numerous accessory minerals. Among others, silica may dissolve close the canister due to high temperature (or high pH), and transported by diffusion outwards into the outer parts where precipitation may take place affecting to the porosity. The presence of siderite and pyrite are of paramount importance for the redox control of the system under oxidized or reducing conditions.

In order to calculate the pore water chemistry, a geochemical modelling has been performed, in which the exchangeable cations, the soluble salts and the mineral equilibrium of different phases observed determine the chemistry of the pore water, and the pH of the pore water is buffered by the surface hydroxyl sites. An important issue in calculating the pore water chemistry is to distinguish between the types of water, their distribution in the clay/water system (absorbed water, interlayer water and pore water), and the respective volumes accessible to cations and anions. The volumes of free water or external water per kg of bentonite are required to know the chloride concentration from the Cl inventory. In the procedure for the case of MX-

80, the free water in compacted bentonite is equivalent to the accessible porosity determined from diffusion tests, which is similar to the determined external porosity. In the procedure employed for the FEBEX bentonite, the free water is equivalent to the external porosity calculated from water adsorption isotherms and statistical calculations.

The pore water chemical composition is controlled by dissolution/precipitation reaction of trace minerals of the bentonite, exchange reactions and the S:L ratios involve in the system. The results obtained as a function of the dry density indicate that at saturated repository conditions, the pore water chemical composition of the MX-80 varies as a function of the dry density from Na-SO<sub>4</sub> water type to Na-Cl-SO<sub>4</sub> water type, with a pH around 8.0 and an ionic strength of 0.3 M. For the FEBEX bentonite, the pore water is Na-Cl water type, increasing the Cl concentration to 2.5 M as a function of the dry density; the pH is between 7.4 to 7.6 and the ionic strength ranges from 0.2 M to 2.5 M. Here we can see the differences in the pore water chemistry from both types of bentonites. The salinity content is quite different, being the FEBEX bentonite the most saline with a higher amount of chlorides.

## CHLORITE FORMATION AT 90 °C BY DIFFUSION OF HYPERALKALINE FLUIDS THROUGH COMPACTED BENTONITE

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Cement and concrete will be used in the construction of geological disposal facilities for radioactive wastes. The hyperalkaline fluids typical of the cement porewater will interact with the bentonite buffer material (engineered barrier), potentially degrading its performance. The diffusion reaction of a synthetic K–Na–OH solution at pH 13.5, representative of the early leaching stage of cement degradation, was studied at 90 °C with a compacted Mg-saturated bentonite column (with dimensions of 2.1 cm length and 7.0 cm diameter, and dry density 1.65 g/cm<sup>3</sup>) for 3 independent time periods (6, 12 and 18 months). Mineralogical and physico-chemical post-mortem analyses were studied on bentonite as a function of distance from the hyperalkaline interface sectioning the column in subsamples of 0.35 mm to 2 mm, according to the reaction time and the expected reactivity in each section.

The mineralogical alteration was limited. A cemented rim of irregular distribution was localized at the interface with an averaged thickness of 2 mm. The reaction is kinetically controlled since the extension of the alteration is not linear with time, nevertheless, mineralogical changes are better observed after 18 months. Brucite precipitation is observed at the interface but also intercalation of brucite in the interlayer of montmorillonite is detected as a consequence of the magnesium reaction with the hydroxide, forming chlorite-type structures. The formation of chlorite is almost complete although X-ray diffractograms also show presence of unaltered montmorillonite. Other than this mineralogical alteration, only traces of analcime were detected in the cemented rim and at inward thicknesses (2–4 mm).

The results on BET surface area decrease notably in the cemented rim and in lower degree beyond this alteration zone, which could indicate partial clogging of the porous medium along the whole bentonite column, hindering the cation diffusion with respect to previous experiments performed at 60 °C. The decrease in BET surface would also agree with the formation of chlorite-type phases with similar morphology to the pre-existent montmorillonite but with lower surface areas, due to the growth of laminar sheets.

K and Na, however, diffuse through the interlayer of montmorillonite displacing Mg over the whole column length. Nevertheless, the pH at the end of the column remains in the range of 8–9. The overall cation exchange capacity (CEC) decreases heterogeneously as a function of distance from the alkaline interface but within a range 0–20% with respect to the reference Mg-bentonite. Under these circumstances,

the swelling capacity, not determined in this study, should decrease accordingly, proportionally to the CEC.

The mineralogical and physico-chemical characterization performed on the samples indicates that the basic structure of the clay changed after the precipitation of  $\text{Mg}(\text{OH})_2$  (either as chlorite or brucite), but was not destroyed. Montmorillonite dissolution is relatively low and heterogeneous at 90 °C.

The observed nano-scale crystallization do not imply important mineralogical changes but could modify the mechanical properties, which indeed, could be the key factor to determine the maximum temperature to be reached at the cement–bentonite contact in the repository system for the optimum performance of the engineered barriers.

## THE INFLUENCE OF RAW MATERIALS IN CO<sub>2</sub> EMISSIONS IN THE BRICK INDUSTRY. THE CASE OF ANDALUSIA (SOUTHERN SPAIN)

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The study of atmospheric contaminating emissions from ceramic industries represents an important challenge for those groups which are responsible for the enforcement of the new (EU) European Community environmental protection policies, and more specifically with the Guideline 96/62/CE for the management and evaluation of air quality. In order to fulfill these guidelines, it is necessary to conduct various partial studies which include research on the origin of the pollution and all of the factors potentially involved. In this way, pollution can be controlled and reduced at the same time.

The main emissions generated during the firing process of the raw materials, in other words clay, are: suspended particles (PS), Fluoride (F), Chlorine (Cl), Nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>). Emissions can be reduced by interceding in the production process, whether by modifying or substituting the raw materials, the type of fuel used, or by installing filters in the factory's chimneys. The most significant carbon dioxide emissions come from the fuel used, but emissions are also due to the decomposition of the carbonates and/or organic material, depending on the composition of the raw materials.

In this work, the possible CO<sub>2</sub> emissions released into the atmosphere during the firing of the ceramic raw materials (clays, marls, shales) used in structural ceramics in Andalusia have been evaluated. Twenty-two representative raw materials samples and their respective fired products have been taken from the Andalusian factories with the greatest production. A mineralogical characterization by X-ray diffraction was performed. The quantification of the carbon dioxide emitted was done by calcimetry (Bernard's calcimeter), element analysis of C (LECO CHNS 932) and by assessing the organic material oxidizable with potassium dichromate (Black's method).

The raw materials are composed of phyllosilicates (mainly illite and smectite) (25-40%) calcite (0-45%), and quartz (25-40%). In lesser proportions, feldspar, dolomite and gypsum were also found. In some samples, kaolinite, pyrophyllite, chlorite, paragonite was detected. The fired products had a mineralogical composition of quartz, plagioclase, mica, gehlenite, wollastonite, kilchoanite in carbonate-rich samples. In those Mg-contain samples (dolomite and smectites) diopside can sometimes be formed. The presence of calcite has not been detected in the fired products. The data obtained from the calcimetry, for those products, indicates that

the  $\text{CO}_2$  is  $<2\%$ . In those special ceramic products which use sericitic shales and kaolinite raw materials, mullite and quartz are the main high temperature phases.

The organic material content is low in all the samples, except in those where sericitic shale is used when producing ceramic pieces, thus they cannot be considered a significant source of  $\text{CO}_2$  emissions. Furthermore, due to the nature of their products, these factories make mixtures without carbonates, which mean that the  $\text{CO}_2$  emissions are less than 1%.

The other factories studied, which represent more the 90% of the total Andalusian industries, can be classified, on the basis of the carbonate contents of the unfired brick and the firing temperatures as follows: a) factories firing products with carbonate content under 20%, regardless of the firing temperature, which have  $\text{CO}_2$  emissions around 5%; b) those which raw materials have a carbonate content raging between 20 and 30%, in these cases the emissions can reach up to 9% especially in those factories where they are fired above 900 °C and c) factories preparing products with carbonate content above 30%, in which case the emissions are high and can even reach 17%. So, given that the production of ceramic materials in Andalusia is very high, and more than 80% are manufactured with raw materials which have a carbonate content of 10-25%,  $\text{CO}_2$  emissions from these industries is significant. In order to diminish these emissions, the compositions of the raw material mixtures should be modified.

## COMPARISON OF WELL-LOG DERIVED MINERAL QUANTITIES WITH XRD RESULTS

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Variation in mineral abundances in the subsurface influences petrophysical properties and other characteristics of hydrocarbon sealing sequences and reservoirs. In geophysical well logs, various proxies, such as gamma ray emission and neutron absorption, are used to assess changes in mineral composition. This study compares X-ray diffraction measurements of mineral percentages in core samples with those derived from well logging. Samples were obtained from a core in the Northern Gulf of Mexico. Whole sample rock powders and mineral intensity factors were used to convert integrated peak areas to relative percent abundances for Quartz, Feldspar, Calcite, Dolomite, Gypsum, Siderite, and Total Clay. Well log values used for comparison were Dry Weight Fraction Clay, Dry Weight Fraction Carbonate, Dry Weight Fraction Anhydrite/Gypsum, Dry Weight Fraction Pyrite, Dry weight Fraction Siderite, Dry Weight Fraction Quartz+Feldspar+Mica, Dry Weight Fraction Coal, and Dry Weight Fraction Salt. A linear correlation analysis was used to assess covariance among the XRD and the log results.

A wide range of mineral correlation values were generated by a 21 x 21 matrix. Mineral correlation factors of  $\geq |0.6|$  were only considered significant. The results yielded seven pairs of significant coefficients, 5 from the XRD analysis and 2 from the well log quantities. The XRD observed results produced: a negative correlation of %Clay to %Quartz (0.98), a negative correlation of %Clay to %Feldspar (0.65), a negative correlation of %Clay to Quartz+Feldspar Fraction (0.98), a positive correlation of %Quartz to %Feldspar (0.63), and a positive correlation of %Calcite to Carbonate Fraction (Dolomite+Calcite+Siderite) (0.86). The log results produced a negative correlation of Dry Weight Clay Fraction to Dry Weight Fraction Quartz+Feldspar+Mica of (0.81) and a positive correlation of Dry Weight Fraction Carbonate to Dry Weight Fraction Siderite of (0.73).

The best correlation in each group of data is simply due to quartz and clay being the major constituents in the sample. The lack of correlation between any well log variables and any XRD result is an indication of poor calibration. Clay and quartz values for the two measurement techniques cannot be compared. Examination of the quartz abundance data reveals very different ranges in the analytical values. XRD Quartz+Feldspar varies from 15.67% to 74.70% with an average of 32.92%, while log Quartz+Feldspar+Mica ranges from 58.85% to 74.92% with an average of 65.07%. Log quartz values may not be as sensitive to the small scale variability detected with the XRD procedures. Additional studies are underway to determine how the calibration of log and XRD values can be established when actual clay species are used.

## STUDIES ON ADSORPTION AND DIFFUSIVITY OF PHENOL IN ANIONIC CLAYS

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This work is devoted to study the sorption processes of phenols by synthetic clay minerals of different composition.

Solving the problem of preventing contamination of the environment depends on the successful solution of the problem of industrial wastewater from pollutants, especially from phenols [1]. Therefore becomes more urgent problem of pollution of natural waters, the growth in waste water and the search for effective methods of cleaning them.

The purpose of work is the search for new anionic sorbents. The application of this sorbent would allow to effectively remove of phenols from wastewater.

The most promising sorbents are those based on double hydroxides of metals with the structure hydrotalcite. They are cheap, accessible and effective, universal sorbents, and they have a high absorption capacity, resistance to environmental stress and can serve as excellent carriers for fixing on the surface of various compounds with their modification.

The using of clay minerals with 2:1 structure type and the changing value of the basal interlayered distances are very effective. Water molecules, as well as the positive and negative ions can be adsorbed in interlayer space of these minerals. Therefore it is possible to place large ions between layers and forming columns. So we can create a system of pores where various small molecules can be placed. The pore sizes resulting in the intercalation process are about several tenths of nanometers. The samples were synthesized with the following ratios of cations in the matrix:  $Mg/(Mg+Al) = 0,52; 0,72; 0,81; 0,86$ .

The specific surface of LDHs was determined by low-temperature nitrogen adsorption chromatographic method with subsequent processing of the results obtained by BET method.

The change of interlayer distance in LDHs after the adsorption of phenol, were investigated.

Adsorption capacity of the obtained sorbents was investigated in the reaction of phenols with LDHs different composition of general formula  $Mg_xAl_y(OH)_z$  with varying degrees of isomorphous substitution. During the adsorption the amount of adsorbed phenol from the aqueous phase were fixed. The kinetic parameters of ion-exchange were studied by means of the sorption kinetic equation:



$$v = k \cdot C_{\text{PhOH}} \cdot m_{\text{sorb}}$$

For :  $\text{Mg}/(\text{Mg}+\text{Al}) = 0,52; 0,72; 0,81; 0,86$   $k = 0,83; 1,29; 1,67; 1,74 \text{ kmol l}^{-1} \text{ s}^{-1}$ ,  
respectively

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## ADSORPTION OF CADMIUM(II) FROM AQUEOUS SOLUTION ONTO SEPIOLITE

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Water pollution caused by heavy metals has attracted much attention in recent years because several of the heavy metals are very toxic. The main sources of metal pollution in superficial waters are the discharges of industrial and municipal wastewaters. Adsorption has been extensively applied for the removal of metals from water solutions. The most frequently tested adsorbents are activated carbon prepared from different sources, natural zeolites, biosorbents, and agricultural by-products. It is very well known that several natural clays have high cation exchange capacities and can be used as heavy metal ion exchanger. The adsorption of heavy metals on sepiolite has been investigated in very few works. Sepiolite ( $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ ) is a natural hydrated magnesium silicate clay mineral and is a trilaminar fibrous clay. The structure of the sepiolite consists of blocks and channels running parallel to the fibre axis. The dimensions of the channels are  $0.376 \times 1.06$  nm and the size of the fibers is normally  $800 \times 25 \times 4$  nm. The structural unit of each block consists of two tetrahedral sheets of 6 tetrahedra and a central octahedral sheet. The tetrahedral sheets alternate their orientation to both sides of the octahedral sheet. Due to its wide channels the sepiolite has a great adsorption capacity.

The sepiolite used in this work was obtained from a deposit located in Madrid, Spain. The clay mineral was characterized by various analytical techniques. The cation-exchange capacity (CEC) of the sepiolite was determined using the ammonium exchange procedure. X-Ray diffraction analysis was used to identify the crystalline species present in the sepiolite employing a Rigaku DMAX 200 diffractometer. The textural properties (surface area, pore volume and average pore diameter) of the sepiolite were determined by the  $\text{N}_2$ -BET method using a Micromeritics model ASP 2010 surface area and porosimetry analyzer. The adsorption equilibrium data were obtained in a batch adsorber which consisted of a conical centrifuge tube. A certain mass of the sepiolite and a given volume of a solution with known initial concentration of Cd(II) were contacted in the batch adsorber and allowed to attain equilibrium. The batch adsorber was partially submerged in a constant temperature water bath. Samples were taken at various times to follow the progress of adsorption, and the concentration of Cd(II) in each sample was determined with a spectrophotometric

Atomic Absorption method. The mass of metal adsorbed on the sepiolite was estimated by mass balance of Cd(II).

The X-ray analysis of the mineral clay revealed that the sepiolite was the main crystalline phase. The surface area and cation exchange capacity of the sepiolite were 203 m<sup>2</sup>/g and 42.8 meq/100g, respectively. These values are within the ranges of values commonly found for a sepiolite.

The experimental adsorption equilibrium data of Cd(II) on sepiolite were interpreted with the Langmuir isotherm and this isotherm model fitted the data reasonably well. The adsorption capacity of sepiolite was largely dependent upon the solution pH. The adsorption isotherm cannot be determined in the whole pH range since at very acidic pH the sepiolite was dissolved and at basic pH the Cd(II) precipitated as Cd(OH)<sub>2</sub>. The effect of the solution pH on the adsorption of Cd(II) on sepiolite was studied determining the adsorption isotherms at pH of 3, 4, 5 and 7. La adsorption capacity of the sepiolite diminished considerably reducing the solution pH from 7 to 3. This tendency was attributed to the interaction between the surface charge of the sepiolite and the Cd<sup>2+</sup> ions present in the aqueous solution. The effect of the temperature on the adsorption isotherm of Cd(II) on sepiolite was studied and the results indicated that the adsorption capacity was reduced by decreasing the temperature from 15 to 35 °C. The isosteric heat of adsorption was estimated to be 22.8 KJ/mol. Hence, the adsorption was endothermic and this explained why the adsorption equilibrium decreased with temperature.

## EFFECT OF MECHANICAL TREATMENTS IN THE ADSORPTION OF DIURON ON MONTMORILLONITE AND SEPIOLITE

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Mechanical treatments of clay minerals are of great interest because produce materials of great specific surface area that can be used as adsorbents of different contaminants. In addition to the grinding, ultrasound is a technique recently used for the reduction of the particle size and enhanced surface. Diuron is an herbicide widely used in agriculture. It has been often found as an emerging pollutant in soils and waters.

The aim of this work was to study the effect of mechanical treatments (grinding and ultrasound) in the adsorption of diuron on montmorillonite from la Provincia de Río Negro, Argentina and sepiolite from Spain. The samples were ground in a mill Herzog HS-100 for 30 to 180 seconds. The raw materials in aqueous suspension underwent an ultrasonic treatment, using a Misonix ultrasonic liquid processor of 600 W during 1 hour.

The samples were characterized by XRD, SEM-EDAX, IEP, and specific surface area using the BET method. The specific surface areas show the effect of grinding with values from 168 to 256 m<sup>2</sup> g<sup>-1</sup> and 30.5 to 122 to m<sup>2</sup> g<sup>-1</sup> for for sepiolite and montmorillonite, respectively. The X-ray diagrams of the samples indicate changes in the cristallinity due to grinding. The sonicated samples, however, were less affected in their cristallinity.

Adsorption experiments were performed on 0.05 g of raw and treated samples of both minerals by treating with 10 mL of diuron solutions ranging from 0 to 30 mg L<sup>-1</sup>. The adsorption of diuron on montmorillonite is very low with values about 0.5 μ mol g<sup>-1</sup>. The adsorption for the untreated and treated samples was very similar.

The adsorption isotherms of sepiolite showed values higher than those for montmorillonite, reaching a plateau at a value of 6.5 μ mol g<sup>-1</sup>. The adsorption capacity of the different samples was correlated with their external surface. The sonicated sepiolite showed the higher adsorption capacity.

## PHOTODEGRADATION OF ANIONIC DYE BY NON-TREATED Zn-AL LAYERED DOUBLE HYDROXIDE IN AQUEOUS SOLUTION

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Photocatalytic reactions are currently attracting a lot of attention as an efficient and sustainable purification procedure in water contamination caused by inorganic or organic hazardous substances. In photocatalytic reactions, degradations of some chemical substances are induced after an approaching or adsorption on the surfaces of photoactive materials. However, major photocatalysts such as  $\text{TiO}_2$ ,  $\text{ZnO}$  and  $\text{CdS}$  show little adsorption performance for ions. On the other hand, layered double hydroxide (LDH) has extremely high anion adsorption capacities, and these are well known as anionic clays. Recently LDH has received considerable attention as environmentally-friendly materials because of its harmless composition. It is also noted that LDH has catalytic and photocatalytic properties associated with its solid basicity or modifications with various polyacids. However, the photocatalytic properties of LDH itself have not yet been fully elucidated.

To examine the photocatalytic activity of non-treated LDH itself, this study focused on the photodegradation of anionic dye by synthetic Zn-Al LDH in aqueous solution under UV light irradiation. It is particularly expected that Zn-Al LDH has a potentially photocatalytic activity since  $\text{ZnO}$  exhibits a remarkable photocatalytic ability. Sulforhodamine B (SRB) was used as an anionic dye adsorbate.

Synthesized LDH was characterized by using XRD, SEM and AFM. The resultant XRD profile was consistent with that of Zn-Al LDH including chloride ions in the interlayer. The crystallinity of synthesized Zn-Al LDH was relatively high, and there were no crystalline by-products such as  $\text{ZnO}$ , zinc hydroxide or aluminum hydroxide. SRB aqueous solution of 0.01 mmol/L was mixed with Zn-Al LDH in polypropylene centrifuge tube. The solid concentration was adjusted at 50 mg/L. The suspension was dispersed in an ultrasonic bath, and then placed in a shaker for 24 hours at room temperature. It was conducted under light shielding. The suspension was added in a quartz cell, and served to UV irradiation experiment with vigorous stirring.

The absorbance of SRB was monitored with an UV-Vis spectrometer during UV light irradiation. The absorption band of SRB was appeared from 450 to 620 nm, and SRB presented absorption peak at 565 nm. The absorbance of SRB with Zn-Al LDH was unchanged after leaving in a dark condition. The result suggests that Zn-Al LDH itself didn't have just a catalytic activity. On the other hand, it was observed that the absorbance of SRB with Zn-Al LDH gradually decreased after UV irradiation. The degradation rate was reached approximately 50 % in 300 minutes of UV irradiation. And degradation rate of SRB with Zn-Al LDH was faster than in SRB without Zn-Al

LDH. Therefore, Zn-Al LDH certainly has the photocatalytic activity for SRB, and the degradation and decolorization reactions are accelerated without being stabilized under UV irradiation. It was expected that Zn-Al LDH could be utilized as an efficient photocatalyst for harmful organic anions.

## APPLICATION OF NATURAL ATTENUATION PROCESS FOR WASTEWATER CONTAMINATED WITH COPPER AND ZINC

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Generally, the removal of copper and zinc from wastewater by using antalkaline to increase pH around 7-10 will produce copper and zinc hydroxides after treatment. However, this method has some disadvantages such as dewaterability and disposal of alkali sludge. Hence, we have to develop more efficient treatment. On the other hand, natural attenuation process for copper and zinc at Dougamaru abandoned mine is achieved at neutral pH 6 and can provide insight on how to develop more efficient and safety treatment by applying this natural attenuation process. Therefore, the objective of this study is to understand and apply the natural attenuation process of copper and zinc in the Dougamaru abandoned mine for real wastewater treatment.

In the copper-zinc-sulphide mining district of Dougamaru in Japan, blue-green precipitate is generated from the drainage. The result of X-ray and chemical analyses revealed that the main mineral component of precipitate was Hydrowoodwardite with average chemical formula of  $\text{Cu}_{0.66}\text{Zn}_{0.09}\text{Fe}_{0.01}\text{Al}_{0.23}(\text{SO}_4)_{0.15}(\text{OH})_2 \cdot m\text{H}_2\text{O}$ . This mineral is composed of positively charged copper-aluminum hydroxide layers and intercalated with sulfate anion and water molecules. Hence, it can be classified as hydrotalcite-like compounds. The results also confirmed that the reduction of copper and zinc concentrations was due to dilution by river water and natural attenuation process caused by the formation of Hydrowoodwardite at lower pH (6.0).

For understanding of the condition to form the Hydrowoodwardite, five synthesis wastewaters, each containing 1.5 g of copper sulfate and aluminum sulfate in 150ml of distilled water, were prepared. The atomic Cu/Al ratios used were 1:0, 9:1, 4:1, 2:1, and 1:1, respectively. After mixing the solution, 0.1M NaOH were added to adjust the pH to 6.0. The dried precipitates were characterized by XRD, while the filtrate solutions were analyzed by ICP-AES. From the XRD data, the peak of Hydrowoodwardite was identified in three samples with Cu/Al ratio of 4, 2 and 1. This result also suggested that the optimum Cu/Al ratio in order to form Hydrowoodardite was 4. Moreover, a similar experiment was conducted for zinc, and resulted into an optimum Zn/Al ratio of 9 to form hydrotalcite-like compounds. From the result of ICP-AES measurements, most of copper in all samples was distributed in the solid phase. Meanwhile, distribution amount for solid phase of zinc depend on the presence of aluminum in which the samples containing aluminum showed the removal efficiency from 42.4 to 58.7 %, but the sample without aluminum

showed 12.7 %. Therefore, the remediation of zinc can be achieved at lower pH 6 by adding aluminum to wastewater. Moreover the interlayer anion of hydrotalcite-like compounds can be exchanged for another anion, as revealed batch adsorption experiment in which the interlayer  $\text{SO}_4^{2-}$  can be exchange for another hazardous anion. Therefore, Hydrowoodawrdite and zinc hydrotalcite-like compounds can also play a role of adsorbent for toxic anions when the drainage contains spontaneously some anions such as As, Se, and Sb.



## MACROSCOPIC AND SPECTROSCOPIC CHARACTERIZATION OF As(V) SORPTION BY BRUCITE AT HYPERALKALINE CONDITION

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The high mobility of As(V) at alkaline pH condition due to its low adsorption on predominantly negatively charged minerals in natural environment proved to be an important factor of consideration for arsenic immobilization in such condition. Due to this paucity of mineralogical host for As(V) at hyperalkaline condition, it is necessary to study other stable mineral phases that can act as major sorbing solid for arsenic.

This study examined brucite as possible sorbent of As(V) at hyperalkaline pH condition. Arsenate sorption was conducted during and after mineral formation at pH of  $11 \pm 0.5$  and conducted in the presence of silicate which is an ubiquitous anion in the natural environment. Solutions containing 0.03 M of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  plus 0.03M of  $\text{NaNO}_3$  (90 mL) and 0.03 M of  $\text{Na}_2\text{SiO}_3$  plus 0.09M of  $\text{NaNO}_3$  (10 mL) were mixed and adjusted to pH 11 by adding 5 M NaOH. The coprecipitation of arsenate during brucite formation was conducted by adding appropriate amounts of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  solution instantaneously during the mixing of Mg and Si solutions (with a final As concentration of 10 and 100 ppm, respectively) and were shaken for 7 days. In the case of adsorption studies, arsenate was added after mineral synthesis for 7 days and was shaken for additional 7 days prior to collection and analysis. The effect of temperature on the sorption behavior of As(V) by brucite was also carried out at 25, 50 and 75°C. To understand arsenic association with brucite, leaching test using phosphate bearing solution was conducted. Moreover, the various binding mechanisms of adsorbed and coprecipitated arsenic with brucite was investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy while the speciation of arsenic was determined from the XANES spectra.

The results of sorption experiments revealed that brucite have very large uptake capacity for As(V) even in the presence of silicate which was also removed in the solution. However, the results of desorption experiments of coprecipitated and adsorbed As(V) by brucite at 25°C indicated that arsenic can be released easily from the brucite surface (more than 80%) by anions with stronger affinity than As(V). The absence of second shell bonding environment for arsenic detected by EXAFS in these

samples may prove that As(V) was only adsorbed via outer-sphere complexation in the brucite surface. On the other hand, the high desorption rate of As(V) was reduced significantly by as much as 40 percent at higher temperature. This strong binding of sorbed arsenic at 50 and 75°C may imply that As(V) could either be imbedded in the brucite surface by displacing the hydroxyl group coordinated to Mg or forming inner-sphere complexes with near surface-exposed Mg. These binding mechanisms were confirmed by the results of EXAFS analysis which indicated that the 4-fold oxygen coordinated arsenic is surrounded by Mg shells only. However, the presence of amorphous and unknown crystalline phase on these samples which could probably be attributed to Mg-arsenate precipitate could not be excluded for this As-Mg bonding environment.

The results of this experiment highlighted the large uptake capacity of brucite for arsenic and can limit arsenic mobility at hyperalkaline condition. However, the long-term immobilization of arsenic by brucite cannot be guaranteed at temperatures typical of most hydrogeological environments since it can only retain arsenic via outer-sphere complexation and can be released easily by competing anions with stronger affinity.

## UPTAKE OF PESTICIDES FLUOMETURON AND NICOSULFURON BY LAYERED DOUBLE HYDROXIDE

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Wide use of pesticides increases the levels of its residues in soils and ground waters so this becomes a current environmental problem. In order to compensate the losses caused by transport and degradation processes, pesticides are applied to agricultural soils in amounts which greatly exceed those required for control of the target organisms, and the excessive quantities added increase the environmental impact, particularly problems related to drinking water quality. So there are many efforts in development of new materials which could be used in water decontamination.

Layered double hydroxides (LDHs), also known as hydrotalcite (HT)-like compounds, have recently been studied as potential sorbents of pesticides to prevent and remediate water contamination. LDHs are layered materials with a general formula  $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}[X_{x/m}^{m-} \cdot n\text{H}_2\text{O}]^x$ , where  $M^{II} = \text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , etc;  $M^{III} = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , etc; and  $X^{m-} = \text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , etc. The intercalation of organic anions in LDHs changes the nature of the interlayer space from hydrophilic to hydrophobic, thus allowing the sorption of nonionic or low-polarity molecules on these materials.

The objective of this work was to investigate the capability of HT ( $\text{Mg-Al-CO}_3$ ) and organo-HTs (where interlayer space is modified to hydrophobic with dodecylsulfate, DDS, anions) on the uptake of Fluometuron and Nicosulfuron herbicides from aqueous solutions, at different conditions of pH, contact time, initial concentration of the pesticide. Both pesticide Fluometuron (pre and post emergency treatment) and Nicosulfuron (post emergency treatment) have a widespread use in cotton and crops fields, respectively. The physico-chemical properties of Fluometuron are solubility 0.12g/L and  $\text{pK}_a=14.55$  and for Nicosulfuron are 4g/L and  $\text{pK}_a=4.3$ .

The adsorption behavior of both pesticides with respect to a hydrotalcite is different, due to its different polarities. Nicosulfuron is more polar and it is adsorbed by the hydrotalcite calcined at 500 °C, not being absorbed by the DDS-treated hydrotalcite. The non-polar Fluometuron is better adsorbed by DDS-treated hydrotalcite.

The kinetics shows that for the case of Nicosulfuron plateau is reached after 24 hours, while for Fluometuron is achieved within 5 hours. The adsorption of both pesticides is not greatly affected by change of initial pH. The adsorption isotherms of both pesticides are of L- type, indicating the high host-guest interaction although the adsorptions were limited by very low pesticides solubilities. In the case of Fluometuron the isotherm plateau is reached at an initial concentration 0.3

mM where the maximum pesticide amount adsorbed was of  $37.8\mu\text{mol}$  per g of adsorbent, whereas for Nicosulfuron it was reached for an initial concentration of 1.25 mM, and the maximum amount adsorbed was  $324\mu\text{mol}$  per g of adsorbent. In addition, desorption isotherm was performed by successive dilutions with water. The desorption curve is different for each pesticide, as in the case of fluometuron this is almost complete while in the case of desorption of Nicosulfuron is practically negligible.

The adsorbents and the adsorption products were characterized by XRD technique and FT-IR spectrophotometry. These techniques confirmed the presence of both pesticides in the adsorption products.

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## CATIONS ABSORPTION IN HIGH TECHNOLOGICAL LAYER SILICATES

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The synthetic highly charged mica Na-Mica-n,<sup>1</sup> which has a high swelling and ion-exchange capacity, is potentially useful for the elimination of harmful pollutants such as radioactive cations, heavy metals, organic compounds and biomolecules.<sup>2,3</sup> The stacking of the layers creates galleries (alternatively referred to as interlayers) that, in the as-made mica, are occupied by Na<sup>+</sup> cations, but the interlayer space can be modified by ion-exchange reactions<sup>4</sup> involving the exchange of inorganic cations by other inorganic cations with technological interest.<sup>5,6</sup> From basic and applied point of view, it is fundamental to have a deep knowledge of the interaction force between the hydrated cations and the clay surface which will controls the swelling, dispersion, and ion exchange properties of these layered silicates.

Although the swelling 2:1 layered silicates have been recognise traditionally as those containing a total layer charge between 0.4 and 1.8 units (smectite and vermiculite groups), a new family of compounds with different layer charge values, ranging between 2.0 and 4.0, has been very recently synthesized, which exhibit swelling properties. Our research group has reported a general method to synthesize these swelling high charge micas in which the layer charge can be adjusted.<sup>3</sup> However, there is not yet available information on the precise location of the interlayer cations in the interlayer space of these materials and on the water structure in these confined spaces with a high electric field, which should be responsible of their relevant properties in several applied fields.

In this work the absorption capacity of a set of cations of the same period but with different oxidation state by expandable high charge micas have been explored. The samples synthesized have been analyzed by characterization methods that provided short as well as long range structural information. To determine the hydration state of the solids, termogravimetric analysis has been used; the swelling capacity of the layers due to this hydration has been determined by XRD. The hydration/deshydration processes was studied using a diffractometer with a reaction chamber and variable temperature. At last, the interactions between the interlayer cations and the silica network have been explored by MAS-NMR.

The results have shown that the cation interchange is effectively achieved and the hydration state of the interlayer space not only depends on the cation charge

but also on the silicate surface. Short order studies have revealed the existence of a complex between the interlamellar cation and the oxygen of pseudohexagonal cavity of the structure, that may affect the hydration/deshydration of the phyllosilicates.

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## **PALYGORSKITE FROM MARRAKECH HIGH-ATLAS (MOROCCO): CHARACTERIZATION, FUNCTIONALIZATION AND PHOTOCATALYTIC ACTIVITY**

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Palygorskite is a fibrous clay mineral with versatile industrial applications. This work introduces the physico-chemical and mineralogical characterization of a clay picked up from Marrakesh High-Atlas (Morocco), by means of several advanced analytical techniques such as STEM-EDX, XRD, FTIR, ICP-MAS, TG-DTA, MAS-NMR. These studies indicated that fine separate fraction ( $< 2 \mu\text{m}$ ) was a monomineral corresponding to a fibrous Mg-rich palygorskite that also contained noticeable amounts of Al and Fe. The CEC of this silicate was about 8 meq/100g and the specific surface area, determined from  $\text{N}_2$  adsorption-desorption isotherms according to the BET method, of around  $40 \text{ m}^2/\text{g}$  with a porous volume of about  $0.2 \text{ cm}^3/\text{g}$ . FTIR spectroscopy indicated the presence of bands ascribed to  $\text{Al}_2\text{OH}$ ,  $\text{Fe}_2\text{OH}$  and  $\text{Mg}_3\text{OH}$  vibration modes, which constituted evidence of the simultaneous occurrence of trioctahedral and dioctahedral domains inside this palygorskite. MAS-NMR spectroscopy revealed that most of the Al was in octahedral sites in this clay mineral, while its two tetrahedral silica pyroxene chains contained two nonequivalents Si sites.

This palygorskite has been used to prepare functionalized nanocomposite materials, made up of  $\text{TiO}_2$  photocatalyst supported on the mineral fibers.  $\text{TiO}_2$ -palygorskite was synthesized according to the colloidal method reported by Aranda et al [1] in which a surfactant was involved as template of the oxide nanoparticles. The inorganic-inorganic hybrid material, developed upon heat treatment under air at  $600^\circ\text{C}$  for 1h of the as-prepared sample, showed homogeneous monodisperse distribution of anatase  $\text{TiO}_2$  nanoparticles (size  $< 15 \text{ nm}$ ) onto palygorskite fibers.

Photocatalytic experiments showed good activity of the nanocomposite based on this material with  $\text{TiO}_2$  nanoparticles covering the surfaces of palygorskite fibers towards the removal of Orange G used as model pollutant.

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## ADSORPTION OF THE PESTICIDE METALAXYL ON PHYLLOSILICATE SURFACES BY FIRST PRINCIPLE CALCULATIONS

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Commonly used pesticides can be harmful to people, pets, and the environment, due to the toxicity and carcinogenesis of some pesticides (1). The development of innovative and effective methods for remediation of soil and water contaminated by toxic organic compounds and/or pesticides is a research area of great interest nowadays. Metalaxyl [N-(2,6-dimethylphenyl)-N-(2-methoxyacetyl)-DL-alanine, Methyl ester] is a systemic fungicide that is widely used in agriculture especially for vineyard and rice exploitations. The fungicide is a racemic mixture (50:50) of R- and S-enantiomeric forms (Fig. 1), although its fungicidal activity is almost entirely due to the R-enantiomeric form.

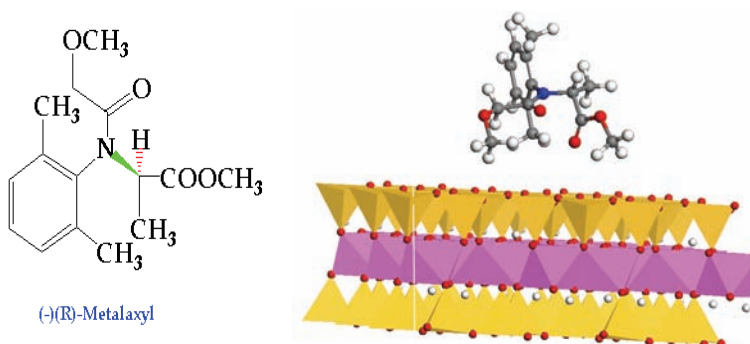


Figure 1: Molecular Structure of Metalaxyl and adsorbed on phyllosilicate surface.

Metalaxyl is very soluble in water, moderately volatile, and weakly adsorbed to soil. Available laboratory and field studies indicate that metalaxyl is stable to hydrolysis under normal environmental pH values. It is also photolytically stable in water and soil when exposed to natural sunlight (2). However, the interactions of this pesticide with the surface of the soil minerals at molecular scale are not well known yet. A better knowledge of these interactions will help to evaluate and control the mobility of this molecule along the soil and to design new usage methods of these pesticides.

In this work we study the adsorption of metalaxyl on the pyrophyllite surface as a model of phyllosilicate. The molecular and electronic structure the metalaxyl have been studied using different theoretical methods of quantum-mechanical calculations based on Hartree–Fock and density functional theory (DFT) comparing different calculation levels. The adsorption of metalaxyl on the surface of phyllosilicate and the spectroscopic properties were calculated using a crystal periodical model of the adsorption. These calculated properties are according to experimental values and help to interpret the vibrational spectra.

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## ADSORPTION OF HYDROPHOBIC ORGANIC COMPOUNDS ONTO A GEOSORBENT MATERIAL

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Xenobiotics are increasingly used in agriculture to enhance food production. Excessive applying of these products (such as herbicides, fungicides and different pesticides) is a matter of environmental concern because these chemicals are recognized as a source of potential adverse impact. Many of these chemicals are mobile in soil and readily migrate into ground water to compromise water quality.

The clean-up of contaminated groundwater by using organo-clays has become a major focus of research and policy debate in a variety of environmental settings.

Organo-clay complexes have the potential to remove heavy metals and organic pollutants thanks to increased adsorption properties.

These complexes show several promising applications in contamination prevention and environmental remediation, including the treatment of waste effluents, as extenders for activated carbon and components of clay barriers, hazardous waste landfills and petroleum tank forms.

The aim of our research was to develop a matrix capable of removing organic contaminants from waters to be purified. Modified organo-clay was obtained by using SWy-2-Na-montmorillonite (Wyoming) and octadecyl-trimethyl-ammonium-bromide (ODTMA) as surfactant. The montmorillonite (MMT) used in this study was supplied by the Clay Minerals Society. The chemical composition of MMT is: SiO<sub>2</sub> 62.9%, Al<sub>2</sub>O<sub>3</sub> 19.6%, Fe<sub>2</sub>O<sub>3</sub> 3.35%, MgO 3.05%, CaO 1.68%, Na<sub>2</sub>O 1.53%. The cation exchange capacity (CEC) is 76.4 cmol<sub>+</sub> Kg<sup>-1</sup>.

At first, simulated water polluted by atrazina, an old xenobiotic, was used as sorption model at rate of 0.35 mol Kg<sup>-1</sup>. Successively, river water, as real sample containing chloroform, dichloromethane and dibrochloromethane, was treated.

The method adopted for the preparation of the organo-modified clay was similar to that described in literature. Basal spacing (*d*001) of the unmodified and modified clay mineral was determined by X-ray diffraction (XRD) using a Rigaku Rint 2200 powder diffractometer with Cu-K $\alpha$  radiation and graphite monochromator. Retention by surfactant-modified MMT was measured by using the Thermo micro ESI/FT-ICR/MS 7T.

The results of chemical analyses confirmed the usefulness of modified organo-clay adsorbent compared to natural montmorillonite.

## SODIUM AND CALCIUM / MAGNESIUM-MONTMORILLONITE: STRUCTURE, FORCES AND SWELLING PROPERTIES

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Na Ca/Mg-montmorillonite and natural Wyoming bentonite (MX-80) have been studied experimentally and theoretically. For a clay system in equilibrium with pure water, Monte Carlo simulations predict a large swelling when the clay counterions are monovalent, while in presence of divalent counterions a limited swelling is obtained with an aqueous layer between the clay platelets of about 10 Å. This latter result is in excellent agreement with small angle x-ray scattering (SAXS), while dialysis experiments give a significantly larger swelling for Ca montmorillonite in pure water. Obviously, there is one "intra-lamellar" and a second "extra-lamellar" swelling.

Montmorillonite in contact with a salt reservoir containing both Na<sup>+</sup> and Ca<sup>2+</sup> counterions will only show a modest swelling unless the Na<sup>+</sup> concentration in the

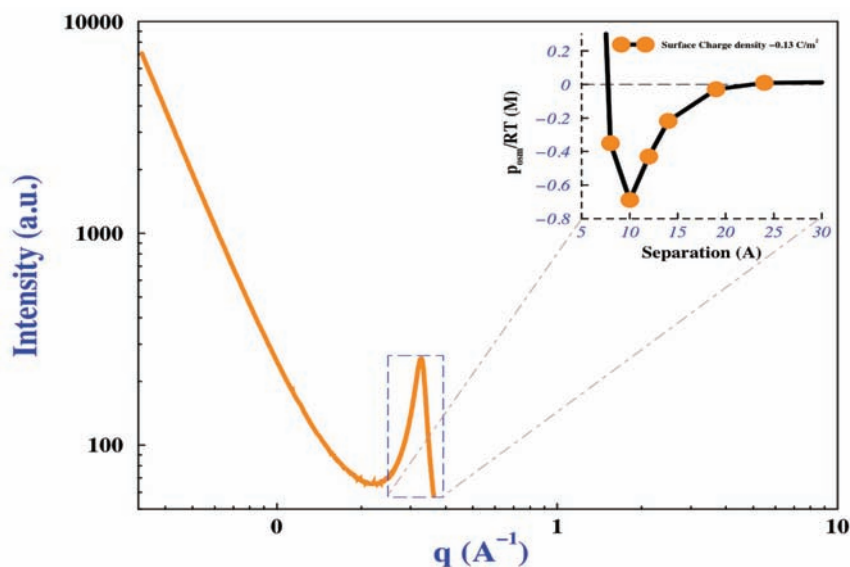


Figure 1: SAXS result for Ca-montmorillonite in excess of Milli-Q water. The peak at the repeat distance in excellent agreement with MC simulations.

bulk is several orders of magnitude larger than the  $\text{Ca}^{2+}$  concentration. The limited swelling of clay in presence of divalent counterions is a consequence of ion-ion correlations, which reduce the entropic repulsion as well as give rise to an attractive component in the total osmotic pressure. Ion-ion correlations also favour divalent counterions in a situation with a competition with monovalent ones. A more fundamental result of ion-ion correlations is that the osmotic pressure as a function of clay sheet separation becomes non-monotonic, which indicates the possibility of a phase separation into a concentrated and a dilute clay phase, which would correspond to the "extra-lamellar" swelling found in dialysis experiments. This idea also finds support in the x-ray scattering spectra, where sometimes two peaks corresponding to different lamellar spacings appear.

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## HIGH PERFORMANCE NEW AMORPHOUS ALUMINUM-SILICATE ADSORBENT WATER VAPOR AND CARBON DIOXIDE

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**Background:** The issues for global warming and energy are increasingly important around the world. To solve these problems, we have developed the amorphous aluminum silicate materials that can contribute to the efficient use of energy and capture carbon dioxide efficiently. This study describes the synthesis and properties of the newly developed materials, which adsorb water-vapor and carbon dioxide efficiently. The present study aims to improve the efficiencies of a desiccant air conditioning system and a carbon dioxide capture system, and to spread these systems to the world.

**Synthetic methods:** An amorphous aluminum-silicate was prepared by the following procedure. Five hundreds mL of 0.45mol/L sodium orthosilicate, and another 500mL of 0.54mol/L aluminum chloride were mixed together and stirred with a stirrer for 10 minutes. The Si/Al molar ratio of this mixed solution was 0.83. Then 35mL of 1.0mol/L sodium hydroxide was added to 1000mL of the stirred solution at a time and stirred for 10 minutes. The mixture was poured into a 2000mL Teflon bottle followed by heating at 98°C for 24 hours. After cooling it to room temperature, the solid product was water-washed by centrifugation three times to remove sodium chloride contained in the suspension. The product, which was collected by centrifugation, was dried at 60°C in a dryer for 2 days.

**Results and Discussions:** The XRD profile of synthesized sample exhibit broad reflection peaks at around 26° and 39° in 2θ, which are typically shown in amorphous aluminum-silicate such as allophane. From the TEM image of this product, it has 2-3 nm ring-shaped particles, and 2-10 nm irregular-shaped particles. Though 2-3 nm ring-shaped particles are similar to allophane, the ring shaped particles is slightly smaller than allophane particles. The <sup>29</sup>Si NMR spectrum of this sample shows a sharp resonance peak at -78ppm and a broad resonance peak at around -86ppm. A sharp resonance peak at -78ppm corresponds to the allophan-like or imogolite-like Si tetrahedron attached to three aluminol groups of the gibbsite sheet and one silanol group. Another broad resonance peak at around -86ppm may correspond to zeolite or layer aluminosilicates such as vermiculite. The <sup>27</sup>Al NMR spectrum of this sample shows a sharp resonance peak at 53 and 0ppm. The peak at 53 ppm shows tetrahedral Al and the peak at 0ppm shows octahedral Al. Tetrahedral Al may be derived from 2:1 layer aluminosilicates with isomorphic substitution in Si

tetrahedral sheets with Al, such as vermiculite and beidelite. Octahedral Al is derived from allophane or imogolite structure.

Nitrogen adsorption: From the pore-size distribution curves of the synthesized sample calculated by the BJH method, the synthetic specimen exhibits nearly flat distribution curve. Small size pore which is less than 5 nm and large size pore larger than 30nm are slightly large in number. The specific surface area calculated by the BET method is 556 m<sup>2</sup>/g.

Water-vapor adsorption and desorption: From the water vapor adsorption/desorption isotherms, the amounts of the adsorbed water in the low range ( $P/P_o=0.0-0.20$ ) and the high range ( $P/P_o=0.85-0.95$ ) of relative water vapor pressure are slightly larger than the amount of the adsorbed water in the middle range ( $P/P_o=0.20-0.85$ ). In the pore-size distribution curves, the volume of pore size at under 5nm and over 20nm is slightly larger than that of any other pore size. The result of pore-size distribution is quite corresponded with the result of water-vapor adsorption, because the phenomenon of water-vapor adsorption is due to capillary condensation within open pores. The amount of water-vapor adsorbed on this sample was 36wt% when the relative water vapor pressure is at 0.6. This value was 1.4 times larger than the amount of water-vapor adsorbed on zeolite A.

Carbon dioxide adsorption/desorption: From carbon dioxide adsorption isotherms, the amount of adsorbed carbon dioxide on the sample and zeolite X are 17.0wt% and 22.6wt%, respectively, when the pressure of carbon dioxide is 0-900kPa. However, if the adsorption starts at atmospheric pressure, the amount of adsorbed carbon dioxide on our sample and zeolite X are 11.1wt% and 5.4wt%, respectively. The amount of adsorbed carbon dioxide on the sample is 2.1 times as larger than that on zeolite X.

## **A COMPARATIVE STUDY OF THE USE OF AN ORGANOCLAY-BASED FORMULATION AND A STANDARD COMMERCIAL FORMULATION OF THE HERBICIDE DIURON UNDER FIELD CONDITIONS**

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Olive is one of the most important crops in the Mediterranean region, where 97 % of the world olive oil is produced. Spain is the main olive oil producing country in the world. In olive groves, soil texture, pronounced slopes, and climatic conditions favor losses of the applied herbicides by leaching and runoff processes. The use of slow release formulations has been proposed as an efficient strategy to reduce the environmental impact of soil-applied pesticides.

In previous studies, we showed the ability of organoclay-based formulations of the herbicide diuron to act as slow release formulations. Laboratory experiments indicated that such organoclay-based formulations retarded the release of the herbicide into water and reduced the herbicide leaching through soil columns compared to a standard commercial formulation containing the herbicide in an immediately available form. Here, one of the organoclay-based formulations of diuron tested in the laboratory was selected and its behavior assayed under field conditions. The organoclay based formulation of diuron was prepared by supporting the herbicide on spermine-exchanged Wyoming montmorillonite (SW-SPERM). The organoclay-based formulation and a standard commercial formulation of diuron were applied to 4 x 1 m field plots at a rate of 3 kg active ingredient/ha. At selected times, triplicate soil samples were taken from different soil depths (0-5, 5-10, 10-20 and 20-30 cm) and extracted to determine their content in diuron and to address the effect of the organoclay-based formulation on herbicide leaching and persistence.

The field experiment revealed that diuron applied as organoclay formulation moved slower through the soil profile than diuron applied as the standard commercial formulation and that SW-SPERM retarded the herbicide dissipation. The results indicated that organoclay-based formulations can be used under field conditions to prolong the persistence of diuron in soils and retard its leaching through the soil profile.

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## SLOW RELEASE FORMULATIONS OF THE HERBICIDE METRIBUZIN: BASED ON PHOSPHATIDYLCHOLINE-MONTMORILLONITE COMPLEXES

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Liposome-clay formulations of the herbicide metribuzin (MTZ) were designed for slow release by incorporating the herbicide into phosphatidylcholine (PC) vesicles, which subsequently were adsorbed on montmorillonite. PC and montmorillonite are classified as substances of minimal toxicological risk by the USEPA. Active ingredient contents of the PC-clay formulations ranged up to 24.8%. Infrared spectroscopy showed hydrophobic interactions of herbicide molecules with the alkyl chains of the adsorbed PC, and replacement of some hydration water of the PC by herbicide molecules, which remain in the vicinity of the polar PC headgroup by forming water bridges.

Release experiments in a sandy soil showed a slower rate when using the PC-clay formulations as compared to the commercial one. Soil column experiments with the sandy soil (AR) and a loam soil (P44) under moderate irrigation were performed (Fig.1). In the upper soil layer (0-4 cm) the reduction in leaching was up to 38-40% for both soils. In the following soil layer (4-8 cm depth), the liposome-clay formulations amounted to a 19% reduction in the AR soil whereas larger reductions (45%) were obtained in the P44 soil. In this soil the herbicide was mainly accumulated in the first 8 cm because of its larger adsorption capacity and hysteresis than the AR soil, where the herbicide leached to a larger extent to deeper soil layers.

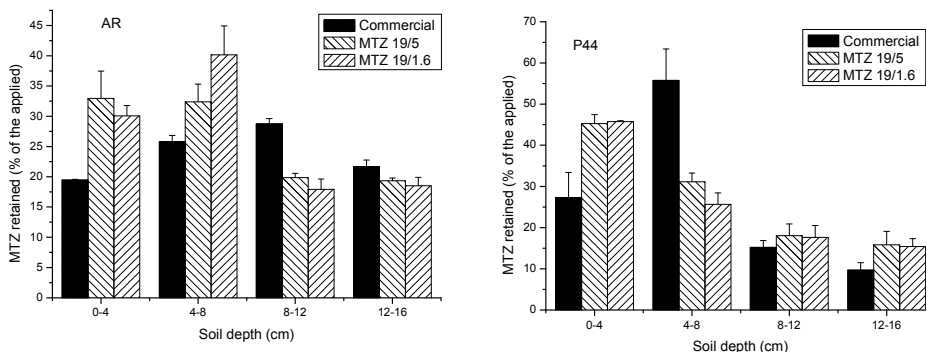


Figure 1. Amounts of metribuzin retained as a function of the depth in soil column experiments from PC-clay (MTZ19/5, MTZ19/1.6) and commercial formulations.

Bioassays were performed in the upper soil layers of the soil column experiments by determining the reduction in shoot fresh weight of a weed (*Setaria Viridis*) relative to a control (untreated soil). The inhibition percents in the upper soil layer (0-4 cm depth) were 6- and 1.6-fold larger for the PC-clay formulations in the AR and P44 soil, respectively, relative to those of the commercial formulation.

In conclusion, the PC-clay formulations show a reduction in leaching and enhanced bioefficacy in the upper soil layers, which are those of prime interest for weed control. Therefore, a reduction in the rate of application of the herbicide can be achieved by using liposome-clay formulations, with the subsequent economic and environmental advantages.

## GEOCHEMISTRY OF THE FINE FRACTION OF SUPERFICIAL SEDIMENTS IN THE OUTLET OF MEDJERDA RIVER (GULF OF TUNIS)

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The outlet of Mejerda River, situated in the North of Tunisia, receives large volumes of mining rejects mainly from Pb, Zn and Ba mines during last decades. Concentration of major and trace elements (Al, Ti, P, K, Mg, Na, Ca, S, Fe, Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, I, Ba and Pb) are determined in different three fractions of 45 surficial sediments. Grain size distribution of fine fractions (<2  $\mu\text{m}$ , 2-20  $\mu\text{m}$ , 20-63  $\mu\text{m}$ ) reveals that clay and fine silt fraction are dominant 75-95% in the deeper estuarine region. Regarding clays, the dominant phases are dioctahedral smectite, illite and kaolinite. Chlorite and interstratified illite-smectite are also present. The total organic carbon (TOC) content in surface sediment of the gulf of Tunis varies between 0.08 and 1.37 %. The determination of total nitrogen permitted to calculate the C/N ratio with an average of ~7. The C/N indicates a marine origin of the organic matter, only in front of the outlet of Mejerda River and Ghar el Melh lagoon where the organic matter has a mixed origin. The use of "Principal Component Analysis" statistical method, helped to establish which organic and/or inorganic phases concentrate the contaminants. There is a significant correlation between TOC and trace element Cu, Zn, in the <2  $\mu\text{m}$  fraction. This correlation is weak with clay minerals. The correlation of  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$  and  $\text{P}_2\text{O}_5$  with traces element, mainly in the <2  $\mu\text{m}$  fraction, reveals that amorphous Fe and Mn are among the most active scavengers of dissolved metals mainly in continental environments (Mejerda River). The cluster analysis, using the similarity matrix with the ratio matching, supplements the results obtained for the metals of the fractions of the sediment (<63  $\mu\text{m}$ ). This test allows classifying the sediments of the study area in terms of their inter-metallic ratios. That is, sediment samples that are similar in origin tend to associate in one group, whereas sediments that are affected by some factor, such as a sediment transport pattern or their closeness to sources of pollution, tend to separate into independent groups. The cluster analysis between sites is applied with data of different grain size fractions of the sediment. The dendrogram suggests a separation of five different groups. The most important groups are in the <2  $\mu\text{m}$  and 2-20  $\mu\text{m}$  fractions. In the fine fraction, Group 1 most of the sites are characterized by relatively low metal concentrations, and the Group 5 contain sites with the highest concentration of Fe, Al and traces elements in the sediments mainly Zn, Pb, Ni Cr, Zr and Ba. In coarser grain size

sediment (2-20 $\mu$ m) most of sites are represented in Group 1 marked by high content in quartz, representing the distribution of continental sediment discharge in the outlet of Mejerda River and the Group 2 contains the lowest contents of detritic sediment.

## EFFECT OF TEMPERATURE AND CATIONS ON THE SWELLING AND SHRINKING BEHAVIOURS OF MONTMORILLONITE-CLAY

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Montmorillonite, a member of the smectite group, is a naturally occurring swelling clay. Due to its low permeability to water, high swelling capacity, high surface area and high retention capacity for cations, this swelling clay is of great interest in geoenvironmental engineering as liners or constituents of the storage of radioactive waste.

Molecular dynamics simulations have been performed to study the diffusive transport properties of water and counterions in 1-, 2- and 3-layer hydrated Wyoming-type montmorillonite (MMT). The considered counterions included in the clay are monovalent cations, such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and divalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ .

The simulation results of the diffusion of water and cations in Na-MMT are compared with available experimental quantities and previous simulations that our simulation results employed NVE ensemble and SPC/E water model are in great agreement with the experimental values. The same methods have been performed in other simulations to predict the coefficient diffusions of water and counterions at different hydrated state.

We have found that at the same hydrated degree, water diffuses much faster than cations. Monovalent cations diffuse more quickly than divalent ones. Both water and cations' diffusion is speeded up by increasing hydrated degree. That means the increasing water content will release cations. However, heavy metal cations are always difficult to release. On the other hand, cations' size, weight and capacity of attracting water molecule affect the diffusion behaviour of water. The existence of heavy metal cations causes high diffusion of water in high hydrated clay.

The effect of temperature on the diffusion behaviour has been also studied. We have found that the diffusion behaviour of interlayer particles becomes important with the increasing of temperature. We show that the temperature effect is more important on diffusion of water than cations. This effect is significant in high hydrated clay than low hydrated ones. The influence of temperature is important on diffusion of monovalent cations and negligible for divalent ones. Pollutants, the heavy metal cations are always hard to release even at high temperature and high hydrated degree.



## TOPIC 5

*Biological Aspects & Health*





# *ORAL PRESENTATIONS*



## KEYNOTE

### ADSORPTION OF PROTEINS ON SAPONITE

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The adsorption of cationic proteins on smectites such as saponite occurs in three distinct steps: (1) strong, quantitative adsorption on the edges of the saponite layers; (2) adsorption of a monolayer of protein molecules in the interlamellar region; (3) weak adsorption in excess of the cation exchange capacity (CEC). The first two steps are mainly ion exchange reactions. From the amount of Na<sup>+</sup> released in solution and the corresponding amount of protein molecules adsorbed the average positive charge per adsorbed protein molecule can be calculated. These charges are 13.5 and 9.5 for protamine and lysozyme respectively (Table 1). The third step results in weakly adsorbed protein molecules, which can be washed off.

Table 1: Proteins and their adsorption characteristics

| protein          | MW (Da) | Size (nm)   | charge   | Edge adsorption (mg/g) | Ion exchange (mg/g) |
|------------------|---------|-------------|----------|------------------------|---------------------|
| protamine        | 4500    |             | +13.5    | 400 <sup>2</sup>       | 400                 |
| lysozyme         | 14500   | 4.6x3.5x3.5 | +9.5     | 150; 230 <sup>3</sup>  | 600                 |
| papain           | 23000   | 5x3.7x3.7   | unstable | unstable               | unstable            |
| BSA <sup>1</sup> | 63000   | 14x4x4      | negative | 70                     | -                   |

<sup>1</sup> BSA: bovine serum albumin; <sup>2</sup> edge adsorption cannot be separated; <sup>3</sup> Cs<sup>+</sup>-saponite

Factors, which determine the adsorption process are: (1) the exchangeable cation on the saponite (Na<sup>+</sup>, Cs<sup>+</sup>); (2) the molecular weight of the proteins; (3) the chemical stability of the proteins. Thus, protamine and lysozyme are ion exchanged on Na<sup>+</sup>-saponite and form a monomolecular layer in the interlamellar space. However, protamine is able to ion exchange only 36% of the Cs ions of a Cs<sup>+</sup>-saponite, while

lysozyme is unable to penetrate in the interlamellar space of  $\text{Cs}^+$ -saponite. Papain is unstable under the conditions of the adsorption experiments and gives erratic adsorption data.

In FTIR the amide I and amide II bands of the adsorbed proteins are essentially the same as in aqueous solution. Thus, no significant conformational changes have occurred upon adsorption. This observation, together with the fact that the obtained biocomposites, protein-saponite, adsorb up to 146  $\text{H}_2\text{O}$  molecules per molecule of lysozyme, lead to the conclusion that the adsorbed proteins are still available for enzymatic activity.

## SYNTHESIS AND CELLULAR UPTAKE OF FLUORESCEIN INTERCALATED LAYERED DOUBLE HYDROXIDE

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Layered double hydroxide (LDH) is widely known as anionic clay, host-guest material and anion-exchanger. The general formula of LDH is represented by  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][Anion^{n-}_{x/n} \cdot yH_2O]$ , where  $M^{2+}$  and  $M^{3+}$  are metallic divalent and trivalent cations, which may be, respectively,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$  or  $Zn^{2+}$  and  $Al^{3+}$ ,  $Cr^{3+}$ , or  $Fe^{3+}$  etc. In addition,  $Anion^{n-}$  signifies an exchangeable inorganic anion such as  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$  or various organic anions. The  $x$  value is equal to the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$ , generally 0.20-0.33. LDH has widely various applications as catalyst, catalyst precursor, adsorbent, optical functional material, flame retardant and polymer stabilizer, particularly it has been used as antacid and antipeptin in the medical field. In recent year, increasing attentions have been devoted to drug/LDH, the synthesis of drug/LDH for uses such as anti-cancer, antibiotic, antibacterial, analgesic and anti-inflammatory drugs have been reported. Interesting researches have focused on a cellular uptake efficiency of drug/LDH. Oh et al. described that the cellular uptake mechanism of LDH was in principle a clathrin-mediate endocytosis by using fluorescein-5-isothiocyanate (FITC) intercalated LDH.<sup>1)</sup> Actually, FITC has been used extensively in a biological labeling, however, isothiocyanate group is reactive toward nucleophiles including amine and sulfhydryl groups on biomolecules. There is a probability of misconception that a released FITC is able to bond to nearby biological molecules. Costantino et al. have been reported an intercalation of fluorescein disodium salt (Fluo) into Zn-Al LDH by using ion-exchange method.<sup>2)</sup> Here, we focus on Fluo as a guest in fluorescence dye, the intercalation behavior of Fluo into Mg-Al LDH by coprecipitation method has been investigated. To further present the abilities of the Fluo/LDH, the cellular uptake behavior of the Fluo/LDH has been studied.

The influence of the solution pH in the 8.0 to 12 range on the intercalation of Fluo is examined. The XRD patterns show that the Fluo/LDH, which the diffraction peaks are  $d_{003}=1.58$  nm (pH 9.0 and 10) and  $d_{003}=0.78$  nm (pH 8.0 and 12), respectively, has an obvious LDH structure. These  $d$ -values depend on the amount of Fluo intercalated, supporting that Fluo has two different arrangements, vertically and horizontally orientations, in the LDH interlayer space. Adsorption peaks by the intercalated Fluo and  $NO_3^-$  from the FT-IR spectra suggest that both guests are intercalated into the LDH. The typical chemical composition of the Fluo/LDH (pH 10) is  $[Mg_{0.68}Al_{0.32}(OH)_2][Fluo_{0.23}(NO_3)_{0.09} \cdot nH_2O]$ . The molar ratios of Fluo/Al and Mg/Al are 0.72 and 2.1, which agree with the anion exchange capacity and the stoichiometry of LDH.

Cellular uptake behavior of the Fluo/LDH in mammalian cell line, L929 (mouse, connective tissue) and HeLa (human, cervix), has been studied. In order to define the Fluo/LDH internalized into cell line, the Fluo/LDH was added with the cell culture medium. Fluorescence images are taken using fluorescence and confocal laser microscopy, and fixed-cell cross section images are also observed by a TEM. The fluorescence microscope images demonstrate the uptake of the Fluo/LDH because the intense fluorescence in the cytoplasm is observed, beside the it cannot be shown in Fluo alone. The internalized Fluo/LDH is dissolved in endosome where pH is weak acidic condition (pH 5.0 to 6.0), since Fluo is released from the LDH and dispersed in the cytoplasm. The tomograms of cells also suggest the uptake of the Fluo/LDH which the fluorescence of the Fluo/LDH particles is observed in the cytoplasm. The TEM images of fixed-cell cross section are clear evidence of the internalization of the Fluo/LDH in the cytoplasm within vesicle structure. The influence of incubation time on the uptake of the Fluo/LDH in L929 cell was also investigated. The TEM images prove that the aggregate Fluo/LDH particles are oriented in the periphery of plasma membrane in 10 min and in the cytoplasm within vesicle structure in 30 min.

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## EVALUATION OF BENTONITES AS AN AMENDMENT IN POULTRY FEED CONTAMINATED WITH HIGH-CONCENTRATION OF AFLATOXINS

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Aflatoxins are toxic metabolites produced by fungi in food and animal feeds. Moderately contaminated grains that cannot be used as food are often directed to animal feed applications. The mycotoxins in feeds can induce health problems such as reduced feed consumption and lower productivity. Economically-feasible detoxification measures for the contaminated feeds are needed. The objectives of this research were to identify effective bentonites as aflatoxin adsorbents and to evaluate the performance of the clays as aflatoxin amendments in feeds for broiler chickens.

Five bentonite samples from Gonzales, Texas, USA were collected and characterized by the published selection criteria for aflatoxin adsorbents (Dixon et al, 2008). Aflatoxin adsorption capacity, pH, CEC, organic carbon, particle size distribution, and mineralogical and structural compositions of the bentonites were analyzed. Two bentonites were identified as potentially good aflatoxin adsorbents based on the analyses. These two bentonites were selected for an *in vivo* poultry experiment to test the efficacy of the clays in detoxifying aflatoxins. Also, detailed mineralogy analyses were conducted on these two samples after size fractionation. The bentonites were added at a rate of 0.5% (wt) into both a clean feed containing <20 ppb aflatoxins and a highly-contaminated feed containing ~1500 ppb aflatoxins. Feeds without the clays were used as controls. There were six treatments in total: (1) aflatoxin feed, (2) aflatoxin feed + clay A, (3) aflatoxin feed + clay B, (4) clean feed, (5) clean feed + clay A, (6) clean feed + clay B. Each of the six treatments had 8 replicas and each replica pen had five chickens initially. A total of 240 chickens were fed and monitored for three weeks. Feed intake and average body weight were recorded every seven days, and mortality was monitored daily. The chickens were sacrificed after three weeks. The weights of body, liver, kidney, heart, and spleen of each chicken were recorded individually. Five chicken livers from each treatment were chosen to quantify AfB1, AfB2, AfG1, AfG2 and AfM1 by HPLC.

Clay A (coded as 4TX) and B (coded as 1TX) contained 87% and 65% clay, respectively. Smectite was the dominant mineral phase in the clay fractions of the

two bentonites. Feldspars and quartz were present in the sand and silt fractions of both samples. Additionally 4TX contained clinoptilolite and 1TX contained pyrite in their sand and silt fractions. It is not likely that the zeolite, quartz, or feldspars will cause harmful effects on the chickens, but the presence of pyrite in 1TX raised concerns about its use in animal feed.

For the feed contaminated by 1500 ppb aflatoxin, adding clays in the feed increased body weight by 21% (clay A) and 12% (clay B); reduced AfB1 level in liver by 22% (clay A) and 47% (clay B), reduced AfG1 level in liver by 54% (clay A) and 33% (clay B), and total aflatoxins by 36% (clays A and B). Those differences (with and without clay) are statistically significant at  $p < 0.05$  level. Adding clays in the aflatoxin-contaminated feed improved the visual appearance of livers from pale red (10R6/6) to more reddish color (10R5/8) resembling the healthy red livers (10R3/6). Adding the clays to the clean feed did not show significant differences in any measured parameters at  $p < 0.05$  level. All chickens fed with clean feed had significantly higher body weights than those fed with highly contaminated feed. The aflatoxin levels in their livers were below the detection limits.

These investigations indicate that certain bentonites can effectively adsorb aflatoxin *in vivo*. Directly mixing the high-adsorbing bentonites as dry powder to highly contaminated poultry feed can reduce the acute aflatoxin toxicity to broiler chickens but does not eliminate it. The clays appear to be safe to use even with the presence pyrite in one of them. Dealing with large variation of the aflatoxin concentration in feed, making the clays well dispersed, finding adequate dose of the clays, and making the clays accessible to the aflatoxin in the feed need to be addressed in practice. More tests should be conducted on moderately contaminated feeds that occur more frequently.

Dixon, Kannewischer, Tenorio Arvide, Barrientos Velazquez. *Applied Clay Science* 40 (2008) 201-208



## ENZYME SUPPORTING PHOSPHOLIPID-SEPIOLITE HYBRIDS INCORPORATED IN POLYMER MATRICES FOR BIOSENSOR AND BIOREACTOR APPLICATIONS

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Preservation of biological activity is a crucial factor for immobilization of biological species on inorganic solid supports. These resulting hybrid materials form the basis of various kinds of biosensors such as enzymatic, immuno- or DNA sensing devices. A versatile approach to achieve biocompatible and robust immobilization host materials is the concept of biomimetic interfaces<sup>1</sup>. It involves molecular modification of a solid surface to create an environment that mimics biological structures and morphologies. A well-studied system is the artificial lipidic cell membrane. Adsorption of lipid molecules on solid supports renders biomimetic layers that are especially suitable for the accommodation of membrane proteins such as enzymes. It has been demonstrated that lipid bilayers adsorbed on different electrode surfaces are versatile supports of recognition moieties in many kinds of biosensors<sup>2</sup>.

In the present work sepiolite-phospholipid hybrids were evaluated as immobilization host for cholesterol oxidase and urease as model enzymes. The microfibrillar silicate sepiolite was used as solid support for the lipid membrane. Sepiolite is inherently biocompatible and its large specific surface area permits the immobilization of a high amount of biological entities. Cholesterol and urea sensors were fabricated to probe the ability of the sepiolite-lipid system to accommodate biological species preserving their activity. Recently developed sepiolite-phospholipid bio-organoclays were prepared from ethanolic phosphatidylcholine (PC) solutions. The resulting membrane morphology can be tuned according to the PC concentration and a mono- or bilayer arrangement is obtained<sup>3</sup>. Biomimetic properties of the clay supported lipid membranes were assayed with two distinct enzymes. Cholesterol oxidase was chosen as intrinsic membrane-bound enzyme, located at the outside of the cell. Contrarily, jack bean urease is a cytoplasmic enzyme which only externally associates to lipid membranes. The enzymes were immobilized from phosphate buffer solution on both mono- and bilayer biohybrids as well as on neat sepiolite and sepiolite modified with a commercial alkyl surfactant (CTAB). Sepiolite-enzyme conjugates were suspended in a polymer and deposited as film on gold electrodes. The enzymatic activity was assessed by cyclic voltammetry (CV) and calorimetrically by UV-Vis photospectroscopy. An immobilization model based on adsorption affinities was developed showing a clear beneficial effect of the supported lipid membrane on enzyme activity. The fabricated biosensors displayed high sensitivity and extended shelf-life up to various months. These results also indicate that the newly developed

materials possibly serve as general support for other types of biological species. Adding yet another level to the composite's hierarchy, enzyme-hybrid conjugates dispersed in a polymeric matrix were processed as macroporous foam, with the modified sepiolite acting as reinforcing agent to improve the mechanical properties.<sup>4</sup> The objective herein is the synergy of highly permeable foams that serve as reaction vessel for the catalytic enzyme-hybrids. By using carbon-doped polymer matrices, conducting foams can also be prepared and employed as high-surface electrode of a biosensing device.

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## *POSTER PRESENTATIONS*



## ADSORPTION OF RADIO CESIUM BY PHARMACEUTICAL CLAY IN STOMACH MEDIUM SIMULATED USING RADIOTRACER TECHNIQUE

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The pharmaceutical clay has been successfully used in treatment to eliminate some toxin and bacterial in body for their adsorption properties. The Smecta drug has been tested in the aim to modify the adsorption of radio cesium in simulated stomach, using the radiotracer technique in batch reactor.

In the first, we characterized the crystalline phases constitute the drug with the DRX and FTIR. In second part, we have evaluated the adsorption kinetics; the results showed that sorption followed pseudo-second-order kinetics. the effect of each parameter in simulated stomach (pH, ionic strength, temperature) and the influence of the alkaline ion ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) on the adsorption process. The Sorption showed spontaneous and exothermic behavior on clay, with  $\Delta H^\circ$  being -15.73 and ( $G_0 = 3.21$  (kJ/mol at 20°C). The equilibrium isotherms in simulated stomach were determined using the six models (Langmuir, Freundlich, Jovanovic, Jovanovic-Freundlich, Langmuir- Freundlich, and Dubinin-Astashov), however, the Cs sorption on Smecta follows the model of Langmuir- Freundlich which is the best result with regression factor close to unity ( $R^2=0.9858$ ) and  $Q_{\max}$  near of experimental result.

The acid medium in the stomach decrease the radio cesium sorption, we have tested some local anti acid drugs in the aim to improve the adsorption of Smecta drug.

## **AFLATOXIN CONTROL IN FEEDS AND FOODS WITH ADSORBENT SMECTITE CLAYS IN BENTONITES**

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It has been 50 years since aflatoxin was discovered and it still is a major problem to the health of animals and possibly for humans in many parts of the world. The chemical and crystal structures of the organic molecule that causes the disease have been determined. The fungi that produce aflatoxin in grains and nuts are propagated by spores throughout the world. Drought and heatstress conditions for the fungi to grow are increasing as the need for corn and other grains for fuel consume more water.

Among the detoxification strategies the use of smectite clay binders is a practical and economical method that has been supported with many in vivo experiments. Aflatoxin-binder clay selections are thorough, based on several chemical, physical, and structural analyses. Adsorbent clays in animal diets reduce aflatoxin infection in the animals and improve their performance. The increasing use of smectite binders of aflatoxin in animal rations serves as a basis for testing of smectite clay binders in food for humans where aflatoxin frequently occurs or is suspected by the severity of other diseases.

Agricultural producers face the seasonal risk of an aflatoxin infestation in a belt of ~30 counties in eastern Texas and a potential threat in another block of counties of limited water supply in north Texas. The increasing demand for corn for fuel and the greater need for water indicates a growing need for control of aflatoxin with adsorbent smectite clays. The need for water for human consumption is likely to continue to grow and more control of aflatoxicosis will be required. More well-selected adsorbent bentonite clays and improved performance clays will be needed.

Wider public education on this subject should strengthen the agricultural economy and improve health for animals and humans. National-international needs are for more public education on aflatoxin and preventative measures to reduce the infection in animals and in humans. There is a need for an improved regulatory policy on consistently blending aflatoxin-infected grains in feeds versus binding aflatoxin with tested and proven-beneficial smectite clays to increase animal performance.

Current needs to prevent aflatoxin infection of feed and food

- Quantitative measure of octahedral ion composition of smectite
- An analytical method of evaluating aflatoxin binding in smectite

- Efficient method for aflatoxin analysis in animal tissue
- Biological means of evaluating smectite adsorption effectiveness

Other current aflatoxin control needs

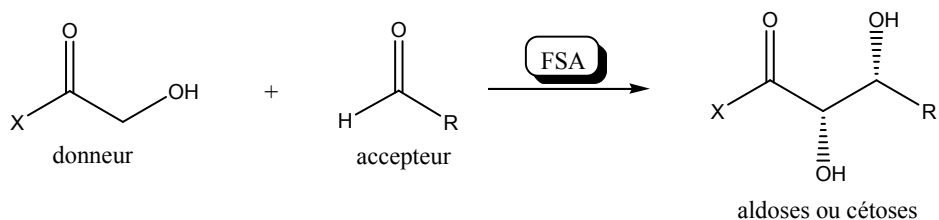
- Improved means of informing the public of preventative and corrective measures
- More annual maps of infection areas: domestic and international
- Methods of evaluating and treating DDGS to control aflatoxin in feed and food
- Financial support for aflatoxin monitoring and corrective measures by adsorption in feed and food

## FRUCTOSE-6-PHOSPHATE ALDOLASE LDH BASED BIOCATALYST FOR ALDOSE AND CETOSE SYNTHESIS

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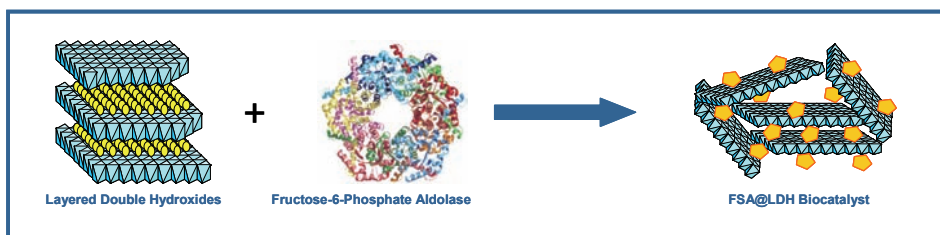
Fructose-6-phosphate aldolase (FSA) from *E. coli* [1] is a member of class I aldolases which catalyse the formation of C-C bonds. FSA displays unique catalytic properties under great investigations. FSA was previously described as a dihydroxyacetone (DHA) aldolase but recent works showed a broader catalytic activity towards hydroxyacetone (HA) [2], hydroxybutanone (HB)[3] and glycolaldéhyde (GA) [4].



DHA: X=CH<sub>2</sub>OH ; HA: X=CH<sub>3</sub>; HB: X=CH<sub>2</sub>CH<sub>3</sub> ; GA: X=H

The exceptional catalytic properties of the FSA allow to prepare in one step a large variety of aldoses and cétooses with interest in diabete and genetic desease therapy. However, its immobilisation on solid supports would allow its use for the scale up of organic synthesis. Layered Double Hydroxides, as unique anion exchange properties and 2-D structure, are suitable host matrices for the immobilization of enzymes [5] with an overall negative charge. FSA has been immobilized in Mg<sub>2</sub>Al-NO<sub>3</sub> LDH, by in situ coprecipitation. The biohybrid material has been fully characterized by chemical analysis, XRD, UV-Vis and FTIR spectroscopies. The biomaterial retains 100% of the free enzyme activity and catalytic testes will be presented.





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## ADSORPTION OF OXALATE ON MONTMORILLONITE

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The mineral/water interface plays a critical role in controlling the exchanges that occur between minerals and fluids present in the Earth's crust, hydrosphere and biosphere. The interaction of the surface reactive groups of the mineral with compounds transported in solution leads to mineral dissolution through a series of adsorption/desorption reactions. The presence of naturally-occurring low molecular weight organic acids, like oxalate, enhances the rate of dissolution. One possible mechanism for observed increase in the rate of dissolution involves the adsorption of the organic acid on the surface. The objective of this study was to investigate the adsorption of the oxalate on smectite using traditional sorption methods coupled with diffuse reflectance Fourier transform infrared (DR-FTIR) spectroscopy.

The adsorption experiments were carried out with bentonite from Cabo de Gata (Almería, SE Spain). Batch adsorption experiments were conducted in the pH range from 2 to 10 (adsorption edges) using 1.5 mM oxalate and constant ionic strength (10 mmol L<sup>-1</sup> KCl). Ion chromatography was used to determinate oxalate concentration. Oxalate adsorption was quantified by comparing the concentration of oxalate in control samples and the concentration remaining in the solution samples after being equilibrated for 5 hours. For the infrared study, the clay suspensions were filtered and allow to air dry.

The sorption of oxalate on the clay was strongly pH dependent. The maximum amount of oxalate sorbed was 13  $\mu$ moles per gram of clay at pH 2 and the amount of oxalate adsorbed decreased with increasing pH. Above pH 8, oxalate does not adsorb on the smectite surface. The DR-FTIR results are in agreement with the adsorption edge results. We observed the oxalate bands in the spectra at pH values below 8. Above pH 8, there was no difference between the spectra of the clay samples with oxalate and the spectra of the clay without oxalate at the same pH value. The DR-FTIR spectra were inconclusive regarding the type of binding oxalate to montmorillonite in our experimental conditions.

The behaviour observed in our study has been note previously for oxalate/kaolinite system (1). The increase in adsorption at low pH and the decrease in adsorption at high pH can be explained by considering the electrostatic interactions between the carboxylic acid species and the edge sites. As the pH decreases, positively charged sites are predominant at the montmorillonite edges due to protonated aluminol sites

(2), leading to an electrostatic interaction with the oxalate (negatively charged at pH > 1.28).

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## GOSSYPOL ADSORPTION BY UZBEKISTAN BENTONITES

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Cotton seed cake has a high content of protein, however use of cotton seed cake in animal feed is limited by the presence of a toxic polyphenol – gossypol. The specific objective of this investigation is to characterize the physical and chemical properties of bentonites from nine Uzbek deposits and to determine whether the properties of the bentonites influence their capacity to adsorb gossypol from water-acetone solutions.

The crushed (<250  $\mu\text{m}$ ) but otherwise raw bentonite samples were equilibrated with different concentrations of gossypol ( $5 \times 10^{-6}$ ;  $10^{-5}$ ;  $2 \times 10^{-5}$  and  $5 \times 10^{-5}$  M  $\text{L}^{-1}$ ) in 0.05 M Na-acetate at three pH balances (pH 4.0; 5.0 and 7.45) and four ionic strengths (0, 0.05, 0.1 and 0.15 M NaCl). The amount of excess gossypol in the supernatant was quantified by UV/vis spectrophotometry using the phloroglucinol reagent method.

The  $K_d$  values ranged from 0.91 to 94.2 (L/kg). Average  $K_d$  values for all 9 bentonites increased from 16.0 to 31.6 as the background NaCl concentration increased from 0 to 0.15 M, and were higher at pH 5 than pH 4 or 7.45 (average  $K_d$  values were 23.8, 31.8, and 18.1 for pH 4, pH5, and pH 7.45, respectively). No significant correlations between  $K_d$  values and measured bentonite properties (bentonite CEC, smectite layer charge, total C, or total N) were observed. Scanning electron microscopy indicated that two of the three bentonites with high gossypol adsorption (the Dehkanabad and Tavoksay bentonites) consisted of aggregate clusters with significant intra aggregate porosity. However the third bentonite with high gossypol adsorption, the Arabdasht bentonite, did not exhibit aggregate cluster morphology. The data so far offer no consistent clues as to why some bentonites adsorb more gossypol than others.

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## MICROBIOLOGICAL ASSESSEMENT OF SOME VOLCANIC MUDS FROM S. MIGUEL, AZORES

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São Miguel is one of the nine volcanic island of Azores archipelago. The island exhibits several secondary volcanic manifestations such as hydrothermal waters and fumaroles. Muds from fumaroles have peculiar characteristics that, for health purposes, can be considered very interesting, like for example their high content in sulphur. However, other several properties should be improved, like pH and abrasivity features which might be enhanced by maturation procedures. This research was performed on laboratory, where three different S. Miguel mud samples were submitted, during 60 days, to mixture with Furnas mineral water under different abiotic conditions. This research intends to study if microbiological community, with focus on diatomological one, have the ability to colonize and develop on these raw materials and identify the best conditions. Three different combinations of light conditions (artificial light/ natural light/ darkness) and two different stirring conditions (remixing/ no mixing) were tested at controlled room temperature (about 18°C during the day and 15°C at night). Therefore, muds samples from Lagoa (16), Furnas (10) and Ribeira Grande (19) (65 up to 68°C and pH=1.7 to 1.8) were collected in November, 2008 and sieved at 500 µm before maturation. Two biological samples were collected from the edges of muds sampling area; one sample was preserved alive for mud inoculation, the second inoculate was immediately preserved with formalin for posterior observation. pH and temperature were measured directly on field and periodically, during the process.

For diatom identification, an aliquot of samples was cleaned using HNO<sub>3</sub> and potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) at room temperature for 24h, followed by several centrifugations for acid removal. Slides were mounted using Naphrax® and observed under light microscope (Leitz Biomed 20 EB) at 1000x under oil immersion for diatom identification and semi-quantification. Taxonomy was based on Floras commonly used for Freshwater diatom studies.

Results revealed the ability of diatom community to develop on samples submitted to light without mixing procedures; samples 16 and 19 submitted to the mentioned conditions developed a continuous biofilm. With the exception of sample 16, mud

samples revealed, after maturation, a decrease on number of taxa comparatively with biological samples from the different sampling area. The species found in biological samples and mud samples are in agreement with several studies on diatom composition of acidic environments. The most representative genus was *Nitzschia* Hass. but *Pinnularia* Ehrenb., *Achnanthes* Bory, *Aulacoseira* Thwaites, *Eunotia* Ehrenb., *Navicula* Bory, *Fragilaria* Lyngbye, *Frustulia* Rabenhorst and *Gomphonema* Ehrenb. genera were also observed.

Our results give more information about natural resources maturation procedures and assume to be very promising because diatoms, mainly from the *Nitzschia* genus, are reported as producers of anti-inflammatory action which can be recognized as an important feature for thermal application.

## PREPARATION AND CHARACTERIZATION OF POLYHYDROXYBUTYRATE NANOCOMPOSITE MICROCAPSULES OBTAINED USING SMECTITIC CLAYS

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Drug delivery systems involving microcapsules are an attractive way to improve the performance of many chemical and biological substances. These systems may be used in several industrial sectors, especially medical, pharmaceuticals and cosmetics allowing the developing of better therapies. Alginate and polylactic acid polymers, and recently the poly(3-hidroxibutirato) (PHB), are examples of polymers used to obtain biodegradable microcapsules. PHB is a polyhydroxyalkanoate available in a chemically pure form, biocompatible, biodegradable and inert towards animal tissues [1]. The preparation of PHB/smectite clay nanocomposite improves the physicochemical properties of PHB, including its biodegradability [2]. In this work, we describe the preparation of microcapsules from two nanocomposites systems: a) PHB and Closite 20A organoclay (PHB1) and b) PHB and natural Brazilian Green polycationic clay (PHB2). The clays were characterized by XRD, CEC, DTA, TGA, IR, SEM and swelling capacity in water and organic solvents. The organoclay sample shows high swell in organic liquids, while the polycationic clay sample shows low swell in both water and organic liquids, although high swell in sodium lauryl sulfate aqueous solution. Nanocomposite films and microcapsules were prepared by the solvent evaporating technique using chloroform as solvent and 0.5% PVA solution as emulsion stabilizer agent. When analyzed by XRD the films and microcapsules do not show  $d_{(001)}$  peak, evidencing an exfoliated structure in the nanocomposites. The films have shown by SEM a homogeneous distribution of the clay mineral particles spread uniformly in the PHB film matrix. The new nanocomposite microcapsules have shown a “hydrangea” or “flower” structure similar to that of PHB microspheres prepared by Shishatskaya et al. [1]. The PHB1 microcapsules with organoclay showed a more open structure than the PHB2 microcapsules with the polycationic clay. The diameters of the microcapsules were in the range 0.5-10  $\mu\text{m}$ . In this work we have demonstrated that it is possible to obtain nanocomposite films and microcapsules of PHB using an organoclay or a polycationic smectitic clay. These nanocomposite microcapsules would have potential application in areas such as drug delivery systems.

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## CHARACTERIZATION OF SOUTH AMERICA SMECTITIC CLAYS AND THEIR POTENTIAL USE IN COSMETICS

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The Brazilian bentonites of the Paraíba State, northeast of the country, and the bentonites from the Argentinean province of Neuquén, represent an important fraction of the smectitic clays used in Brazil. The traditional applications for these clays are as ligands for foundry sands and iron ores, tixotropic additives for the oil drilling well industries and as pet litter sands. Nowadays, the social changes caused by the developing of new materials, the expressive scientific discoveries involving clays as nanocomposites with biodegradable polymers and biopolymers and its application in several industry sectors and the new look from people towards our planet, about uses and care of natural resources, have rescued the interest for the use of clays as *in natura* materials for use in the cosmetic and pharmaceutical industries. The aim of this work is to investigate if the South American bentonites present potential for application in cosmetic and medicinal products. We have characterized five natural clays: four polycationic smectites (green, clear green, white and beige colors) from the Brazilian state of Paraíba and one natural sodic bentonite from the Argentinian province of Neuquén (brown color). The objectives were to determine structural differences and to establish parameters for their use in cosmetics. The clays were firstly purified by sedimentation. The deflocculated fractions were then dried and analyzed by chemical analysis, XRD, thermal analysis, SEM, cation exchange capacity, exchangeable cations, FT-IR spectroscopy, swelling capacity in water and organic solvents and viscosity of water dispersions (Fann and Brookfield). Dermatologic studies and microbiological assays were conducted to determine the implications of these clays on the skin. The clays, all containing basically montmorillonite, presented low percentage of heavy metals and no contamination by bacteria, being within the recommendation of the Brazilian, American and European Pharmacopoeias for bentonites. These results aside the dermatological ones indicate a high potential for the use of these clays in cosmetics and toiletry products.



## TOPIC 6

*Industrial and Other Applications*



## *ORAL PRESENTATIONS*



## KEYNOTE

### LAYERED DOUBLE HYDROXIDES AND THEIR USE AS PRECURSORS OF CERAMIC PIGMENTS

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The colour of ceramic pigments depends on their chemical composition and the size of the particles. Most of the compounds used as ceramic pigments are oxides or mixed oxides. These pigments can be classified into three types: (i) *structural pigments*, where the chromophore is one component in a well defined structure, e. g.,  $\text{CoAl}_2\text{O}_4$ ; (ii) *solid solutions* (e. g.,  $\text{V}^{\text{IV}}/\text{ZrSiO}_4$ ), where the chromophore is dissolved in a crystalline structure, and (iii) *encapsulated pigments*, where the chromophore is occluded in a protective crystalline structure, as CdS (or CdSe) in  $\text{ZrSiO}_4$ . Main drawbacks of these pigments is that preparation of types (ii) and (iii) is limited by the solubility and encapsulation difficulties, respectively, while all three types usually need the use of mineralisers for their preparation, with negative effects on the environment. So, development of scalable methods to prepare structural pigments avoiding the use of mineralisers and excessively high temperatures is a current challenge in the ceramic industry.

Layered double hydroxides (LDHs) constitute a family of compounds with increasing interest among the scientific and technological communities because of their easy preparation and the different fields where they find applications.

Their structure permits incorporation of a large diversity of cations, only limited by their ionic radii and formal charge, as well as of anions, although for many of the applications the preferred anion is carbonate, as it is easily evolved as carbon dioxide upon calcination, leaving a mixed oxide with homogeneous dispersion of the components, large specific surface area and other properties. These oxides can be used as adsorbents, heterogeneous catalysts and, if coloured cations (from transition metals with incomplete *d* shells) exist, also as ceramic pigments.

We here report on the main procedures available to prepare these materials (coprecipitation, ionic exchange, reconstruction from mildly calcined LDH precursors, induced hydrolysis, sol-gel, etc.), highlighting their advantages and drawbacks, the post-synthesis treatments (ageing, hydrothermal, or microwave treatments) usually applied, and their main features, as concluded from their physicochemical characterisation.

The preparation of non-stoichiometric systems containing transition metal cations has been also claimed to produce mixed oxides with a wider colour palette. Calcination of the parent LDHs gives rise to a mixture of the oxide of the divalent cation, together with the  $M^{II}/M^{III}$  mixed oxide (generally with the spinel structure). By preparing non-stoichiometric LDHs, where the  $M^{II}/M^{III}$  ratio is below the limiting value of 2.0 for a single LDH structure, we can obtain a more precise colour.

We conclude that the use of LDH precursors to prepare non-stoichiometric spinels containing transition metal cations is an attractive route to obtain ceramic pigments. These show a high purity, without the use of mineralisers, calcination is carried out at temperatures noticeably lower than those required by the ceramic procedure, and a fine tuning of the colour can be attained through selection of the nature of the cations and their relative concentrations.

Standing challenges, however, still remain, concerning the preparation of these pigments with a definite particle size and narrow particle size distribution for being used in ink-jet ceramic printers, substituting coordination compounds solutions.

Acknowledgments: Financial support from MICINN (grant MAT2009-08526), Junta de Castilla y León (grant SA111A09) and ERDF is greatly acknowledged.



## EXPLORING THE COMPETITIVE ADSORPTION OF STARCH AND PLASTICISERS IN THE CLAY INTERLAYER AND ITS INFLUENCE ON THE BARRIER PROPERTIES OF STARCH NANOCOMPOSITE PAPER COATINGS

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Clays have been used in traditional paper coating technologies for many years but the focus has been on non-swelling clays because these exert the least effect on the rheological properties of a formulated coating. However, recent work in the SUSTAINPACK project has demonstrated that combining swelling clays, particularly the smectites, with starch and plasticisers, to form a sustainable coating, results in water vapour transmission rates (WVTR) that are competitive with oil-derived barrier coatings. This concept is being further developed in the FLEXPARENEW project and has amplified the need to better understand the interaction of starch, clays, plasticizer and water both in the clay and in the coating.

Achieving the low WVTR value required depends on the type of plasticiser used in the coating formulation. The plasticiser is also a critical ingredient needed to overcome the inherent brittleness of the starch which becomes a major factor when the coated paper or board is bent or creased.

The simultaneous presence of both starch and plasticizer in the clay gallery appears to be critical in order to achieve the required WVTR values. Unfortunately, it is difficult to unequivocally identify what proportion of starch and plasticizer is present in the gallery of those coatings which present the largest barrier to permeation of water vapour.

In order to better understand the contribution of the different components in the coating formulation the interaction of plasticisers such as glycerol, sorbitol and polyethyleneglycol with the bentonite used has been studied in the absence and presence of starch using XRD. Particular attention was focussed on how the d-spacings were influenced by factors including the type of plasticiser, the starch and plasticiser loading, the ambient humidity and the processing temperature.

The interpretation of the data is complicated by the heterogeneous nature of the starch(es) used. Consequently, parallel studies in which the starch has been replaced by PVOH, of molecular weight 30,000, have been undertaken to support the interpretation of the behavior in the starch/clay/plasticizer coating formulations.

## ORGANOMODIFICATION OF CLAYS USING DIFFERENT SOLVENTS

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Traditionally, organoclays are prepared using water. The main reason for this is that individual layers in natural clays containing interlayer sodium or calcium cations are significantly swollen, if not exfoliated, and thus present a large surface area for the organic modifier to interact with. Another advantage is that water is an environmentally friendly solvent that raises few problems in use or during subsequent disposal. A recent study focussed on the development and use of mixed modifier clays, i.e. clays with more than one organic modifier, served to illustrate the difficulty in producing a homogeneous distribution of both organomodifiers over the clay surface when water was used as the solvent. Several alternative solvent systems were subsequently investigated and the findings are reported herein.

Initial experiments investigated the redistribution of a single organomodifier on commercially available high purity bentonites which included Cloisite 10A and Cloisite 30B. These products are prepared using dimethylbenzylhydrogenatedtallow ammonium and methyltallow, bis-2-hydroxethyl ammonium cations, in quantities higher than the CEC, as organomodifiers. Several solvents were chosen based on their solubility parameters and polarities and included; ethanol/water mixtures, dimethylformamide, tetrahydrofuran, nitrobenzene and chloroform. Further experiments investigated the re-distribution of excess organomodifier when in the presence of additional sodium montmorillonite (Cloisite Na<sup>+</sup>). As anticipated it was found that solvents with a polarity matching that of the modifier (ethanol/water and nitrobenzene) were more able to facilitate re-distribution or wash away the excess organomodifier, whereas those in which the polarity match was poorer (water and chloroform) promoted little, if any, further distribution/modification. The next parameter investigated was the addition of a second organomodifier (choline) to one of the commercially available clays that had previously been mixed with sodium montmorillonite. The best result in terms of producing a homogeneous distribution of organomodifiers was achieved using nitrobenzene, which was attributed to its ability to swell the clay combined with its particular balance between polar and non-polar character.

X-ray diffraction, thermogravimetry mass spectrometry, carbon and nitrogen analysis and infrared spectroscopy were used to characterise the systems.

## EFFICIENCY OF LIME TREATMENT ON MICASCHIST SOIL

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Nowadays interest of environment protection and sustainable development is growing up, leading to improve natural resources management. Land settlement, and more precisely earthworks, is directly concerned with this new policy in order to limit using of external materials.

Nevertheless, some crude soils as soft clays or clayed silt do not satisfy geotechnics criteria for a safe use. Several earthworks on North West of France have met difficulties with fine grained soils of micaschist type, which do not verify mechanical and swelling requirements even if they are treated with different common mixtures of lime and/or hydraulic binders.

Generally, soil treatment failed because of strong water sensitivity inducing a volumic swelling of about 11% for a crude material. These clayed silts are a mixture of quartz, kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) muscovite ( $\text{K}(\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ ) and some accessory minerals as titanium oxide and iron hydroxide. Chemical analyses show the absence of sulphates, phosphates, and organics matter, which are know to have a negative effect on the lime treatment. Swelling characteristic of these soils is not well understood but one explanation could come from physical interactions between clay minerals.

Even if these treated soils are considered as non convenient, lime treatment makes important changes on hydromechanical properties on these soils. To focus on lime effect for the worst behaviour of these soils, i.e. swelling behaviour, we have delayed water introduction from 1 hour to 28 days before swelling measurement under 3kPa load on oedometer device. One hour of treatment can decrease by the half the swelling. Moreover with a curing time of 28 days swelling is almost suppressed. In the same time the volumic swelling decreases, shear strain increases. Microstructural measurements like saturation degree and pore size are used to follow lime effect on soil microstructure.

In order to understand these improvements of mechanical performance we have completed geotechnical measurement by a physicochemical study. The clear goal is to explain macroscopic behaviour by microscopic changes. In this report, we will show the results obtained by thermal analysis and by nuclear magnetic resonance in function of time reaction and rate muscovite/kaolinite. Lime consumption and cement phases formation can explain macroscopic observations.

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## SEPIOLITE - SUPPORTED METALLIC NANOPARTICLES

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Gold nanoparticles were deposited on the external surfaces of the clay mineral sepiolite previously functionalized by an organosilane. The effect of the pre-acidification treatment of sepiolite on the size and the dispersion of gold nanoparticles was studied. Well dispersed nanoparticles with an average size of 2-3 nm were obtained in the case of the clay mineral treated with HCl under soft conditions, whereas in the case of the untreated sample, the deposition of gold was not homogeneous.

These sepiolite-supported gold nanoparticles were used as catalyst for the reaction of esterification of phenols under soft conditions and organic solvent-free conditions with acetic anhydride as acetyl donor. Reactions were done using conventional heating (C.H) and Microwave irradiation (MW.I). Improved yields with dramatic reduction of the reaction time were obtained under microwave irradiation.

This work was extended to other metallic nanoparticles. In general, the nanoparticles are aligned on the external surfaces of the sepiolite fibers, plausibly along the external silanol Q<sub>2</sub> sites.

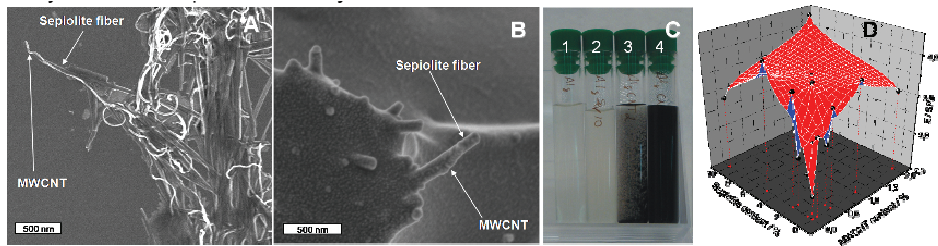
## ON THE SYNERGY BETWEEN SEPIOLITE AND CARBON NANOTUBES IN BIONANOCOMPOSITES

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Bionanocomposites are a new class of hybrid materials that concerns the use of nanosized particles within a continuous biopolymer matrix. The research and use of these materials has gained thrust since its recent appointment by our research group, mostly due to the wide use in functional and structural applications in the biotechnology field that is expected<sup>1, 2</sup>. Within the bionanocomposite field of work, one of the chief concepts is that of nanofillers. These can be roughly divided into two major groups. Firstly, silica and silicate based nanofillers, which aside from being the initial nanocomposite fillers after the pioneering work by Fukushima<sup>3</sup>, represent ideal functional fillers as they present multiple functionalization pathways, mostly due to their easily accessible surface and intra-particle chemistry. Secondly, carbon based nanofillers like carbon nanotubes (CNTs) represent the paradigm of the structural reinforcement nanoparticle, holding the highest known elastic modulus<sup>4</sup>, and presenting a remarkable electronic conductivity alongside with high aspect ratio. Nevertheless, these materials show specific features such as poor surface chemistry, that have continuously postponed its wide application in the nanocomposite field, mostly due to its extreme insolubility in a wide range of media. In fact, a simple comparison between the properties of these two types of nanofillers reveals how complimentary the two types of particles are. Where sepiolite is highly functionalizable, water soluble and mechanically fragile ( $E \sim 55$  GPa), CNTs are very difficult to functionalize, highly insoluble and mechanically outstanding ( $E \sim 1$  TPa).

Recently, a patented work<sup>5</sup> by our group disclosed the homogeneous colloidal suspension of CNTs in the presence of sepiolite fibers obtained by a synergistic effect between the two components. This work takes advantage of the referred complementarity to achieve stability in aqueous conditions and to prepare bionanocomposite films and fibers with improved mechanical and electronic properties. It also aims at deepening both the synergetic and anti-cooperative effects observed in mechanical reinforcement and electronic properties by means of a systematic compositional study.



**Figure 1** - Association between sepiolite fibers and CNTs as viewed by TEM and SEM (image A and B) respectively. Alginate solution C1, alginate solution in presence of 10% sepiolite (referred to alginate mass) C2, alginate solution in presence of 2% CNTs (also referred to alginate mass) C3 and alginate solution in presence of both 2% CNT and 10% sepiolite C4. Image D presents the resulting Young's modulus of the alginate/sepiolite/CNT bionanocomposites at different loadings.

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## PREPARATION AND CHARACTERIZATION OF POLYIMIDE/ LAYERED DOUBLE HYDROXIDE NANOHYBRIDS

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Polyimide (PI)/layered double hydroxide (LDH) nanohybrids were prepared. For this work, LDHs were modified with pyromellitic dianhydride (PMDA), succinic acid and terephthalic acid by anionic exchange reaction. For PI, PMDA and 4,4'-oxydianiline were used to make the precursor poly(amic acid)(PAA). From FT-IR spectroscopy, X-ray diffraction and transmission electron microscope measurements, we confirmed that the PMDA-modified LDH (PMH) and terephthalic acid modified LDH(TMh) were well dispersed in PI matrix. For succinic acid modified LDH(SMH), some parts of LDH were intercalated by succinic acid molecules but most part of LDH were remained with original structure. Thus, PI/PMH and PI/TMH hybrids showed significantly improved mechanical, thermal, and electrical properties as compared to pure PI. It is expected that PMH has aromatic group and better interactions with PI chains than any other m-LDHs. The PMH might react with the end group of PAA and thus show good tensile strength and high T<sub>g</sub>. It was concluded that PI/PMH hybrids exhibited best performance properties than other nanohybrid materials.



## THERMALLY MODIFIED CLAYS AS ADSORBENTS FOR INDUSTRIAL APPLICATIONS

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The additives fulfill several useful functions in the food, which often we give for sat. Nevertheless the widespread use of food additives in the food production also influences the public health. The food industries, which are very important for the economy, spill residues proved from its activity that they have to be controlled to evaluate the environmental impact and to offer the necessary information about the quantitative evaluation of the chemical risk of the use of food additives for the public health.

We have studied the adsorption of several food additives by thermally modified clays, searching their interaction mechanisms and the possible recycling of these materials for environmental purposes and prevention of the public health.

Among the strategies used at present to preserve the quality of the water and this way to diminish the environmental risk that supposes the chemical pollution, stands out the use of adsorbents of under cost, already they are natural or modified, to immobilize these compounds and to avoid the pollution of the water with the consequent reduction of environmental and economic costs. Regarding innocuous and low cost materials, it is necessary to mention clays and clay minerals, which colloidal properties, facility of generating structural modifications, abundance in the nature and low cost make them very adapted for the adsorption of chemical pollutants. The clayey materials have given place to numerous applications in the field of the public health (1, 2) and its efficiency having being demonstrated as natural or modified adsorbents of all kinds of pollutants (3).

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## **ADSORPTION OF CLUSTERS OF PHOTO-FUNCTIONAL DYES ONTO CLAY MINERALS EXFOLIATED TO SINGLE LAYERS**

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Composites consisting of dyes and clay minerals are promising candidates of future nonlinear optical (NLO) materials because of their salient NLO properties [1-3]. NLO materials must satisfy the properties of optical materials, such as an optical flat surface, reasonable size and low light-scattering characteristics. We have fabricated several such dye-clay composites through ion-exchange reactions of aqueous dispersion of exfoliated clay minerals with solutions of dyes [2, 4]. In the course of our study for obtaining efficient NLO clay-dye composites, we have found that most of cationic NLO dyes prefer to form clusters when they are adsorbed onto the surface of exfoliated clay minerals [3]. The average size of the cluster was found to depend on the fabrication conditions, such as temperature, concentration of the dyes and so forth. Depending on the size of the cluster, the composites were found to exhibit various optical characteristics. In this paper, the examples will be introduced.

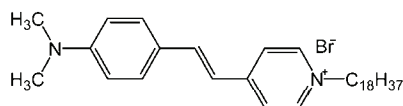


Figure 1. Chemical structure of ODEP<sup>+</sup>Br<sup>-</sup>.

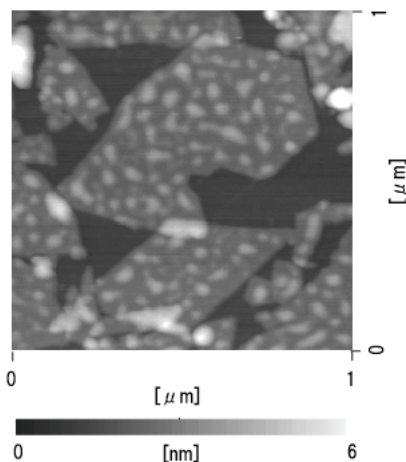


Figure 2. An AFM image of a hybrid LB film fabricated at 40 °C.

One example is a hybrid Langmuir-Blodgett (LB) film [2] of *N*-*n*-octadecyl-4-[2-(4-dimethylaminophenyl)ethenyl] pyridinium bromide (ODEP<sup>+</sup>Br<sup>-</sup>; figure 1) and sodium montmorillonite (Kunipia-P, Kunimine Ind. Co. (Japan), CEC: 1.17 meq g<sup>-1</sup>). An atomic force microscope (AFM) image of an obtained film is shown in figure 2. Formation of clusters on the surface of Kunipia-P can be seen. We fabricated hybrid LB film using subphases at various temperatures. As shown in figure 3, the sizes of the clusters estimated from AFM images were found to vary depending on the temperature. Figure 4 indicates the wavelength of the absorption maxima of the obtained hybrid LB films shifted depending on the cluster size.

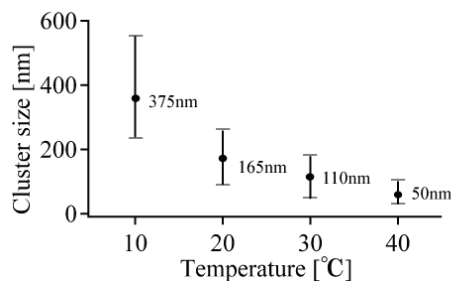


Figure 3. The size of the cluster of ODEP<sup>+</sup>Br found on the surface of Kunipia-P.

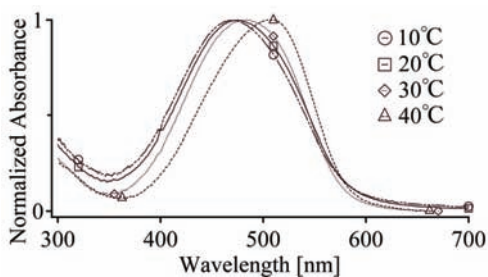


Figure 4. Absorption spectra of the hybrid LB film obtained at different temperatures.

Not only linear optical properties but also NLO properties depended significantly on the cluster size. The detail will be also discussed.

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## CLAYS IN THE GEOMETALLURGY OF COPPER MINING: EXAMPLES FROM CHILE

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Geometallurgy is a field with diverging definitions ranging from the straightforward translation of geological-mineralogical information to metallurgical processing parameters to the implementation of a complete integrated data management systems from exploration over mining and ore processing to product and waste quality monitoring. The field is gaining importance as old mines have to extract ore that has not been treated at the early stages of operation either due to geomechanical problems, complex mineralogy (many clay phases are included here) or environmentally complex minor and trace element chemistry.

Key issues at the geology-mineralogy-metallurgy interface are how to translate/transfer clay mineralogical information obtained often at nanometric scale to giant scale comminution, heap leach or flotation operations. This implies compatibilizing a highly specialized mineralogical language or terminology with the essential parameters of ore processing, thus screening and “reformatting” mineralogical and related data as decision tools in metallurgy.

Examples of geometallurgical concerns involving clay minerals in Chilean copper mining include:

(1) The adequate calibration of field IR equipment based on macroscopic sample/core description, microscopy, qualitative and semiquantitative XRD information, quantitative microchemistry (e.g. Qemscan) and wet chemical data. (2) The transformations of different phyllosilicate families (or even species) during heap leaching with sulphuric acid in terms of acid consumption, delamination, initial expandability and Cu exchange or adsorption. (3) The nanometric intergrowth of chrysocolla or atacamite and kaolinite or smectite (copper clays) and the possibility of Cu recovery from them. (4) Rock texture and clay phases and how does the distribution of clay microdomains influence metal extraction (5) The adaption of tests from the petroleum industry, civil engineering, soil science and colloidal chemistry to predict leach comportment at least on a large bench scale. (6) The understanding of problems caused by phyllosilicates (e.g. pyrophyllite, talc) in flotation. (7) The recovery of process water avoiding irregularities in sedimentation due to e.g. smectite. (8) The capacity of heavy metal retention by phyllosilicates (in particular smectites) downstream of old tailings impoundments. (9) The relevance of clay phases in bioleach operations, as one of the most recent subjects.

With virtually all senior professionals and academics working in this field being autodidacts, emphasis is placed - beside very applied approaches to offer solutions or at least partial or incipient solutions to the above problems – on teaching clay mineralogy to metallurgical and mining engineers. Still there is much need to refer to advances in the fields of the ceramic industries, civil and petroleum engineering, where clays are already long term protagonists.

## CHARACTERIZATION OF ORGANOCCLAYS FOR COMPOSITES WITH NATURAL RUBBER

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Sodium-saturated  $<2\ \mu\text{m}$  fraction (Na-JP) separated from bentonite Jelšovský Potok (Slovakia) was used for preparation of eight montmorillonite-based organoclays. Organic cations were carefully selected to allow more ways of comparisons of the properties within the series. Four samples contain different numbers of octylammonium chains: monoctylammonium (1C8), dioctylammonium (2C8), trioctylammonium (4C8), tetraoctylammonium (4C8), while two others have chains of double length with 16 carbons each, hexadecylammonium (1C16) and dihexadecyldimethylammonium (2C16). Last two cations are of different structure containing aromatic benzene, either without reactive double bonds (benzyltrimethylammonium, C10) or with a reactive double bond present in styrenyl-like surfmer (4-vinylbenzyl-trimethylammonium, C12).

Powder XRD analysis showed that the  $d_{001}$  distances depended to a large extent on the size and structure of the organocation. After subtracting the montmorillonite layer thickness of 0.96 nm from the  $d_{001}$  values obtained for the 1C8-, 2C8-, 3C8- and 4C8-JP series, the interlayer distances increased from 0.45 through 1.02, 1.48 to 1.68 nm, respectively. Adding of each octyl chain into the organocation caused expansion of the interlayer space by  $\sim 0.5$  nm up to the trioctylammonium cation, while the difference between the 4C8-JP and 3C8-JP was only  $\sim 0.2$  nm. The  $d_{001}$  distances in the samples with 16 carbon atoms showed that the 2C8 cation was able to open the interlayers up to 1.02 nm, more than the 1C16 (0.85 nm). The data for the cations with 32 carbon atoms 4C8 (1.68 nm) and 2C16 (2.28 nm) proved that the later cation was more effective for this purpose. The MIR spectra of the organomontmorillonites showed similar shape of the IR patterns of  $\text{CH}_3$  and  $\text{CH}_2$  stretching ( $3000\text{--}2800\ \text{cm}^{-1}$ ) and bending ( $1500\text{--}1300\ \text{cm}^{-1}$ ) vibrations within the 1C8-4C8 and 1C16-2C16 series. However, the spectra of the samples with 16 C atoms - 2C8 and 1C16, and 32 C atoms - 4C8 and 2C16, were significantly different due to altered ratios of  $\text{CH}_3$  and  $\text{CH}_2$  groups in the cations. Only weak absorption bands corresponding to stretching  $\text{NH}_3^+$  and  $\text{NH}_2^+$  vibrations ( $\sim 3270\text{--}3190\ \text{cm}^{-1}$ ) were resolved in the MIR spectra of 2C8, 3C8 and 1C16, the  $\text{NH}^+$  band was overlapped with the CH or  $\text{H}_2\text{O}$  vibrations. As expected, much lower interlayer expansion of 0.55 nm was obtained with both smaller cations, C10 and C12. Only absorption bands due to vibrations of trimethylammonium cations were clearly identified in the MIR spectra of C10 and C12 containing benzene, weak bands near  $3100\ \text{cm}^{-1}$  should correspond to Ar-CH. Vibrational modes of Ar-C-C, or  $\text{H}_2\text{C}=\text{C}$  (vinyl) group were overlapped with more

intense vibrations of aliphatic CH groups. The NIR spectra showed bands assigned to the first overtones ( $2\nu_{\text{XH}}$ ) and combination ( $\nu+\delta$ )<sub>XH</sub> bands of XH groups (X = O, C, N); they were found extremely useful to identify NH and vinyl groups of the cations, which were difficult to recognize in the MIR region. The first overtone and combination bands of  $\text{NH}_3^+$  and  $\text{NH}_2^+$  were found in the 6600-6050  $\text{cm}^{-1}$  and 5000-4600  $\text{cm}^{-1}$  regions, respectively. Only ( $\nu+\delta$ )<sub>NH+</sub> combination mode near 4750  $\text{cm}^{-1}$  was observed in the NIR spectrum of 3C8. The characteristic band assigned to  $2\nu_{\text{CH}_2}$  in  $\text{H}_2\text{C}=\text{C}$  at 6130  $\text{cm}^{-1}$  was detected in the spectrum of Ar-C12. Thermogravimetric analysis performed in  $\text{N}_2$  flow showed the mass losses in the temperature range of 150-800 °C of 13.0 %, 26.9 %, 41.3 % and 37.6 % for 1C8-4C8-JP, respectively, covering the desorption of water; thermal degradation and pyrolysis of the surfactant, and the dehydroxylation of the mineral. The values for the other organoclays were 24.6% (1C16-JP), 40.4 % (2C16-JP), 15.2 % (C10-JP) and 15.3 % (C12-JP).

The organoclays were used as fillers for preparation of composites with natural rubber. The blends for mechanical tests of the composites were prepared by mixing the rubber with the filler and the vulcanization ingredients, the slabs were obtained by compression moulding and the specimens were mechanically cut out from the vulkanized slabs. Reinforcing effect of the fillers increased with the number of the octyl chains in the series C8-4C8 and C16-2C16; the same effect was observed for both tensile strength and elongation at break. The highest elongation and strength values of all composites were obtained for those containing the 4C8 filler. The double bond in C12 did not affect considerably the mechanical properties.

## NANOTUBULAR KAOLINITE AS AN ADDITIVE FOR PREPARATION OF POLYLACTIDE/CLAY COMPOSITES

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Polymer/clay nanocomposites receive much attention due to their interesting mechanical and thermal properties. Interaction between organic polymer matrix and highly dispersed inorganic nanoscale particles leads to a significant change of polymer properties. Among important factors that determine the composite properties are size and shape of filler particles and its surface chemistry. Currently, the vast majority of plastics are made from petroleum-based synthetic polymers that do not degrade in a natural environment and their disposal poses a serious problem. An environmentally-conscious alternative is to design polymers that are biodegradable. In the present work we investigate the synthesis and properties of a novel polymer/clay nanocomposites based on polylactide (PLA) and kaolinite. PLA is a highly biodegradable polymer produced at commercial scale from cornstarch and sugarcanes, with potential to replace undegradable materials produced from fossil fuels in food packaging applications. Kaolinite clays of different grain morphologies are used as fillers.

For the experiments PLA polymer 3051D obtained from NatureWorks® dissolved in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was used. The sample of platey kaolinite of high degree of structural order (M40) was obtained from "Maria III" deposit (Poland). The nanotubular kaolinite (M40MOT) was produced from M40 sample by using octadecylamine intercalation/deintercalation procedure. The new nanocomposites were obtained by mixing PLA solution with the 0.5, 1.0 and 2.0% wt. additives of M40 or M40MOT samples calculated with respect to the amount of PLA. The obtained polymer/mineral suspension after ultrasound treatment was mechanically stirred for 24 hours. Afterwards it was dried at room temperature for 48 hours and finally vacuum dried for 24 hours. The structural characterization was carried out using infrared spectroscopy (IR). Mechanical properties such as: tensile strength ( $S_U$ ) and Young's modulus (E) were measured using Zwick 1435 universal testing machine. The surface of the formed polymer derivatives was examined by AFM (Atomic Force Microscopy). Nanocomposites surface wettability was studied by measuring the contact angle using DSA10Mk2 Kruss instrument.



The mechanical tests revealed that both  $S_U$  and  $E$  values increased significantly after addition of the nano-filler in comparison to the pure PLA. Regardless of the filler content the increase of  $S_U$  and  $E$  values was higher in the case of the nanotubular kaolinite. In particular, a threefold increase of  $E$  value was noticed. For the most homogenous 1% M40MOT/PLA nanocomposite  $S_U$  increased from ~29 MPa (pure PLA) to ~43 MPa, while  $E$  increased from ~0.7 GPa (pure PLA) to ~2.3 GPa. These mechanical parameters were comparable with those measured for polypropylene ( $S_U$  = 40 MPa;  $E$  = 1.5-2.0 GPa) and polystyrene ( $S_U$  = 40 MPa;  $E$  = 3.0-3.5 GPa). It is worth to underline that 1% M40MOT/PLA nanocomposite is biodegradable as opposed to hydrocarbon polymers. Differential IR spectra of the nanocomposites indicated an interaction of kaolinite's inner surface hydroxyls with PLA which was confirmed by an intensity decrease of a band at ~3690  $\text{cm}^{-1}$ . The presence of highly dispersed nanotubular kaolinite particles in the polymer matrix which contributed to the improvement of PLA mechanical properties was observed using AFM. The contact angle measurements showed that addition of the kaolinites led to changes of wettability, however the synthesized materials still possessed hydrophilic surfaces.

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## INTERACTIONS BETWEEN LIME AND CLAY MINERALS – COUPLING BETWEEN THE PHYSICOCHEMICAL AND GEOTECHNICAL ASPECTS

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Sustainable development is marked by an increasing need of re-using the materials directly encountered on earthwork projects. Lime stabilization appears to be a potential way since it can improve workability and mechanical properties of soils presenting low mechanical characteristics and sensitivity to water. Interactions between lime and soil particles lead a succession of complexes physicochemical reactions with variable kinetics (cationic exchange reaction, flocculation, pozzolanic reaction, carbonation...) which modify the mechanical behaviour of soil. However, following the nature of clay minerals present in the soil, the expected modifications and the improvement of mechanical behaviour are not always observed. A more precise knowledge about the development of physicochemical processes is then necessary to understand and determine how materials can be reemployed on substructure sites.

In the present work, the approach undertaking consists to study the effects of lime on two clays in mechanical and physicochemical points of view. A coupling between these two aspects is doing in order to link the reactions to mechanical behaviour of materials.

Two materials, a kaolinite and a bentonite, with different structural and geotechnical characteristics, were used in this study. They were treated with 10% of lime over a period from 1 hour to 98 days, at 20°C and at constant water content. The mechanical behaviour of these materials was investigated by compressive strength tests and materials are analyzed in details by NMR, XRD, SEM and thermal analysis.

Results showed a notable increase of mechanical resistance for bentonite, when it was treated with lime. In contrast, for the period studied, the addition of lime to the kaolinite does not improve significantly the mechanical behaviour. These differences can be explained by a reactivity which is different between the two materials. In the case of kaolinite, the hypothesis to describe the mechanical behaviour is the modification of the clay mineral surfaces which promotes interactions and cohesion between particles. For bentonite, cementitious phases like calcium aluminate hydrates and calcium silicate hydrates form during the first days of cure. The presence of these phases increases the cohesion between particles and also the mechanical performances of the material.

## APPLYING ZETA POTENTIAL MEASUREMENTS TO CHARACTERIZE THE ADSORPTION OF INORGANIC, ORGANIC, MICELLAR AND POLYMERIC CATIONS ON MONTMORILLONITE

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A systemic study was carried out to characterize the adsorption of inorganic, organic, micellar and polymeric cations on montmorillonite by monitoring zeta potential ( $\xi$ ) as a function of cation loading on the clay. The degree of the decrease (less negative) in the clay's  $\xi$  increases with charge of the inorganic cations ( $\text{Na}^+$ ,  $\text{Cs}^+ < \text{Ca}^{+2} < \text{Al}^{+3}$ ) (as predicted by the Double Layer Theory) and at high concentration of  $\text{Al}^{+3}$  surface charge reversal was obtained. As expected  $\text{Cs}^+$  had more of an effect than  $\text{Na}^+$  on the clay's  $\xi$  due to its small hydration shell. An unexpected increase in  $\xi$  was measured at moderate concentrations of these monovalent cations which was explained by the effect of the counter anions. A linear correlation between the adsorption of small organic cations on the clay and  $\xi$  potential of the composites was found. This linear correlation was obtained also for the adsorption, up to the cation exchange capacity (CEC), of larger organic cations, cationic surfactants as monomers and as micelles. Such a correlation enables to predict the amount of cation adsorbed by measuring  $\xi$  or *vice versa* predicting  $\xi$  when the amount of cation adsorbed is known. However, when cation adsorption exceeded the clays CEC a non-linear increase in  $\xi$ , was measured. The degree of increase in  $\xi$ , upon adsorption above the CEC, corresponds to cation size and affinity to the clay surfactant < dye dimmers < micelles. The measured  $\xi$  was approximately zero for the adsorption of these cations at the CEC of the clay. In contrast,  $\xi$  reached zero at polycation loadings below the calculated CEC which was explained in terms polymer extension into the solution and surface screening. The adsorption isotherms of the polycations on montmorillonite did not fit the Langmuir model, however, so called zeta-adsorption isotherms of the polycations were derived and were in good agreement with the model. We suggest that the derived Langmuir-like constants may be a good comparative tool to describe polycation adsorption.

## PHOTOCHEMICAL REACTIONS IN COLLOIDAL MIXTURES OF EXFOLIATED CLAY AND SEMICONDUCTOR NANOSHEETS

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We report photochemical events in multicomponent colloids including oxide nanosheets yielded by exfoliation of hectorite clay (Laponite) and photocatalytically active layered hexaniobate. Colloidal mixtures of the clay and niobate nanosheets, which will be called clay-niobate colloids hereafter, show a characteristic microdomain structure where the phase-separated clay and niobate nanosheets are dispersed with forming their own microdomains.<sup>1)</sup> We have recently found that the clay-niobate colloids added by electron acceptor methylviologen show photoinduced electron transfer, the behavior which is characterized by stability of the charge-separated state.<sup>2)</sup> Thus, it is worthy of investigating photoprocesses in the clay-niobate colloids other than the electron transfer to the acceptor. Here, we show photochemical behavior of the clay-niobate colloids in the absence of electron acceptor.

The colloid samples were prepared by hectorite clay (Laponite RD) and layered hexaniobate  $K_4Nb_6O_{17}$ . The colloidal dispersions were irradiated with UV-light under a nitrogen atmosphere. Photochemical response of the colloids was monitored by visible spectroscopy, and hydrogen evolution was detected by gas chromatography.

Electron accumulation in the semiconducting nanosheets was observed when the clay-niobate colloids were irradiated without additives under static conditions. The clay-niobate colloids turned green with irradiation of UV-light. Fig. 1 indicates visible spectra of a colloid sample before and after the irradiation. The irradiated sample shows a broad absorption band, which is assigned to a lower-valent niobium species produced by accumulation of electrons in the niobate nanosheets; the reduced niobate species is hereafter denoted as niobate(e<sup>-</sup>). This is explained by the photocatalytic activity of the niobate nanosheets. The semiconducting niobate nanosheets absorb UV-light to generate

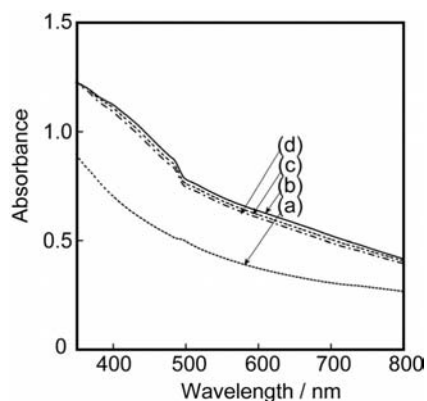


Fig. 1. Visible absorption spectra of the clay-niobate colloid ([clay] = 10 g L<sup>-1</sup>, [niobate] = 1 g L<sup>-1</sup>) (a) before UV irradiation and (b) 1, (c) 30, and (d) 60 min after termination of the irradiation.

conduction-band electrons and valence-band holes. Since the niobate nanosheets are dispersed in water together with propylammonium ions, which are introduced to the system as the exfoliating reagent and present as counter cations of the negatively charged niobate nanosheets, the holes are scavenged by the propylammonium ions. The photogenerated electrons are consequently accumulated in the niobate nanosheets.

The niobate( $e^-$ ) species was stably kept in the colloids after the irradiation was terminated, as indicated by the slow decay occurring over hours, as shown in Fig. 1 where the absorption due to niobate( $e^-$ ) little decreases 1 h after the termination of the irradiation. The amount and lifetime of the niobate( $e^-$ ) species both depended on the clay content of the colloids. For the colloids with  $[\text{niobate}] = 1 \text{ g L}^{-1}$ , the largest yield and lifetime of niobate( $e^-$ ) were obtained at  $[\text{clay}] = 10 \text{ g L}^{-1}$ , whereas formation of the niobate( $e^-$ ) species was not observed in the colloid of  $[\text{clay}] = 30 \text{ g L}^{-1}$ . Thus, too low or too high clay concentration is inappropriate to obtain the niobate( $e^-$ ) species with high yield and stability. These results demonstrate that photoreduction of the niobate nanosheets in the clay-niobate colloids is controlled by the coexisting clay nanosheets.

The niobate nanosheets photocatalytically decompose water to generate hydrogen under stirred conditions. However, the hydrogen evolution was rather suppressed in the clay-niobate colloids compared with the clay-free colloids. This fact suggests that the clay nanosheets assists the electron accumulation in the photocatalyst nanosheets but inhibit the utilization of the accumulated electrons.

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## LOTUS CERAMICS FROM KAOLIN CLAYS AND ITS CAPILLARY RISE ABILITY

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Due to vast consumption of thermal energy by industrial and social activities especially at big cities, those cities are facing to increase temperatures in summer and this phenomenon is called as "heat island effect". Many trials to suppress this heat island effect are proposed and performed actions now. One of the effective ways is usage of water by spraying as fine mists, surface wetting using superhydrophilic property of  $\text{TiO}_2$ , evaporating of water using porous ceramics as the building and pavement materials, etc. Porous ceramics are considered to be important key materials for this purpose because they have abilities to absorb, reserve and evaporate water, which makes lowering of temperature by the endothermic reaction.

Various types of porous ceramics have been prepared by a variety of methods. We used an extrusion method with flammable fibers as the pore former<sup>1-3)</sup>. The starting materials for ceramics used were kaolin clay (Kentucky, USA), alumina (Showa Denko, Japan) and Chinese earthen clay (Inagaki Mining, Japan). The chemical composition was 36, 56 and 5 mass% of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , respectively. Rayon fibers with 800  $\mu\text{m}$  in length and 16.5  $\mu\text{m}$  in diameter were used as the pore former. The ceramic raw materials were dry mixed with 20 mass% of the fibers and kneaded with 40 mass% of water. The resulting paste was molded using an extruder to tubular green bodies with inner and outer diameters of 20-30, 30-50 and 20-50 mm. The extruded bodies were dried at room temperature for three days, then at 120°C for 18 h. They were fired at 1500°C for 4h in air.

The bulk density and porosity of the samples was measured by the Archimedes technique using water. The pore size distribution and pore volume was measured by an Hg intrusion porosimetry. The microstructure of the cut surface was observed using a SEM. The crystalline phases were examined by powder X-ray diffraction. The capillary rise ability of the sample (50 mm $\phi$ -20 mm $\phi$ x1800 mm) was measured by immersing the one side (15 mm) in water at various time intervals by visual observation. The measurement was performed under ambient conditions, the room

temperature and RH during the measurements ranging between 15-22.5°C and 32-61%, respectively.

The bulk density was 1.57 g/cm<sup>3</sup> and the apparent porosity was 46.6%. The pore size distribution showed a sharp peak at 15.6 µm slightly shrunk from the fiber diameter and the total pore volume was 0.28 ml/g. SEM observation revealed that cylindrical throughhole pores introduced by the fibers were highly oriented along the extruded direction, thus, the porous ceramics are called as “lotus ceramics” from the similarity of the microstructures. The capillary rise curve showed very steep increase by 2-3 h, milder the rising with longer time and approaching to an equilibrium height of about 1.3 m, of which height is the highest of all materials so far reported. Such an excellent result is realized by controlling of the porous microstructure by the present preparation method. Among the variously proposed equations, the experimental data were best fitted using the equation reported by Fries and Dreyer<sup>3)</sup> adopting the parameters of the contact angle as 69.5° and effective pore radius as 4 µm. The lotus ceramics were very effective to lower the surface temperature by the passive vapor evaporation ability.

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## POROUS MATERIALS FROM ACID LEACHED GROUND VERMICULITE

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Selective leaching with acid has been used to prepare porous silica from various clay minerals, including vermiculite. The presence of iron in this mineral plays an important role in the specific surface area obtained after acid treatment. Grinding of clay minerals significantly influences their leaching behaviour (Maqueda et al. 2008).

Vermiculite from Santa Olalla (Huelva, Spain) was used as starting material. Its half-unit cell composition is  $(\text{Si}_{2.64}\text{Al}_{1.36}) (\text{Mg}_{2.48}\text{Fe}^{3+}_{0.324}\text{Fe}^{2+}_{0.036}\text{Al}_{0.14}\text{Ti}_{0.01}\text{Mn}_{0.01})\text{O}_{10}(\text{OH})_2\text{Mg}_{0.439}$ . Vermiculite particles less than 80  $\mu\text{m}$  in size were obtained with a knife-mill (Retsch ultracentrifuge mill, model 255 M-1 equipped with a suitable sieve) and used for all experiments.

Grinding experiments were carried out using a vibratory mill (Herzog HSM-100). The sample ground for 3 minutes was used for subsequent acid treatments since it was found to have the maximum specific surface area (BET) before leaching. Vermiculite samples (<80  $\mu\text{m}$ ) left untreated and ground for three minutes were leached with HCl solutions at three different concentrations, 0.25 M, 0.50 M, and 1.0 M at a solid/acid mass ratio of 1:20. The suspensions were maintained at 80 °C and stirred for 24 h.

The ground vermiculite from Santa Olalla treated with 1M HCl produced a residue constituted by silica and iron oxides. Quantitative estimation from XRD analysis showed that the sample consisted of 13% crystalline material and 87% amorphous material. The crystalline portion consisted of 91.2% of akaganeite and 8.8% nanocrystalline  $\text{SiO}_2$ . The porosity studies showed that the high surface area of this residue about 700  $\text{m}^2 \text{g}^{-1}$  may be attributed to the presence of iron coming from structural iron. Using HRTEM it was found that the HCl treated ground vermiculite sample consists of amorphous silica and  $\beta\text{-FeOOH}$  (akaganeite) microcrystals containing a small amount of Ti and Cl as impurities. As it was proved by electron microscopy, the acid leached materials consist of spindle shape particles approx. 0.1 x 0.5  $\mu\text{m}$  assigned to  $\beta\text{-FeOOH}$  and irregular aggregates of amorphous hydrated silica nanoparticles few nm in size.



The XRD diagrams of the residue heated in a high temperature chamber from 30 to 1200°C at 10° min<sup>-1</sup> were registered every 50°C. Whereas the starting ground 1 M HCl leached vermiculite was partially crystalline on account of presence of the crystalline  $\beta$ -FeOOH. This phase is present until 150 °C. The sample heated between 150 and 800°C was practically amorphous. This is in agreement with the observations that  $\beta$ -FeOOH decomposes to amorphous or poorly crystalline phase  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> transforming only slowly to crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. At 850 °C the sample showed the first signs of crystallinity fully developed at 1050°C. At this temperature the sample was crystalline, consisting of quartz, cristobalite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>.

It is known that nanoparticles of amorphous Fe<sub>2</sub>O<sub>3</sub> crystallize into nanocrystalline maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and this transformation is normally characterized by an exothermic peak at 280 °C. However, it has been reported that Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> amorphous nanoparticle systems show a major difference from the case of pure amorphous nanoparticles of Fe<sub>2</sub>O<sub>3</sub>, in spite of the fact that the same transformation phase product (i.e.,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was observed. The difference appears in the shifting of the transformation temperature toward higher crystallization temperature (ca. 700 °C). The shifting of the crystallization temperature toward higher temperature and the consequent stabilization of the amorphous Fe<sub>2</sub>O<sub>3</sub> nanophase is attributed to what is called the preventive role of the silica matrix. This effect results in fact that well crystalline iron oxide nanoparticles embedded into the silica matrix are formed usually at relative high temperatures in range 600-1000°C in contrast to silica free material.

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## MAYA BLUE ORIGINS TRACED WITH SYNCHROTRON RADIATION CLAY ANALYSIS

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Maya blue is a mysterious artificial pigment invented by the Maya about 800 A.D. It spread in Prehispanic times from the southern Maya region to most Mesoamerican cultures. It continued to be used for religious paints until the end of the XVIth century in colonial Mexico and even later for civil decoration in Cuba. Rediscovered in 1931, this light blue pigment still intrigues material scientists because of its surprising resistance to degradation in adverse environmental conditions. It is made by moderate heating of indigotin from the leaves of the *Indigofera sufruticosa* plant, mixed with palygorskite.

We performed X-ray diffraction experiments using synchrotron radiation on several archaeological pigments containing Maya blue. The samples were selected from a wide range of cultures that inhabited Mesoamerica over almost a millenium: one of each from Maya (Mayapán), Olmec-Xicalanca (Cacaxtla), Totonac (El Tajín), Huastec (Tamuín) and Aztec (Tenochtitlan), as well as one colonial sample (Jiutepec convent). The high brilliance of the synchrotron source was essential to obtain a good quality signal-to-noise ratio from pigment microsamples.

We identified that some features in the diffraction patterns of palygorskite, the main ingredient of Maya Blue, that can be used as fingerprint to trace the provenance of the clay. The peak 310 exists for both palygorskite phases (orthorhombic and monoclinic), but with much less intensity for the orthorhombic. The X-ray data revealed that the diffractograms for all the prehispanic and colonial samples -except for the Aztec- are in agreement with the palygorskite from Yucatan, the place where it is believed that the Mayas obtained this clay to manufacture Maya blue [1]. Strikingly, the Aztec samples either do not present the 310 peak, characteristic of the monoclinic phase, or its intensity is extremely low. Therefore, the palygorskite used to make the Aztec pigment is almost pure orthorhombic. Furthermore, when using the ratio of the peak intensities the archaeological samples can clearly be separated into two groups: Non-Aztec versus Aztec samples.

We demonstrate that the palygorskite present in all the Aztec samples analyzed do not come from Yucatan. This evidence, resulting from analytical work on the archaeological samples, has important implications for our knowledge of Aztec

history and technology. It shows that the Aztecs, as well as the Maya, possessed the technology to manufacture a sophisticated product, the pigment Maya blue, know as the ancestor of the new hybrid materials.

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## POLYMER NANOCOMPOSITE USING A SECOND-STAGED ALKYLAMMONIUM-SERICITE COMPLEX

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The intercalation dynamics of layered materials, such as graphite, clays, and transition-metal dichalcogenides, has been reported in detail, both experimentally and theoretically. In particular, the phenomenon of staging has generated a large amount of interest in these materials. Staging is a process by which layered host materials intercalate guest compounds. A staged layered compound has a regularly repeating series of interlayers, alternating periodically between an intercalated layer and non-intercalated layer.

We have conducted ion exchange experiments using sericite (SE) and dehydrated sericite (dhSE) with dodecylammonium (DDA) solutions of various initial concentrations (7.3, 21.9, and 73.3 mM, corresponding to  $\text{DDA}^+/\text{K}^+$  mole ratio = 1.0, 3.0 and 10.0, respectively), at 70 °C. In the case of the SE complexes, two separated phases, 1.0 and 2.3 nm, were obtained, which were ascribed to the non-intercalated layers, and vertical (perpendicular to the layers) orientations of the incorporated DDA, respectively. On the other hand, in the case of the dhSE complexes treated with  $\text{DDA}^+/\text{K}^+$  mole ratio = 1.0, a large basal spacing of 3.3 nm was observed. The 3.3 nm basal spacing is close to the sum of the basal spacing for the vertical (perpendicular to the layers) orientations and that for the non-intercalated layers, so it can be interpreted as regular alternation of the 2.3 nm layer and the 1.0 nm layer, exhibiting  $c = 3.3$  nm supercell ("1:1 ordered interstratifications" or "second-staging").

The nanocomposite was prepared by dispersing the resulting DDA-dhSE (that had the second staging structure) in an epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) with subsequent curing in the presence of nadic methyl anhydride (NMA) and benzyldimethylamine (BDMA) at 180°C. The morphology of the nanocomposite, as deduced from the TEM images, showed silicate nanolayers with extremely high aspect ratios that are at levels of several dozens times greater than that of conventional exfoliated clay-polymer nanocomposites. Moreover, most of the dispersed nanolayers were actually comprised of 2 nanolayers in one group. This would appear to be a new method in polymer nanocomposite technology that will enable the control of the number of dispersed layers in a nanocomposite.

## CHARACTERIZATION OF HECTORITE SYNTHESISED WITH MICROWAVES AND DISPERSION IN PU

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Hectorite is a trioctahedral smectite with formula  $(\text{Si}_{8.0})[\text{Mg}_{6.0-x}\text{Li}_x](\text{OH.F})_4 \text{O}_{20} \text{M}^{n+}_{x/n} \cdot m\text{H}_2\text{O}$ . Hectorite can be used as catalyst, in ion adsorption and ion exchange processes, in nanoparticle synthesis, and in the preparation of nanocomposites obtaining the best results when clay particles are individually dispersed. Hectorite can be found in nature, however, in order to work with a reproducible material it must be synthesised. Preparation methods usually involve long time hydrothermal treatments, and other natural clays are still used for main applications [1]. Microwaves interact with polar molecules such as water, heating the sample in an homogeneous way, and are an alternative to conventional methods where heat is irregularly distributed via convection. The introduction of microwave technology in clay synthesis not only reduces the synthesis times, but can also confer interesting properties to the prepared materials. In a previous study, we synthesised hectorite clay in a short time using microwaves [2]. The objective of this work is to characterize a microwave synthesised hectorite and study its dispersion in a commercial polyurethane.

$\text{Li}^+$ -Hectorite (H1) was synthesized according to the reported procedure [2]. A slurry (3 wt. % solids) containing  $\text{SiO}_2$ , fresh brucite  $\text{Mg}(\text{OH})_2$ , and  $\text{LiF}$ , was aged in an autoclave under microwave irradiation at 373 K for 8 h. The samples were studied using X-Ray diffraction (XRD), Diffuse Reflectance Fourier Transform InfraRed Spectroscopy (DRIFTS),  $\text{N}_2$  physisorption, TGA, TEM and determination of the cationic exchange capacity (CEC). Laponite, a commercial hectorite sample, was used in parallel experiments to provide a benchmark for comparison.

The XRD patterns of both samples, confirmed that hectorite was the only crystalline phase and there was no broad band related to amorphous silica. The XRD pattern of sample H1 showed the 001 peak related to stacking of clay layers with a basal spacing of 13.4 Å. This reflection was not observed for Laponite. Patterns of both samples showed the (060) reflection typical for these materials having a  $d(060) = 1.52$  Å. The crystallite size value calculated from this reflection was slightly higher for Laponite than for sample H1.

DRIFTS spectra of both samples exhibited the Si-O-Si stretching band around 1000  $\text{cm}^{-1}$  suggesting an ordered clay mineral layer. Some broad bands in Laponite spectrum related to varying quantities of unused reactants were observed.

However many differences between the samples were observed when comparing the derivative of TGA curve. The peak related to dehydroxylation was sharp and occurred at higher temperature in H1 than in Laponite which may suggest a higher homogeneity in H1 sample. This result agrees with  $N_2$  physisorption results where Laponite exhibits a higher surface area arising from disorder in the layers.

Preliminary investigations of the dispersion of H1 in polyurethane (PU) were carried out. A selection of nanocomposite samples were prepared, using a commercial PU and with clay contents of 1, 2, 5 and 20 wt% (related to the total composite). The same samples were prepared using Laponite for comparison. The dispersion of 1 and 2 wt% of H1 in PU appeared to be good since no clay aggregation was observed in the XRD patterns of the nanocomposite films. Thermal decomposition of H1-PU samples occurred at higher temperatures than the Laponite-PU samples.

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## *POSTER PRESENTATIONS*





## EFFECT OF SURFACTANT ON THE ELECTROKINETIC PROPERTIES OF NATURAL CLAY

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Pollution caused by organic compounds is a common problem faced by many countries and is likely to cause health hazards, harm to ecology, damage to structures or amenities, and interference with legitimate use of water. Hence, numerous researchers studied the removal of pollutants from the waste waters. Surfactant modified clays (SMC) are also extensively used removal of pollutants.

The aim of this paper is to prepare the surfactant modified clay and is also to research the effect of surfactants on the some electrokinetic properties. Electrokinetic properties are important to clarify clay soils behavior. The electrokinetic properties observed in this study are zeta potential, electrical conductivity-EC, pH, CEC and contact angle of clay. For this reason, the clay is modified by surfactants for improving their engineering properties. In this study; DAMS (Dialkyl ammonium meta sulphate) was used as surfactants.

From the test results the modified clays gave the lower cation exchange capacity and EC values than the natural clay. However, pH values were not significantly changed as compared with those of natural clay. Additionally, the contact angle and zeta potential of modified clay significantly increased.

## ZEIN-CLAY BIO-HYBRID SYSTEMS AS FILLERS IN ALGINATE FILMS

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It is well known the use of certain biopolymers processed as coatings and films for food packaging. Among them, polysaccharides (cellulose derivatives, starch, alginate...) and proteins (collagen, gelatin, soy and casein) are the most widely employed in food industry due to its high biocompatibility and biodegradability.<sup>1,2</sup> Many of them possess oxygen barrier properties and flavour passage acceptable, but they are very sensitive to moisture. This inconvenience is usually overcome by incorporating additives into the biopolymer matrix, which help to improve the vapour barrier properties, to reduce gas transport (oxygen and carbon dioxide), as well as to enhance the mechanical handling properties and provide additional structural integrity. Natural or synthetic clay minerals (layered silicates such as montmorillonite or fibrous minerals such as sepiolite and palygorskite) are additives usually incorporated into the biopolymer matrix giving rise to the so-called nanocomposites.<sup>2</sup>

Among the wide range of biopolymers extracted directly from biomass, zein is a storage protein found in abundance in corn. It is characterized by its hydrophobic nature due to its high content of nonpolar amino acids. Such biopolymer is used in the food sector because of its antibacterial activity and good barrier properties to gases and water vapor, in addition to biodegradability and biocompatibility.<sup>3</sup> The association of zein with clays<sup>4,5</sup> can be an alternative of great interest in finding new bio-hybrid additives for bioplastic applications, conferring the properties associated to zein to those of usually employed clay minerals. In the present work we have prepared a new system using zein-clay bio-hybrid composites as fillers into polymeric matrices of alginate and the resulting nanocomposites have been processed as films. The incorporation of the zein-clay bio-hybrid in alginate reduces the solubility of the film, optimizing its barrier properties to the passage of water vapour, yielding values up to  $0.17 \text{ mg h}^{-1} \text{ cm}^{-2}$  for samples containing up to 75% (w/w) of incorporated hybrid. The resulting composites have a tensile elastic modulus of up to 3.8 GPa and an elongation at break of about 21% compared to 5.78% of unmodified alginate films. The films may also have anti-bacterial nature associated with the presence of zein, and, therefore, they are promising materials in the food sector.

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## LIME-METAKAOLIN MORTARS WITH INCORPORATION OF SEPIOLITE

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Some cases of restoration and conservation works on historic buildings require the application of mortars that must harden in conditions of no air contact and usually high humidity; however, some setting speed is needed, mainly in order to assure the adequate performance of the whole preservation work. In building conservation practice, there is some difficulty in formulating compatible mortars for use in renders and joints, due to requisites of low elastic modulus, sufficient flexural and compressive strength and adequate behaviour in terms of water intake and drying. For these reasons air lime is the most adequate binder; however it encloses some problems such as slow setting, inability to harden under water, microcracking and lack of durability. The use of pozzolanic materials in lime mortars such as metakaolin is a matter of recent studies and the results suggest that, in adequate proportions, they produce an increase in mechanical strength and durability of mortars, meeting water intake and drying requirements.

With the purpose of developing mortars for applications in building rehabilitation, two sets of mortars were prepared: mortars with 1:3 air lime : sand volumetric ratio, in which a) lime binder was replaced by 10 % and 20 % of metakaolin (commercial product, Portuguese origin); b) the same mortar compositions in which air lime was substituted by 5 % of sepiolite (commercial product, Spanish origin). Water was added in order to achieve the required workability for this typology of mortars, calculated to reach a consistency with flow table values of around 130. Samples were cured for 28 and 90 days according to EN 1015-11 standard. The characterization of the mortars was carried out by X-Ray diffraction (XRD), X-Ray fluorescence (XRF), differential thermal analysis (DTA), scanning electron microscopy (SEM), mechanical testing (compressive and flexural strength) and elasticity modulus.

The aim of this research was to study the influence of the metakaolin addition on mechanical properties and hydration products formed in lime mortars and the influence of the sepiolite on the carbonation process of lime-metakaolin mortars, as well as the microstructural characteristics of mortars.

The obtained results showed the increase of the mechanical properties in lime-metakaolin mortars when compared to lime mortar, as well as the improvement of flexural and compressive strength with the addition of metakaolin content. Compared

to the lime mortar, flexural and compressive strengths increased by ~20 % and ~12 % for lime-metakaolin mortars, respectively. XRD patterns and SEM images after 28 days in all the specimens, showed an excess of portlandite compared to calcite, but its presence decreased with increased substitution of metakaolin. After 90 days of curing, almost 90 % of portlandite is transformed to calcite. Due to the carbonation process, calcite appears in all the mortars confirmed by the phenolphthalein test and its amount increased with curing time. Also, calcium-silicate and calcium-aluminium-silicate mineral phases were identified in mortars containing metakaolin inducing higher mechanical strength in metakaolin-blended mortars. Incorporation of sepiolite in mortars increased the flexural strength by 15 % and 8 % for lime and lime-metakaolin mortars, respectively. Sepiolite addition to lime and lime-metakaolin mortars improved the compressive strength values, too. Considerable enhancement is related to sepiolite-lime-metakaolin mortars, where compressive strength increased 24 % in comparison with lime-metakaolin mortars, while 6 % improvement is associated with addition of sepiolite to lime mortar without metakaolin.

As expected, the incorporation of sepiolite in lime-metakaolin mortars resulted in higher water demand (4 %) during mortar preparation. It is a consequence of high specific surface area and absorbent properties of sepiolite. For the tested curing days, it was proved that sepiolite slows down the rate of carbonation process due to its capacity for water adsorption without affecting the mechanical behaviour of these lime mortars. Otherwise, the fibrous habit of sepiolite caused enhanced compatibility with the individual components and a comprehensive densification is achieved in the mortar system.

The pozzolanic activity of metakaolin and the specific characteristics and properties of sepiolite expressed an improvement of mechanical properties and water behaviour in mortars for application in conservation and restoration of cultural heritage.

## **ECONOMIC EVALUATION OF SPENT BLEACHING CLAY RECYCLING USED IN REREFINING OF WASTE LUBRICATING OIL IN SULAIMANI CITY-IRAQ**

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The current production of the rerefined lubricating oils in Sulaimani city is about 150 ton per day. The estimated amount of the spent clays produced in the rerefining process is 15 ton/day. The oil content of the spent bleaching clay is in the range from 30 to 40 w/w % which is dumped in landfills near Tanjero River.

In our previous work, a process for the recovery of oil from the spent bleaching clay by solvent extraction and regeneration of the deoiled clay by calcination has been described on laboratory scale. The cost of the spent clay with its oil contents comprises a considerable portion of the total refining cost.

In the present study, a preliminary economical analysis of oil recovery and recycling of spent bleaching clay on industrial scale in Sulaimani city was done.

Tanjero region is selected for the suggested plant with a total capacity of 1.5 ton/batch. Assuming 10 batches per day, the plant capacity will be 1.5 ton/batch. The process is assumed to be batch except for the distillation column which operates in continuous mode. A flow sheet diagram of the suggested plant is presented with all dimensions of extraction vessel, column, furnace, etc. Assuming 15% free space in the extractor, the volume of the extraction vessel is estimated to be 8.3m<sup>3</sup>. A rotary furnace is recommended for the calcination process. Assuming 50% free space for ventilation and mixing, the volume of the furnace is estimated to be 1.5 m<sup>3</sup>.

Detail of cost estimation and earning shows that the profitability of the suggested plant is estimated to be more than 50,000 US \$/month, in addition to pollution prevention in the area.

## THE EFFECT OF (ORGANO) CLAY ADDITION ON THE PROPERTIES AND USES OF U.V. POLYMERISED ACRYLATE SHAPE MEMORY POLYMERS

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Shape Memory Polymers (SMP), as their title suggest, have the intriguing ability to change from a pre-deformed intermediate shape back to a fixed original shape<sup>1</sup>. In thermoresponsive SMPs the intermediate shape is conferred on the polymer by heating it to a given temperature,  $T_{trans}$ , deforming it into the intermediate shape using a physical force, then cooling it below its  $T_{trans}$  temperature. The intermediate shape is retained after the physical force is removed until the sample is reheated to  $T_{trans}$  at which point the polymer returns to its original shape. These polymers have been used to produce, among other things, medical devices such as stents and catheters. Typical examples of polymers which can exhibit this shape memory effect include (meth)acrylates, polyurethanes, and blends of polystyrene and polyurethane and polyvinylchloride.

The incorporation of clays and organoclays into polymers, at addition levels of 1 to 5 wt%, have been shown to dramatically increase the mechanical, barrier and fire resistant properties of a wide range of polymers. Moreover, they have been shown to increase tensile properties and increase storage modulus, this would allow more energy to be stored within an intermediate shape of a SMP which would allow a broader range of applications.

Results are presented from a benchmark study designed to create SMP systems, based on clay-polymer nanocomposites, with transformable properties at room temperature. It aims to identify the factors influencing the (organo)clay dispersion in UV polymerised tBA/PEGDMA blends and their subsequent physical properties<sup>2</sup>. The effect of (organo)clay type and loading on the glass transition temperature, the (organo)clay loading required to influence the shape memory effect and the extent/reproducibility of shape recovery as well as the time required to return to the original shape are reported. These results will be correlated with the extent of dispersion of the (organo)clay in the tBA/PEGDMA blend.

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## SILICA/ALUMINA CLAY NANOCOMPOSITES AS HETEROGENEOUS ACID CATALYSTS

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In order to design new adsorbents or catalysts based on smectite clays, these last are generally functionalized through the modification of their exchanged cations (size and nature). The main aim of these modifications is approached to control the thermal stability, porosity and acidity of the final materials. In this work, a different approach has been used to prepare silica/alumina clay nanocomposites based on the controlled hydrolysis and polycondensation of metal alkoxides that coagulates within the galleries of a commercial organo-modified montmorillonite. This procedure has proved for silica-clay nanocomposites [1,2] to produce high exfoliation degrees of the clay layers, making accessible their internal surface. In the present case, the incorporation of a silica/alumina phase allows to create acid sites (Brønsted and Lewis), therefore appears as an optimum way to design functional materials with applications in acid catalysis.

The Cloisite30B organoclay (Southern Clay Products) dispersed in alcohol was treated with a mixture of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  alkoxides (molar ratios 1:4 / 3:2), controlling their hydrolysis with stoichiometric water content. The suspension was stirred at 50 °C until a spontaneous coagulation was produced, obtaining a viscous gel. The gels were dried at 50°C or frozen at -196°C and lyophilized. The solids were finally heated at 560 °C (2 h in  $\text{N}_2$  and 6 h in air). The final solids were characterized by several techniques and evaluated as acid catalysts. Important reactions in sustainable chemistry will be considered, such as the synthesis of *solketal* (1,2-isopropilidenglycerol) from glycerine and acetone. This reaction has great relevance because it allows using glycerine, a by-product from biodiesel production currently regarded almost as a waste [3], and produces *solketal*, a solvent that could be used as an additive for biodiesel, reducing its cloud point, and for the production of monoglycerides and other surfactants.

The main structural change suffered by the montmorillonite in the nanocomposites was the lost of the stacking (00l) reflection orders. Clay suffered delamination when low contents of aluminium are used. Higher contents caused the fast  $\text{Al}^{3+}$ -alkoxide hydrolysis at the expense of the exfoliation process, leading to the collapse of clay layers after calcination. The clay modification by metal alkoxides improved textural properties on the starting clay. The mesophases showed high specific surface areas prior to calcination, increasing from ca. 11  $\text{m}^2\text{g}^{-1}$  of cloisite 30B to values in the range 80-300  $\text{m}^2\text{g}^{-1}$ . The calcination of these mesophases enhanced the surface area,

reaching values between 200 and 600 m<sup>2</sup>g<sup>-1</sup>. The amorphization of the clay yields to materials with microporous and mesoporous regions, whose morphology changes noteworthy. The stacked silicate layers are turning into dispersed layers surrounded by nanoparticles of the silica/alumina oxides incorporated.

The inclusion of silica/alumina promotes the acidity of the systems, increasing from 0.44 mmol/g for Cloisite30B to 0.80 mmol/g for the systems with low aluminium contents (4Si1Al and 3Si2Al). The acid sites of these solids are related to the number of aluminium centres incorporated to the silica/alumina framework, increasing the number of Si-OH-Al species. Preliminary reaction tests will be described for further verification of the acidic and textural properties of the nanocomposites prepared, comparing the activity of these systems to those described by homogeneous and commercial catalysts. The final goal is to get similar selectivities to those described by HCl or H<sub>2</sub>SO<sub>4</sub> catalysts (23 %), while avoiding the corrosion and catalyst separation involving these homogenous syntheses. Seemingly, the catalytic activity depends on the Si/Al relationship and textural properties, being controlled by the number and accessibility of the acid active sites involved in this reaction.

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## STRUCTURE AND RHEOLOGY RELATIONSHIP OF ORGANOCLAY W/O MACROEMULSION FOR DRILLING FLUIDS

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In the field of oil extraction, bentonites are extensively used worldwide as drilling-fluid additives. Their main functions are to viscosify the mud and to reduce the loss of fluids in the formation (1). Bentonites (commercial organoclays) are commonly added at low volume fraction to water in oil emulsions in order to obtain drilling fluids with a moderate steady-shear viscosity, a sufficient thermal stability and a low permeability towards hydrocarbon bearing rocks.

These emulsions are generally kinetically stabilized by the adsorption of surfactant or low molecular weight polymers at the oil interface even if the ability of clay-like solid particles to stabilize emulsions without any other surfactant (pickering emulsions) is demonstrated. Two mechanisms are thus commonly proposed to explain the flow behaviour of clay loaded emulsions, i) the stabilisation of the emulsion by the formation of an organoclay film at the W/O interface and ii) the formation in the organic phase of a network of linked Mt-layers which acts as a barrier against the coalescence of oil droplets.

In this frame, the interest of this present work is to study the relationship, on the one hand, between the behaviour under lamellar flow of clay loaded emulsions, and on the other hand, the dispersion state of clays in the continuous oil phase with in situ SAXS measurements. SAXS and viscosity measurements are combined by placing under the X-ray beam the Couette-geometry cell of a rheometer. SAXS measurements are performed under flow at different shear rate in the range (0.1-1000 s<sup>-1</sup>). Thanks to SANS used in contrast matching, we obtain complementary features on the composition of the interlamellar space after dispersion in oil.

We study a water in dodecane 10/90 emulsion stabilized with commercial surfactants usually used in oil-based drilling fluids formulation and viscosified by addition of organoclays. Three different organoclays are investigated at different concentrations. Clay loaded emulsions stabilized by surfactant are steady and exhibit a shear thinning behaviour with a yield stress for the higher clay volume fraction. Even at higher shear rate the structure of clay particles is unchanged and clay particles are isotropically dispersed. At a same concentration, the viscosity of emulsions depends on the type of organoclay and more precisely on the dispersion state of clay particles inferred

with a fit of SAXS profiles using a scattering model of stacking of  $N$  core-layer platelets. Concerning the studied system, it is clear that the addition of organoclays together with surfactants has a synergetic effect on the stability of the system which is thoroughly instable without organoclay or without surfactant addition. Different mechanisms explaining this synergy are discussed.

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## **PALYGORSKITE CLAYS FROM BORSHHOVSKOE DEPOSIT (KALUGA REGION, RUSSIA): COMPOSITION, CRYSTAL CHEMICAL PARTICULARITIES OF CLAY MINERALS AND COLLOIDAL PROPERTIES**

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Palygorskite clays are used in various branches of industry, such as pharmaceuticals, constructing, drilling, wine-making etc. Palygorskite clays as a component of drilling fluid are the main application. Clays can form a stable suspension with surplus water. Main technological characteristics of the raw clays are cation-exchange capacity, slurry yield with fixed viscosity etc.

Clays from production horizon of Borshhovskoe clay deposit (Kaluga region, Russia) were used as a test subject. Detailed research which includes study of relation between mineral composition, crystal chemical particularities and colloidal properties of clays should provide better exploitation of deposit and their proper use as a raw material.

The following methods have been used during this study: x-ray diffraction analysis, differential thermal analysis, near-infrared spectroscopy, middle-infrared spectroscopy, grain-size analysis, viscosity measurement (according to API requirements), and measurement of cation-exchange capacity. Characteristics of mineral composition and quantitative mineral analysis were carried out using the data received from XRD-analysis conducted in MSU. Thermal analysis was performed in MSU, infrared spectroscopy was carried out in MSU and TPCI. Technological testing took place in MITHT.

Clays from different areas of upcoming quarry were studied during the research. It was found that clay composition varies from primary palygorskite to montmorillonite clays within the limits of deposit. Montmorillonite has quite stable composition while palygorskite has the complex one. NIR examination results clarified that palygorskite

represents mechanical mixture of Al- and Al-Fe-varieties in different proportion with overall prevalence of Al-variety.

Testing the colloidal properties of clay suspensions has demonstrated generally good properties. The application range of these clays is determined chiefly by the quantitative ratio of clay and non-clay minerals, the suspension viscosity and the cation-exchange capacity. Standard technological tests require considerable amounts of time and sample volume. This work will underlie in development of express methods which could be used as fast and precise evaluation of the main characteristics of colloidal properties (used in grade of clay powder analysis) based on mineral composition and particularities of clay minerals structure.

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## THE EFFECT OF CROSS-LINK TYPE, CROSS-LINK CONCENTRATION AND INITIATION METHOD ON THE SWELLING/ DESWELLING CAPABILITIES OF PNIPAM HYDROGELS IN AQUEOUS AND ALCOHOLIC SOLUTIONS

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A hydrogel is an intricate polymer chain network that is insoluble in aqueous media and capable of absorbing very large quantities of water due to chemical and/ or physical cross-links between polymer chains. Their extremely high water content gives rise to a high degree of flexibility and enables the gel to behave in a manner similar to that of natural tissue. Common uses for hydrogel materials include tissue engineering, stimuli-responsive materials, biosensors, and as disposable absorbent materials; e.g. contact lenses. Adaptive behaviour which permits macroscopic transformation can be given to synthetic hydrogel homopolymers or copolymers, such that changes in solubility and/ or secondary structure occurs in response to changes in secondary forces such as hydrophobic effects, hydrogen bonding and electrostatic interactions.

The successful development of polymer-clay nanocomposite involves the optimisation of polymer/ clay ratio together with the processing method and an exploration of the effect of different clays (and organomodifiers) on the properties of the resulting material. This study reports the comparison of poly(n-isopropylacrylamide), PNIPAM, which has been prepared using a chemical cross-linking agent or physically cross-linked using well dispersed laponite, a synthetic hectorite. The swelling/ deswelling response of four different cross-linked PNIPAM systems in water alone, and in mixtures with alcohol, has been studied.

Within the PNIPAM/ laponite structure, the laponite behaves as a physical, rather than chemical, multifunctional cross-linker. This type of physical interaction between the polymer chain and the cross-linking agent has been shown to vastly improve the swelling and deswelling capabilities of the hydrogel, with far greater expansion/ contraction in response to external stimuli. The results reported here show that the initiation method, cross-link type and cross-link concentration all have a profound effect on the deswelling behaviour of the gels when heated, with chemically cross-linked gels showing an inhibited volume decrease compared to the clay nanocomposites. Cross-link concentration appears to have little or no effect on volume change when gels are deswollen in alcohol/ water solutions, although it was observed that increased deswelling was achieved by increasing the alcohol chain length.

## NOVEL REACTIVE AMINO-COMPOUND: TRIS(HYDROXYMETHYL)AMINOMETHANE COVALENTLY GRAFTED ON KAOLINITE

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The covalently grafting of organic units on an inorganic matrix leads to materials combining functionalities of the organic ligands, such as light absorption, reactivity, and flexibility, with the specific properties of the support, such as chemical and thermal stability, giving rise to new materials with high functionalities and unique properties. Various inorganic matrices such as silica, zeolite, and titania have been employed in the development of hybrid organic-inorganic matrices. In this context, natural clays, and kaolinite in particular, have attracted attention due to their structural features, which consist of two types of interlayer surfaces, one formed by silicon tetrahedral sheets and another composed by aluminum octahedral sheets. In the case of an octahedral aluminum surface (gibbsite), there is a higher density of hydroxyl groups that can be modified by intercalation, reacting with organic molecules and resulting in hybrid materials. A novel reactive solid containing amine groups was prepared by functionalization of the Brazilian São Simão kaolinite with tris(hydroxymethyl)aminomethane, designated TRIS. The functionalization involved refluxing of the molten TRIS in the presence of kaolinite previously intercalated with dimethylsulfoxide (DMSO). TRIS effectively displaced DMSO from the clay interlayer, giving rise to Al-O-C bonds, thereby characterizing formation of a hybrid organic-inorganic matrix. The resulting material was characterized by X-ray diffraction, thermal analysis, infrared absorption spectroscopy, and C and N elemental analysis. The X-ray diffractograms revealed incorporation of the organic molecules of TRIS into the interlayer space of kaolinite. The thermogravimetric curves of the kaolinite samples functionalized with TRIS indicated that the materials were thermally stable up to 300°C. Resistance of Ka-TRIS to hydrolysis was tested by two treatments, namely by washing with ethanol by several times and by magnetic stirring in aqueous solution for 48h, clearly showing that the organic units are covalently bound to the hydroxyl groups of kaolinite and not only intercalated. Displacement of the bands due to interlayer hydroxyls in the infrared absorption



spectra and the presence of vibrations due to  $\text{NH}_2$  groups at 3349, 3331, 3290, and  $1589\text{ cm}^{-1}$  also confirmed functionalization of the kaolinite with TRIS.

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## CERAMIC PROPERTIES OF CLAYS FROM THE LITHOSTRATIGRAPHIC UNIT “ARGILAS DE AVEIRO”: A 3D MODEL VARIABILITY

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Clays from the Upper Cretaceous lithostratigraphic unit “Argilas de Aveiro” (Portugal) have been used for the manufacturing of traditional ceramic products. This unit covers an area of about 100 km<sup>2</sup> extended along N-S direction, the outcrops represent about 30% of the area referred to. The assessed ceramic properties showed that the clays have high potentialities for the manufacturing of by high added values products such as extruded floor tile and vertically perforated brick.

The studied clays are geologically included into the Upper Cretaceous (Senonian) sedimentary sequence named “Argilas de Aveiro”. The outcropping clay layers are characterized by diversified ceramic properties which make possible their blends their blending and consequently the supply of distinct ceramic markets.

The selected clay raw materials were characterized by XRD, WLXRF, PSA and Atterberg plasticity. The high temperature reactions and changes which have occurred along firing were identified by TG, DSC, and TD. The green test bodies which have been prepared by extrusion were dried at 105 °C, were submitted to slow firing at 875 °C, 950 °C; 1025 °C and 1100°C. Drying and firing shrinkages, mechanical bending strengths and water absorption were determined too.

Clay minerals assemblages show regional variation from illite – kaolinite assemblage to smectite – illite assemblage. Particle size distribution shows an increase of clay content from north to south of the lithostratigraphic unit. Chemical analysis data shows a variation correlative with the mineralogical analysis data and particle size distribution, particularly expressed by the decrease of SiO<sub>2</sub> and the increase of Al<sub>2</sub>O<sub>3</sub> from north to south of the lithostratigraphic unit. At relatively low firing temperature (875 °C) the test bodies showed low water absorption (less than 6%), high mechanical bending strength values (ranging from 31 MPa to 53 MPa), and total shrinkage values close to 10%.

In the studied clays the determined mineralogical and chemical data, together with the determined ceramic parameters, allowed with other parameters of the lithostratigraphic unit “Argilas de Aveiro”, to establish a 3D model for the lithostratigraphic unit variability.

This model allowed the definition of the potential zones more favourable for extractive works and both thickness and volume of overburden materials (mostly sand) that should be removed. The typology of raw clay and sand that could be defined in the different zones have provided a good contribution for the better planning and use of the geological resources within the lithostratigraphic unit “Argilas de Aveiro” and have provided also a good contribution for the better territorial planning and administration.

## BUILDING REJECTS INCORPORATION ON RED CERAMICS

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In Brazil, rejects originated by civil building activities achieves the impressive sum of thousands of tons a day, more specifically in São Paulo State. Most of these rejects don't have yet an adequate destination, being just a small fraction recycled as raw materials raw materials to roads and highways refurbishment. The other and biggest fraction ends on landfill, wasting big areas and collaborating to the proliferation of regional epidemic diseases such dengue fever.

It has being studied a procedure for the reuse of these rejects as an component of red ceramics, which market segment have good importance in Brazil, using significant amounts of natural raw materials.

The objective of this work is to analyze the results of this study. The base clay is a red industrial type from Ibetel<sup>TM</sup> ceramic. To determine an adequate reject percentage for industrial use, spherical test bodies with 1%, 5%, 10% 20% and 30% of incorporated material were conformed. The test bodies were dried at 110°C and tested about their compression strength. The same tests were also conducted after a 950°C burn in addition to color, loss of mass and dimensional retraction verification. It was chosen due to its best results, the clay with 5% of incorporated reject to more detailed experiments. The test bodies were conformed 20.0 x 100.0 x 10.0 cm bars, which were characterized about their ceramics properties: water absorption after 950°C burn and compression strength after dried at 110°C and burned at 950°C. The bricks produced on this test shown similar ceramic properties when compared to the base clay proving to the best incorporation proportion. This incorporation percentage is also compatible with the regional amount of rejects in case of industrial application.

So it was determined that an industrial test should be conducted with 5% of incorporation. About of 1500 bricks were produced and tested after dried about water absorption and compression strength. They were finally burned and tested with respect to color, compression strength, water absorption and lixiviation. The testing procedures were conducted by certified laboratories and shown ceramic properties similar with the base clay. By the end, the lixiviation analysis proved that the new resultant material is in compliance with the Brazilians environment regulations.

Given the good results achieved, the use of these rejects on the ceramic industry would result in a adequate end, eliminating a great part of the discharged rejects. This reuse would also contribute to a longer life to the clay reserves that are already running out. as another environment benefit.

## SEPIOLITE-BASED NANOCOMPOSITE FOAMS

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Cellular or macroporous materials employed in insulation are typically prepared from synthetic polymers such as polyurethane or polystyrene, and using foaming techniques that generate cellular structures by embedding gas or air bubbles into the polymer matrix. In case of fire, the main problem with this kind of materials is the generation of toxic gases during the polymer burning. Thus, the current efforts are addressed to overcome this problem, using other types of polymers or incorporating fire retardant agents to the polymer matrix. In this sense, the use of polymers from biological origin in combination with clay minerals may represent an appropriate alternative to commonly employed synthetic polymer cellular materials. As well known, polymer-clay nanocomposites offer improved mechanical properties and better thermal stability than the pristine polymer, even when small amounts of clays are added, usually up to ca. 5% [1]. The dispersion of the clay particles into the polymer, with interaction at the nanometer scale between both components, has also been proved to enhance the fire resistance [2].

The novel rigid foams presented in this work belong to the class of bio-nanocomposite materials, derived in this case from the assembly of microfibrinous clays and different polysaccharides extracted from the biomass. Due to the natural origin of all the components, the resulting bio-nanocomposites are biocompatible, biodegradable and eco-friendly materials, also commonly denoted as green nanocomposites [3]. The strong interaction between the sepiolite and the polysaccharide chains was confirmed by means of infrared spectroscopy, since the stretching vibration band of the OH bond in the silanol groups of the sepiolite surface was considerably perturbed in the bio-nanocomposites. The macroporosity in these foams was achieved by means of freeze-drying. The formation and subsequent sublimation of ice crystals generated materials with a hierarchical porous architecture, with pore size in the micrometre range, which is responsible for the low density of these composite foams, less than 0.05 g/cm<sup>3</sup> [4,5]. This porous structure may provide the foams with acoustic or thermal insulating properties. The association of clay particles to the biopolymer matrix contributed to improve the mechanical properties of the foams, which showed compression modulus in the range of MPa in spite of their low density. These materials also showed fire resistancy, which was evaluated following an established procedure (ASTM D4986), as well as by means of cone calorimetry. In conclusion, the prepared foams could be considered as auto-extinguishable materials, with ability to prevent fire propagation. Because of all these interesting properties, the sepiolite-based composite foams seem

appropriate for application as insulating materials in the construction or in the transport sectors.

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## REACTIVITY OF COMPACTED CLAYEY SOIL PERCOLATED WITH AN ALKALINE SOLUTION

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In the French concept deep nuclear wastes repositories, the galleries should be backfilled with excavated argillite after the site has been filled. Some additives could be used, and previous experimental part showed that the lime addition could improve the mechanical characteristics of the argillite. This study present the effect of a  $\text{Ca}(\text{OH})_2$  saturated solution circulation through lime treated sample for 3, 6 and 12 months at 60°C. Different techniques were used in order to assess the effect of such circulation on the microstructure of the samples. So, mercury intrusion porosimetry tests, scanning electron microscopy equipped with energy dispersive X-ray analyser (EDX) and image analysis of soil pieces were used to understand the link between the mineralogical transformations, the textural and mechanical changes produced in the compacted clayey soil as the consequence of the circulation of the alkaline solution.

The  $\text{Ca}(\text{OH})_2$  saturated solution induced a significant dissolution of the lime treated-argillite with a progressive dissolution of the soil grains, isolating the soil aggregates and creating some flow-paths enhancing the solution transport. That explains the initial macropore formation observed by MIP and SEM during the first three months whereas there are no major modifications at the macropore level between 3 and 12 months of alkaline fluid circulation. Most modification of the shear strength behaviour of the lime-treated argillite occurred during the first three months of water circulation, as a consequence of the dissolution of the argillite and the cementitious product formed during the interaction of the lime with the soil minerals.

## MICROWAVE ASSISTED ACID TREATMENT OF SEPIOLITE

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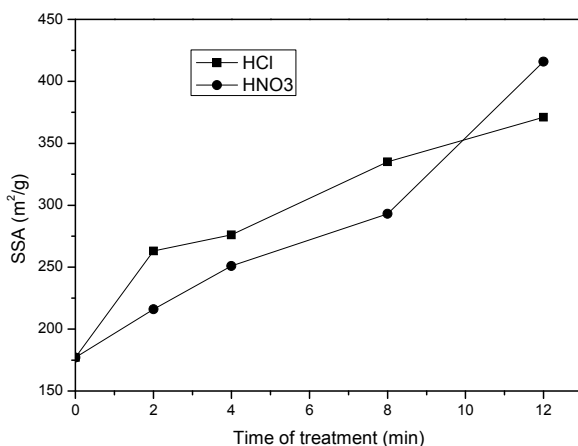
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Microwave techniques for heating are actually used in many chemical processes. The use of microwave radiation in the activation of clays offers higher heating rate in shorter times, and uniform heating. The effect of microwave assisted acid treatment on the texture and structure of a sepiolite from Vicálvaro (Madrid, Spain) was investigated. 5 grams of sepiolite were treated with 50 ml of 0.2 N HCl or HNO<sub>3</sub> for 2, 4, 8 and 12 min under 700 W of microwave radiation. The resulting materials were characterized by X-ray diffraction, FTIR spectroscopy, S<sub>BET</sub> and SEM.

The XRD pattern of the untreated sepiolite shows that this sample contains a certain amount of Mg smectite which, according to Cuevas et al., (2003), consists of a complex mixture of stevensite, saponite and mica-type minerals. The XRD profile of the treated materials shows a progressive decrease in the intensity of the diffraction peaks, which is more evident in the 12-Å reflection, and an increase of the background between 18 and 27°2θ. On the contrary, peak positions do not change throughout the entire treatment. These results are similar to that of Yebra-Rodríguez et al., (2003), and suggest the formation of a large amount of amorphous phase as a result of the partial dissolution of the structure.

FTIR spectra of the obtained materials suggest that the treatment causes the dissolution of the octahedral layer and the generation of free silica.

S<sub>BET</sub> results showed that the acid treatments assisted with microwave radiation increase the specific surface area of sepiolite from 177 to 371 m<sup>2</sup>/g, after 12 min of





treatment with HCl, and to 416 m<sup>2</sup>/g, after this same time of treatments with HNO<sub>3</sub>. This result indicates that the assistance of microwave radiation leads to obtain greater increments of specific surface areas in shorter times of activation, compared with those obtained with conventional methods of acid digestion.

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## SILICA-SEPIOLITE ORGANO-HETEROSTRUCTURES AND HETEROSTRUCTURES

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Since long time ago, the development of porous heterostructures based on clay minerals is a topic of great importance in view to develop alternative catalysts to zeolites. Thus, pillared clays incorporating alumina, iron oxides, titania, and other metal oxides have been largely studied [1]. New approaches, as the one reported by Pinnavaia and co-workers for preparation of silica-smectite derivatives [2], intend to create porous clay heterostructures with modulate and larger porosity than those achievable by common pillaring strategies. In this context, our Group has recently introduced an original approach to prepare a new type of heterostructures based on layered silicate that may give rise to delamination of the layered silicate, for instance smectites and vermiculites, resulting in materials of elevated surface area [3,4]. This method implies the controlled hydrolysis and polycondensation of alkoxysilanes, and other metalalkoxides, previously incorporated in the interlayer space of organoclays that, after a heterocoagulation process and a controlled thermal treatment, results in the formation for instance of highly porous delaminated silica-clay and titania-clay solids [3-5]. This methodology can be extended to clays with a microfibrillar morphology, such as sepiolite, resulting instead in the formation of nanoparticles on the surface of the silicate fibres that may be relevant for different purposes [6]. For instance,  $\text{TiO}_2$ -sepiolite materials show interesting properties as photocatalysts.

In the present work, we have applied this colloidal route to prepare a series of  $\text{SiO}_2$ -sepiolite heterostructures using tetramethylortosilicate (TMOS) as precursor of the silica nanoparticles. We have explored the influence of the nature of the alkylammonium in the starting organosepiolite as well as the TMOS:sepiolite ratio in the characteristics of the resulting materials. Attention was equally devoted to the morphological and textural features of the different  $\text{SiO}_2$ -sepiolite materials before (organo-heterostructures) and after (heterostructures) thermal treatment, which was performed to eliminate the organocation and consolidate the silica network. Final solids describe sepiolite microfibrils surrounding by silica nanoparticles, yielding to materials with surface areas ca. to  $350 \text{ m}^2/\text{g}$  without microporous contribution. Furthermore, preliminary tests regarding the use of the  $\text{SiO}_2$ -sepiolite heterostructures and organo-heterostructures as nanofillers for epoxy resin reinforcement were also explored. The resulting composites mechanical properties are discussed considering the different nature of the external surface of organo-heterostructures and heterostructures as well as its implications on the filler-polymer interface.

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## DIOXIN IN BLEACHING EARTH: MASS BALANCE ISSUES

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Bleaching earths, clays used to remove impurities from vegetable oil, may contain ultratrace amounts of organic compounds such as polychlorinated-p-dioxins (PCDDs) and polychlorinated-p-furans (PCDFs), in this paper referred to collectively as dioxin unless otherwise specified. Since these compounds are considered toxic, their presence in bleaching earths and their fate during oil processing is of interest.

An issue confronting bleaching earth suppliers is the fate of dioxin during the bleaching process. Bleaching earths are used to remove contaminants from oils such as metals, peroxides, chlorophyll, carotenoids, etc. To our knowledge, no one has definitively shown the fate of the dioxins through the bleaching process, either dioxin moving into the oil or dioxin moving from the oil to the bleaching earth. Early work showed neither a reduction nor an increase in measured dioxin content of an oil and a measured decrease in the spent bleaching earth. The question then arose if the dioxin in the bleaching earth had moved into the oil. Since bleaching earths have naturally low levels of dioxins, it becomes difficult to determine dioxin fate through bleaching. Analytical issues with the bleaching earth itself notwithstanding, a bleaching earth is commonly used at ~0.5 wt. % of an oil. If the bleaching earth had a measured dioxin content of 1 ppt (part per trillion), and all the dioxin moved into the oil, the oil dioxin content would increase by 0.005 ppt. This is likely immeasurable. Nevertheless interest remains.

This study examined the fate of the 17 toxic dioxin congeners through the bleaching process. To ensure detection, the study employed bleaching earth containing dioxin at vastly higher amounts than encountered in such products (338 ppt, TEQ), and used  $^{13}\text{C}_{12}$  isotopes of PCDDs and PCDFs to avoid interferences by naturally-occurring dioxins. To further ensure detection, soybean oil was bleached with 10 times the normal amount of clay used (5 wt. %) with a clay prespiked with the 17 PCDD and PCDF congeners. The dioxin concentration was measured in the bleached oil, spent filter cake, and vacuum condensate using high resolution gas chromatography/high resolution mass spectroscopy (HRGS/HRMS). Even at the high loadings used, virtually no dioxin was apparent either in the oil, the filter cake, or the vacuum condensate. The authors could not establish a true mass balance. Even though the dioxin in the spiked bleaching earth may not be held as tightly as native dioxin, the dioxin is either adsorbed strongly, the extraction technique not adequate to extract the dioxin from the spent filter cake, or the dioxin is catalytically degraded. Additional work is ongoing.

## PA6.6/Mg,Al/AD-LDH NANOCOMPOSITES OBTAINED BY SOLID STATE POLYMERIZATION

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In recent years, the dispersion of low loadings (ca. 5%) of inorganic nanoparticles in organic polymers is a challenge for the preparation of new composite materials with enhanced mechanical, gas barrier and flame retardant properties, when compared to those of composites prepared with micron size particles [1,2]. Although fillers like alumina, silica, etc., can be added, layered inorganic compounds show unique properties to be active as fillers in polymeric nanocomposites. They can be, in fact, exfoliated into single layers, each of them having a thickness of the order of nanometers (from ca 0.7-2.5 nm) and the surface of the layers may be functionalized by ion exchange or grafting reactions with organic groups that increase the compatibility with the polymers. In the last years, “anionic clays”, also known as hydrotalcite-type compounds or layered double hydroxides (LDHs), have been used as lamellar materials in nanocomposites synthesis. LDHs are brucite-like layered materials, with hydrated anionic counterions in the gallery space [3]. The positive layer charge is originated by partial isomorphic substitution of divalent cations by trivalent ones. In order to attain electroneutrality, an appropriate number of anions must be incorporated into the interlamellar domain. The flexibility in their composition allows preparing LDH with a wide variety of properties, finding a wide range of applications; they can be used as catalysts or catalyst supports, anion exchangers, polymer stabilizers, ... When these materials are to be used as hydrophobic polymer fillers, pristine LDH is not suitable and the insertion of anionic organic species with a long hydrophobic tail is necessary, which on one hand causes swelling of the interlayer distance and on the other one makes the LDH materials more compatible with organic polymers [2]. Several methods have been developed to produce LDH/polymer nanocomposites [4]. However, *in situ* polymerization is the most appropriate method, in order to produce well-exfoliated nanocomposites. This method enables significant control over both the polymer architecture and the final structure of the composite.

In this work, a new nanocomposite was obtained by dispersing an adipate-modified layered double hydroxide (LDH) with adipic acid and hexamethylene diamine. The samples were polymerized in the solid phase under a nitrogen flow for 200 min at 190

<sup>2</sup>C. The structural and compositional details of the nanocomposite were determined by powder X-ray diffraction (PXRD), Fourier Transform Infrared (FTIR) spectroscopy, focused ion beam (FIB), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The PXRD patterns and FIB images show a partially intercalated and partially exfoliated dispersed layered crystalline particles in the polyamide 6.6 matrix. The best dispersion level is achieved in polyamide 6.6/LDH nanocomposites with low LDH loading. Some residual tactoids and particle agglomerates are also evident at high concentration. The best thermal stability of the nanocomposites is shown by the sample with 0.1% LDH content, for which it is higher than that of pure polyamide.

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## EFFECTIVE AND SELECTIVE ADSORPTION OF ZINC ION ON A LAYERED ALKALI SILICATE FROM SEAWATER

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The concentration of certain ions and molecular species in the environment is a topic of a wide range of scientific and practical viewpoints such as the removal of toxic compounds and the concentration of noble elements. Layered inorganic solids like layered clay minerals are one promising materials for the goal, therefore searching and designing of layered materials and the derivatives for target ions and molecules are widely conducting.<sup>1</sup> As to the ion exchange selectivity on layered inorganic solids, it has been recognized that anions with higher charge and smaller size is preferred on layered double hydroxides.<sup>2</sup> For the concentration of inorganic cations, although there are a variety of possible materials such as smectite clays, synthetic micas, layered metal phosphates, and layered titanates, the selectivity has been scarcely communicated for the concentration of heavy metals and radioactive ions.<sup>3</sup> More recently, the organic modification of nanoporous materials such as layered and mesoporous solids has been conducted to concentrate heavy metal ions.<sup>4</sup> The attached thiol functionality played a role to adsorb Hg though the origin of the selectivity is not clear. Due to the demands for the environmental purification and concentration of noble ions (the situation for the requirement is changing after the consumption of natural resources), it is worth conducting to look for selective ion exchange processes using environmentally friendly materials for a wide variety of target elements.

In this study, we investigated the adsorption of  $\text{Zn}^{2+}$  on a pristine layered alkali silicate, magadiite, from aqueous mixture mimicking seawater.  $\text{Zn}^{2+}$  is an element essential for life; on the other hand, exists in seawater and has been pointed out to be harmful to human or aquatic animal health. Accordingly, the concentration of  $\text{Zn}^{2+}$  from the dilute aqueous mixture is a topic of interest.  $\text{Cd}^{2+}$  was added to the seawater-mimicking aqueous mixture, since it is known that comparable amounts of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  exist in seawater and consequently it is interesting to separate the two cations for the development of adsorbents which efficiently concentrate  $\text{Zn}^{2+}$  from seawater. We have found that magadiite selectively and efficiently adsorbs  $\text{Zn}^{2+}$  from the mixed electrolyte solution by the ion exchange of the interlayer  $\text{Na}^+$  with  $\text{Zn}^{2+}$ . On the other hand, the concentration was not achieved on another sodium-type layered alkali silicate, octosilicate, and a commercially available ion exchange resin. Moreover, it was found that the adsorbed  $\text{Zn}^{2+}$  was replaced by sodium ion for possible  $\text{Zn}^{2+}$

collection, in other word, magadiite was able to be used repeatedly. Magadiite is a naturally occurring layered alkali silicate and can be readily synthesized on a large scale by a simple hydrothermal reaction between silica, sodium hydroxide, and water. Therefore, the present success opens up a new opportunity for collecting  $\text{Zn}^{2+}$  from seawater.

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## EFFICIENT EXCITED ENERGY TRANSFER REACTION BETWEEN PORPHYRINS ON CLAY SURFACE THE EFFECTS OF ADSORPTION CONDITIONS

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In photosynthetic bacteria, regularly-arranged bacteriochlorophylls collect sunlight efficiently. The light-harvesting system carried the energy smoothly to the reaction center.

We aim to realize the artificial light-harvesting system by using clay mineral as host material. We have already reported a formation of an interesting porphyrin-clay complex in which the porphyrin molecules densely adsorb on the clay sheets without aggregation. In this work, the energy transfer reaction between a number of porphyrins on clay was investigated. We found out intermolecular distance between porphyrin dyes affects the efficiency of energy transfer. *m*-TMPyP and *p*-TMPyP were adopted as a energy donor and acceptor (Figure.2) and synthetic saponite was used as a clay minerals. The complex was obtained by mixing porphyrins and clay aqueous solution. The total concentrations of *m*-TMPyP and *p*-TMPyP were set to be constant and the ratio of two porphyrins was changed. Under these conditions, the clay sheets exist as exfoliated form.

As a result, we observed efficient energy transfer reactions from excited singlet *m*-TMPyP to the ground-state *p*-TMPyP. The energy transfer efficiency increased as loading levels and ratios of acceptors increased. Amazingly, the maximum efficiency was almost 100% under the optimum condition.

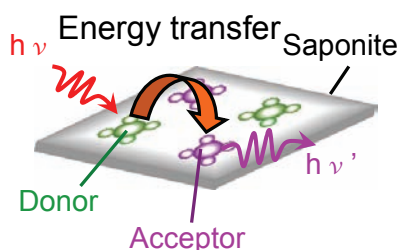


Figure.1 Excited energy transfer on clay surface

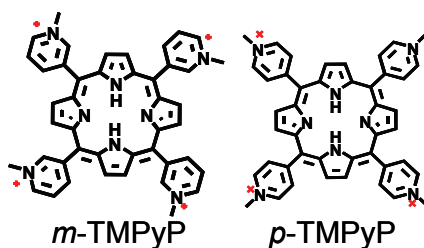


Figure. 2 The structure of porphyrins

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## AN EVALUATION OF CHILEAN CLAYS FOR INDUSTRIALS APPLICATIONS

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This study is focussed on the behavior of clays from Chile which has an important local ceramic industry. Five deposits of clays with industrial application have been selected. The clays come from Monte Patria (A), La Herradura (B), Las Compañías (C), Litueche (D) and San Vicente de Tagua-Tagua (E). The chemical and mineralogical compositions of clays were determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. Also the plasticity index (PI) was measured for each sample. Test samples were prepared by pressing and firing in range of 800 up to 1150°C. Linear contraction (LC), water absorption capacity (WAC) and thermogravimetric analysis (TGA) were completed in order to characterize clays and firing development.

The chemical and mineralogical compositions of samples differ considerably. The chemical composition showed high iron content (5-11%), except for D clay (<1%). B and E clays showed the highest relative amounts of alkalis. A and B samples showed the higher amounts of carbonates. D clay is a carbonate-free sample richest in silica. Albite, quartz, talc, kaolinite and chlorite were the main phases found in A bulk samples. Other minerals found in minor quantities were K-feldspars, calcite, hematite and tremolite. The main clay minerals found in A clay fraction were kaolinite, chlorite and montmorillonite. Other minor phases in the clay fraction are quartz and calcite. The main phases found in B bulk samples were quartz, albite, K-feldspar, and calcite. The main phases in clay fraction were calcite, kaolinite, chlorite and illite/muscovite. Hematite and sepiolite were found in trace amounts in bulk samples and clay fraction, respectively. In C bulk samples albite, quartz and chlorite were the dominant phases; tremolite, hematites and kaolinite were present in lesser quantities. In C clay fraction the mineral phases found were: illite/muscovite, chlorite, kaolinite, albite and traces of quartz, pyrophyllite, sepiolite, vermiculite and palygorskite. The mineral composition of D samples, both in bulk rock and clay fraction, consisted of quartz, K-feldspar and kaolinite with a small amount of illite/muscovite. Finally, E bulk samples consisted mainly of albite and quartz, and contain K-feldspars, hematite, kaolinite and chlorite in minor amounts. Illite/muscovite, kaolinite and palygorskite were the dominant phases in E clay fraction. Other components found in slighter quantities in this fraction were quartz and albite.

The plastic behaviour of the samples and their adaptability for pressing are closely linked. Sample A was considerably more plastic ( $PI=36$ ) than others ( $PI = 23-27$ ), explaining its excellent aptitude for pressing. According to the results, the behaviour of A, B and D were somewhat similar although they have different values of shrinkage, moisture and critical point. On the other hand, the curves of C and E were quite similar. By contrast A and B showed more suitable behaviour. A considerable decrease in the WAC coinciding with the beginning of vitrification, was observed between 1050 and 1100 °C. At 1150°C the porosity of the tile bodies decreases significantly and the tile bodies became earthenware. All studied clays seem to be easily adaptable to a correct dry pressing ceramic process. In particular, illite-kaolinite-rich samples show the best behaviour. Samples from San Vicente de Tagua-Tagua are suitable for production of fast vitreous pieces. Litueche samples present the highest refractory behaviour. The thermogravimetric curves can be classified in two groups. One group is for calcite-rich samples (B and E), and the second group is for the rest of samples (A, C and D), very poor in carbonates. The firing process should therefore be conducted with precaution by creating a low-heating rate stage in the decarbonation zone (850-1000 °C). The general behaviour of C, D, and E were similar because the decarbonation reaction is weaker or inexistent, due to these samples not having calcite.

The positive results obtained in this set of preliminary tests lead us to envisage new research programs in Chile, focused on testing these and other raw materials on a semi-industrial scale, assessing the effective possibility of using them as ceramic raw materials in the local ceramic industry.

## UPTAKE OF HEAVY METAL IONS FROM AQUEOUS SOLUTION BY Mg–Al LAYERED DOUBLE HYDROXIDES INTERCALATED WITH ORGANIC ACID ANIONS, AND ITS KINETICS

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Mg–Al layered double hydroxide (Mg–Al LDH) has anion-exchange capability. In this study, Mg–Al LDH was modified with organic acid anions using a coprecipitation technique, and the uptake of heavy metal ions from aqueous solution by the Mg–Al LDH was studied [1]. Citrate•Mg–Al LDH, malate•Mg–Al LDH, or tartrate•Mg–Al LDH, which had citrate<sup>3-</sup> (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>), malate<sup>2-</sup> (C<sub>4</sub>H<sub>4</sub>O<sub>5</sub><sup>2-</sup>), or tartrate<sup>2-</sup> (C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>) anions intercalated in the interlayer, was prepared by dropwise addition of a mixed aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> to a citrate, malate, or tartrate solution at a constant pH of 10.5. These Mg–Al LDHs were found to take up Cu<sup>2+</sup> and Cd<sup>2+</sup> rapidly from an aqueous solution at a constant pH of 5.0. This capacity was mainly attributable to the formation of the citrate–metal, malate–metal, and tartrate–metal complexes in the interlayers of the Mg–Al LDHs. The uptake of Cu<sup>2+</sup> increased in the order malate•Mg–Al LDH < tartrate•Mg–Al LDH < citrate•Mg–Al LDH. The uptake of Cd<sup>2+</sup> increased in the order malate•Mg–Al LDH < tartrate•Mg–Al LDH = citrate•Mg–Al LDH. These differences in Cu<sup>2+</sup> and Cd<sup>2+</sup> uptake were attributable to differences in the stabilities of the citrate–metal, malate–metal, and tartrate–metal complexes. These results indicate that citrate<sup>3-</sup>, malate<sup>2-</sup>, and tartrate<sup>2-</sup> were adequately active as chelating agents in the interlayers of Mg–Al LDHs.

Furthermore, the uptakes of Cu<sup>2+</sup> and Cd<sup>2+</sup> by the Mg–Al LDHs were examined kinetically [2]. The uptake was shown to occur as the chelation between the heavy metal ions and the organic acid anions. The uptake rate equation was dependent on the type of chelate formed. The apparent activation energies for the uptake of Cu<sup>2+</sup> by citrate•Mg–Al LDH, malate•Mg–Al LDH, and tartrate•Mg–Al LDH were 53.1, 71.2, and 47.9 kJ mol<sup>-1</sup>, respectively. Further, the apparent activation energies for the uptake of Cd<sup>2+</sup> by citrate•Mg–Al LDH, malate•Mg–Al LDH, and tartrate•Mg–Al LDH were 53.6, 50.8, and 106.5 kJ mol<sup>-1</sup>, respectively. These values confirm that the uptake proceeded under chemical reaction control, namely, the reaction simply proceeded according to the chelation with a certain rate, different for each combination.

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## COMPETITIVE ADSORPTION OF POLYMER AND PLASTICIZER INTO THE CLAY GALLERY

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New bio-based packaging materials are of growing interest due to their sustainable and biodegradable nature, especially where there is considerable effort to reduce the dependence on oil based plastics. Unfortunately, the use of biodegradable films for food packaging has so far been strongly limited because of the poor barrier and weak mechanical properties shown by natural polymers. The incorporation of clay can help improve these deficiencies, together with plasticizers to promote flexibility of the resulting biopolymer films. Generally, when polymer and plasticizer are mixed with clay to produce nanocomposites, preferential adsorption of the polymer and/or plasticizer into the clay gallery can occur.

It is difficult to quantify the amount of plasticizer and biopolymer that resides in or outside the clay gallery, but their quantification is very important as the polymer-plasticizer compositions determine the final properties of the nanocomposites. In this study, Poly(vinyl alcohol)(PVOH) has been selected as a 'model' hydrophilic polymer in an attempt to investigate its competitive adsorption with polyethylene glycol (PEG) into the clay gallery. Quantification of the individual loading of PEG and PVOH in the clay gallery has now been evaluated.

In this study, the influence of plasticizer and loading combined with the amount of polyvinyl alcohol offered to the clay has been systematically investigated. The resulting systems have been studied using X ray diffraction (XRD), Thermogravimetric analysis (TGA), and Dynamic Mechanical Analysis (DMA). The clay used is based on Na montmorillonite (Cloisite Na<sup>+</sup>) sourced from Southern Clay Products, the polymer PVOH has a molecular weight of 30,000 and the plasticizer, polyethylene glycol (PEG), has a molecular weight of 600.

## PREPARATION OF ZINC OXIDE – MONTMORILLONITE HYBRIDS

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There is a great interest in hybrid materials of semiconductor particles with organic or inorganic matrices for tailoring the properties of the particles as well as for the materials application. Various kinds of semiconductors have been embedded in organic or inorganic materials using different methods. Smectite, a 2:1 layered clay mineral, exhibits numerous characteristics including adsorptive property, ion exchange property, swelling behavior and large surface area, which may enable its efficient features for conducting novel hybrid materials. In the present study, we investigate the new hybrids materials of zinc oxide (ZnO) particles with montmorillonite, a clay mineral in smectite group, and study the effect of two-dimensional layered inorganic solid in the optical properties. ZnO has been extensively investigated due to its unique electrical and optical properties for optoelectronic devices and so on.

ZnO particle was synthesized from aqueous solution of zinc chloride and sodium hydroxide. The molar ratio of  $\text{Zn}^{2+}:\text{OH}^-$  was 1:15. ZnO-montmorillonite or ZnO-organomontmorillonite was prepared by adding the precursor solutions of ZnO into the suspension of Na-montmorillonite or organomontmorillonite during continuous stirring at 70 °C for 24 h. The hybrid materials of ZnO with montmorillonite were characterized by XRD, UV-Vis and photoluminescence spectroscopies. The diffraction peaks of ZnO particles were located at  $d = 0.28$ ,  $0.26$  and  $0.25$  nm, indicating the hexagonal wurtzite crystals. The XRD patterns of the hybrids showed the diffraction peaks at  $d = 1.52$  nm for ZnO-montmorillonite, at  $d = 2.02$  nm for ZnO-organomontmorillonite together with the peaks ascribed to hexagonal wurtzite ZnO. The absorption onset of ZnO was seen at 383 nm and those of the hybrid products appeared at 375 nm for ZnO-montmorillonite and 378 nm for ZnO-organomontmorillonite, suggesting the formation of ZnO particles in hybrid materials. The emission was observed at 544 nm for ZnO and at 548 nm for ZnO-montmorillonite and ZnO-organomontmorillonite, interpreting to the singly ionized oxygen vacancy in ZnO. The increase in the emission intensity by the hybridization was thought that the oxygen vacancies defects is be probably arisen by the surrounding environment of montmorillonite.

**Keywords:** Montmorillonite, Organomontmorillonite, Zinc oxide, Optical properties

## MODIFICATION OF CALCINED CLAY FOR ARTIFICIAL GROWING MEDIA AND PHYSICAL PROPERTIES

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Calcined clay is granular agglomerate of clay. Traditionally this has been used in pot plant substrates at a volume ratio of up to 1/3 as a subsidiary materials. It has the advantage of slowly releasing fertilizers, germicide, etc. due to its myriad small pore and large surface but also has low EAW (Easily Available Water) and WBC (Water Buffering Capacity) value since the water-holding force of its small pores exceeds the plant root suction power.

This research modified calcined clay to enhance the low EAW and WBC and to substitute for subsidiary materials of growing media. To find out the proper size of unit particles constituting the agglomerate for the matric potential of 1 to 10kPa, several sizes of feldspar was agglomerated and its water suction tests were conducted. Based on the proper size, calcined clay was modified and made with kaolin through two steps: the first step is consolidation of kaolin by mixing with water and drying. It was crashed and classified into the proper size. The second step is agglomerating it spherically by using a pan-type pelletizer. The modified calcined clay (MCC) is finished up by heating at 900°C for 2 hours.

MCC has bimodal pores: small pore of about 1μm and pore larger than 10μm. Water suction tests verified that MCC has higher EAW and WBC than those of typical subsidiary materials of a growing media. MCC with the size of 2~4mm was mixed with a Canadian sphagnum peat at several ratios, and the physical properties of the mixture and the appropriate mixing rate were investigated.



## INVESTIGATION OF DYES ADSORPTION BEHAVIOR ON THE CLAY SHEET ~TOWARDS EFFICIENT PHOTOCHEMICAL REACTION SYSTEM~

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Clay minerals have attracted recent interest regarding their application potential to photochemical reactions. The clay-dye complexes are very interesting as photo-functional materials. The adsorption behavior control of dyes on the inorganic surfaces has been an important factor to construct efficient artificial photosynthetic system. It is known that methylviologen(MV<sup>2+</sup>) suffers dynamic fluorescence quenching on clay surfaces. It indicates that MV<sup>2+</sup> molecules adsorb on clay surfaces as cluster assembly. In the present work, we examined dye adsorption behavior on clay surfaces by using MV<sup>2+</sup> as a probe molecule.

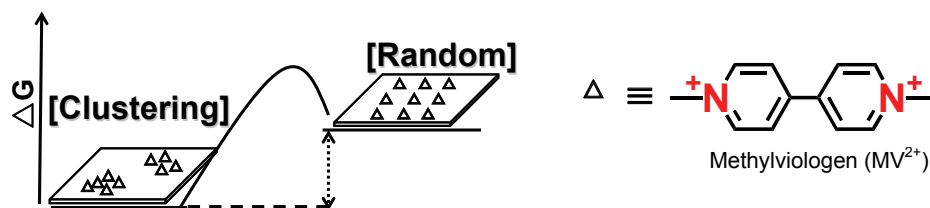


Fig.1 Thermodynamic equilibrium of the dyes on clay surfaces.

We evaluated the cluster assembly formation behavior of MV<sup>2+</sup> adsorbed on clay surfaces by the observation of fluorescence. We have found that clustering form is thermodynamically more stable than random form (Fig. 1). By the analysis of thermodynamic parameters such as entropy and enthalpy, we have found that the hydrophobic interaction causes the clustering form of dyes, thus, the selection of dyes turned out to be very important to control the adsorption behavior. These adsorption behaviors found in the present study are useful to control the photochemical reaction such as an electron transfer and an energy transfer.

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## PRELIMINARY RESULTS OF INVESTIGATIONS OF PHYSICAL AND CHEMICAL CHARACTERISTICS OF CLAY IN THE CONTINENTAL PART OF MONTENEGRO

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Ceramic materials have been used since ancient times, particularly products from baked clay.

With the development of civilization has been increased consumption of their brick and ceramic products. The modern technique and technology ceramic products have found their application.

Thus a broad application and annual production growth in the worldwide level about 15% and the fact that in Montenegro clay occur in several places as products of transformation of the rock on which they are formed, justifying the research in the field of the process of sintering of clay materials.

Most of the clay deposits in Montenegro is closely connected with the creation of coal (Pljevlja, Berane), degradation and transformation of sediments (Ulcinj, Tivat, Spuz), part of the other rocks (Kolasin, Bijelo Polje).

Exploitation of sites with clay localities continental part of Montenegro has not yet performed or for any purposes and not for industrial. So this study with certainty point to something which should be paid more attention to the scientific research and in industrial production.

The experimental part of the work is based on samples that are treated under the same conditions (pressure, temperature, time, the atmosphere in the furnace and sample mass) and so we provide a comparison feature sintered samples. All this opens the possibility to choose the quality and parameters of technological process.

Research is based on an examination of physical-chemical characteristics of the starting materials and products sintered.

The aim of this study was a comparison of characteristics of clay and sintered products with locations continental part of Montenegro, based on the results of completed research and development enabling the industrial production.

Brick building has a value of <20MPa, Tested samples have higher values of 20MPa-150MPa (for power) which indicates a high quality product sintered.

Based on preliminary research results and imposes the conclusion that the clay from the continental localities of Montenegro meet the purpose in the industry and brick making fine ceramics: ceramics, ceramic pottery, porcelain and more.

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## THE BOLE USED IN GILDED PLASTERWORK IN SALÃO ÁRABE, PALÁCIO DA BOLSA (OPORTO, PORTUGAL)

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Gilded plasterwork has played an important role in the Decorative Arts in Portugal, either in religious or in civil buildings, in particular on the north part of the country, reaching a paramount importance along the XVIII and XIX centuries.

Several materials are used in this artistic technique, one of them being the so-called bole. Bole, an argillaceous material, is usually applied as a preparatory layer in order to provide a flat smooth surface before the application of the gold leaf to the surface of the plasterwork.

The Salão Árabe (Arab Room) of the Palácio da Bolsa, in Oporto (North of Portugal), built between 1862 and 1880 is an emblematic symbol of the city due to its intense decoration, particularly the gilded and polychromatic plasterwork of its walls and ceilings. Throughout its existence, this salon has experienced several restoration interventions, some of them without any adequate scientific supervision or technical support.

The aim of this study is to analyze and compare the various types of boles used in selected gilded areas of the Arab Room, assessing the original and the restored areas.

The studied samples were carefully collected and submitted to analytical characterization using optical microscopy, scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDAX) and X-ray diffraction (XRD), carried out on the research facilities of the University of Aveiro.

The obtained results allowed us to delineate the sequence of each intervention.

## LIQUID CRYSTAL PHASES OF CLAY MINERAL COLLOIDS AND ITS APPLICATION FOR FABRICATING ANISOTROPIC GEL MATERIALS

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**Introduction.** Liquid crystal (LC) phases in the colloids of anisotropic inorganic particles were recently rediscovered and are attracting keen interest.<sup>1-6</sup> Although LC phases had not been identified in clay mineral systems due to its gelation behavior,<sup>5-7</sup> Michot et al. recently reported truly LC phases of montmorillonite<sup>8</sup> and beidellite<sup>9</sup>. We also found that the size-controlled fluorinated clay minerals, fluorotetrasilicic mica (FTSM) and fluorohectorite (FHT), form LC phases. These new inorganic LCs are useful to fabricate various advanced materials with anisotropy or controlled hierarchical structures.<sup>10</sup>

Here we show the application of the LC clay colloids (FHT and FTSM) for the synthesis of anisotropic polymer gel materials: we demonstrate that the poly(*N*-isopropylacrylamide) (PNIPA) hydrogel hybridized with the LC clays show macroscopic anisotropy the structure, refractive index, and volume phase transition behavior. For rational design of a polymer gel material with desired functions and properties, introducing well-defined anisotropic structure is important<sup>11</sup> as exemplified by living biological systems such as animal's muscle. Further, hybridization of polymer materials with nano-structured inorganic materials is an excellent way to improve mechanical and other important properties.<sup>12</sup>

**Experimental.** LC clay colloids were obtained by exfoliating a synthetic clay mineral, FHT or FTSM, in water, followed by ultrasonication to control the lateral size of the exfoliated clay nanosheets. Anisotropic hybrid gels were synthesized by radical polymerization of NIPA in the LC colloids under N<sub>2</sub> atmosphere in a glass capillary, by using ammoniumperoxide and *N,N,N',N'*-tetramethylethylenediamine to initiate the reaction. The gels were characterized by polarized light microscopy and small angle X-ray scattering (SAXS).

**Results and Discussion.** The hybrid gels observed with crossed polarizers equipped with wave plate showed uniformly blue/yellow colors at two diagonal directions. Swollen lamellar structures with the basal spacing of 30-60 nm were identified in the LC colloid/monomer mixture before polymerization by SAXS. Although these structures were partially lost in the product gels, the 2D-SAXS of the gels still showed

strongly anisotropic profiles. These results indicate macroscopic orientation of the clay nanosheets in the gel matrix along the capillary wall in the gel.

Due to the anisotropy in the structure, the hybrid gels also showed anisotropy in thermally induced volume phase transition. The hybrid gel shrunk by up to 60 % along the direction perpendicular to the optical axis, while it shrunk only by 34 % along the parallel direction.

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## THE FORMATION OF MAYA BLUE MONITORED BY NEUTRON SCATTERING

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Maya blue is an organo-clay complex used as a pigment. It is, perhaps, the first hybrid material in the history, a great invention of the ancient Maya who managed to encapsulate indigo into palygorskite creating in this way one of the most amazing pigments in the World. Indigo  $C_{16}H_{10}H_2O_2$  was obtained from the leaves of the *Indigofera suffruticosa* plant, and palygorskite  $Si_8(Mg_2Al_2)O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ . Maya blue is the “standard” blue pigment in ancient Mesoamerica (VII-XVI centuries) and it was also used during the colonization in Mexico (XVI c.) and in Cuba (XVII-XVIII c.). Since its rediscovering in 1932, it has attracted the attention of scientists because its coloration and resistance to chemicals and environmental aggressions, making possible the conservation of artworks in hostile environments as the tropical forest. Perhaps its most striking property is its resistance to acids: it is not destroyed (decoloured) even if boiled in nitric acid. The chemical reasons explaining how the indigo becomes inert to the chemical aggressions are still under debate.

We monitored the formation of Maya blue by heating a palygorskite-indigo mixture and measuring the  $S(Q,W)$  response function on the IN6 neutron spectrometer at the ILL, France. The recorded data gave rich information on several aspects of the processes. The elastic scattering  $S(Q)$  gives essentially the structure of the system. The incoherent scattering in our samples comes only from hydrogen atoms. Therefore, the flat background in  $Q$  (incoherent scattering) is very sensitive to the amount of released water and gives information on the dehydration process. This information can be directly compared with thermogravimetry data. The inelastic scattering gives information on the water dynamics. The simultaneous analysis of the elastic scattering and the incoherent scattering gave us the possibility to observe in parallel the dehydration process and the change of clay structure (folding). We observed

that the folding temperature in palygorskite depends very much on the atmosphere (experiments were under vacuum). We quantified the amount of zeolitic water released during the Maya blue formation and how the presence of indigo influences the folding of the clay. We also demonstrate that a quite resistant pigment can be obtained by zeolitically dehydrating the palygorskite-indigo mixture by means of vacuum, without any thermal treatment.



## NANOSPACE ENGINEERING IN METHYLVIOLGEN MODIFIED HECTORITE-LIKE LAYERED SILICATES WITH VARIED LAYERED CHARGE DENSITY FOR THE ADSORBENT DESIGN

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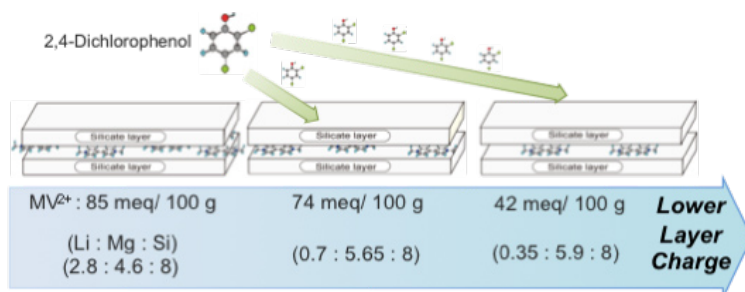
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Controlling spatial distribution (homogeneous distribution or clustering) of organic species in a confined nanospace is an important subject to bring out novel functions of the adsorbed molecules and to produce a specific reaction container with nanometer-scale. Smectites are useful scaffolds to create nanospace by the intercalation of organic species into the two-dimensional expandable interlayer spaces as so-called "pillar".<sup>1,2</sup> Selecting pillaring agents with different molecular structure and smectites with different cation exchange capacity (CEC) results in the controlled molecular sieving functions for nonionic organic compounds<sup>1,3</sup> and photofunctions derived from molecular distribution of photoactive molecules.<sup>4</sup> However, some characteristics, which depend on the origin of smectites, as position of isomorphous substitution and particle size make it difficult to discuss the effects of CEC on the physicochemical properties of smectites and their intercalation compounds. Therefore, there is a need to prepare smectites with a series of CEC. We recently reported the preparation of smectites (tri-octahedral group, hectorite-like) with CEC ranges from 40 to 90 meq/100 g of clay by the reaction of LiF,  $\text{Mg}(\text{OH})_2$  and colloidal silica.<sup>5</sup>

Here, we report the adsorptive properties of the hectorite-like silicates (cation exchange capacity derived from the amount of the cation exchanged: 42, 74 and 85 meq/100 g clay) after the cation exchange with 1,1'-dimethyl-4,4'-bipyridinium (abbreviated as  $\text{MV}^{2+}$ ) ions to investigate effects of the spatial distribution of  $\text{MV}^{2+}$  on the adsorption of nonionic organic compounds. The nanospace created with silicate layers and  $\text{MV}^{2+}$  cations has been used for the adsorption of organic compounds (*N,N*-dimethylaniline and 2,4-dichlorophenol) in the interlayer spaces of a series of the  $\text{MV}^{2+}$ -layered silicate intercalation compounds.

All the intercalation compounds adsorbed *N,N*-dimethylaniline from aqueous solution. The basal spacing of the intercalates (1.3 nm) did not change by the adsorption, indicating that the adsorbed *N,N*-dimethylaniline existed in the interlayer nanospace. The intercalated *N,N*-dimethylaniline polymerized to develop purple color when the layered silicates with the cation exchange capacities of 74 and 42 meq /100 g were used. On the other hand, the intercalation compound with larger content of  $\text{MV}^{2+}$  (cation exchange capacity: 85 meq /100 g) suppressed the polymerization (to dimer or trimer) of *N,N*-dimethylaniline as a result of the smaller size created by  $\text{MV}^{2+}$  in

the interlayer space. The adsorption capacity of 2,4-dichlorophenol was larger when the  $MV^{2+}$  content was smaller, also indicating the variation of the nanospace formed with  $MV^{2+}$  and silicate layers (Scheme). It is found that the volume of the nanospace formed with  $MV^{2+}$  and silicate layers is controllable by using the layered silicate with varied layer charge density.



**Scheme** Variation in the adsorption capacity of 2,4-dichlorophenol depending on the layer charge density

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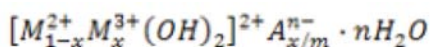
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## SYNTHESIS AND MODIFICATION OF HYDROTALCITE FOR ENHANCED FLAME RESISTANCE

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In recent years there has been considerable interest in the synthesis and use of natural and hydrotalcite-like compounds. Natural hydrotalcites are essentially hydrated magnesium-aluminium-hydroxy-carbonates with a typical formula being  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ; hydrotalcite-like compounds, normally referred to as layered double hydroxides (LDH), have the general molecular formula shown below, where  $\text{M}^{2+}$ ,  $\text{M}^{3+}$ ,  $\text{A}^{n-}$  are the divalent, trivalent metal cations and an anion, respectively.



The structure consists of layers of magnesium hydroxide and aluminium hydroxide with anionic interlayers, typically carbonate. These double-layered hydroxides have the capacity to undergo anion exchange reactions and so the carbonate can be substituted for other anions such as chloride, sulphate, nitrate or larger organic molecules. This anion exchange ability makes the materials suitable for catalysis, ion scavenging, molecular sieves, drug delivery systems and more. A specific use of an LDH, in combination with poly(vinyl chloride), allows hydrotalcite to scavenge chlorine; thus, enhancing the thermal stability of the polymer.

Thermogravimetry-Mass Spectrometry can be used to follow the decomposition of PVC via the evolution of HCl and benzene during pyrolysis. This contribution will describe how the temperature interval over which HCl and benzene are released can be influenced by LDHs containing different anions. The results are benchmarked against standard additives including titania and calcium carbonate. The increased thermal stability offered by the LDH-based modifiers offers the potential to reduce the fire risks associated with PVC and extend the processing temperature range for PVC.

The LDHs used were thoroughly characterised in order to understand the influence of the different preparation procedures on the particle size, crystallinity, and subsequent performance as fire retardant. Characterisation techniques used included; XRD, XRF, CHN, DRIFTS and TG-MS.

## INDONITE®: A MICROPOROUS SYNTHETIC CLAY-LIKE MATERIAL

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Indonite® is a synthetic silicate of nanometric particle size manufactured by ShayoNano Singapore Pte Ltd Company under a patented procedure. The company has expertise in synthesis of nanomaterials with the use of electromagnetic waves as an energy source. The successful synthesis of the synthetic nanoclay-like called "Indonite®", which shows high microporosity, large specific surface area and good thermal stability has potential applications particularly in adsorption, catalysis, nanocomposites.

Indonite® shows a silica/magnesia composition with Mg/Si ratio in range of 1 to 2, sometimes with presence of small amounts of other elements such as Na, Ca, Li and Al. It is a nanosized powder of low crystalline degree contributes to various characteristics of magnesium clays, like saponites, with XRD reflections at around 0.15 nm (060) typical of trioctahedral smectites. However, this material differs from smectite clays because of no charges which could be contributing to its non-swelling behaviour. Its spectroscopic characterization reveals the presence of silicon tetrahedral sites typical of sheet silicates.

Typically, nanoparticles of Indonite are in the 30-100 nm range, showing a plate-like morphology that resembles to certain natural smectites. Thinness of nanoparticles is one of the main special characteristics of these solids.

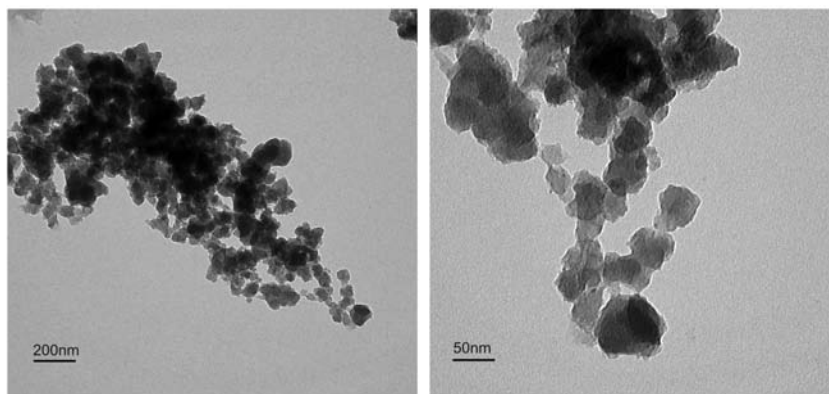


Figure 1. TEM images for Indonite®.

Other important properties of Indonite are their textural characteristics. Indonite is a microporous material with specific surface area (BET) in the range of  $650 \text{ m}^2/\text{g}$ . The total pore volume and the micropore volume are  $0.63$  and  $0.25 \text{ cm}^3/\text{g}$  respectively. The microporosity studied by the Horvath-Kawazoe method shows a narrow and uniform pore size distribution, showing a maximum at  $0.52 \text{ nm}$ , being the average pore diameter of ca.  $0.7 \text{ nm}$ .

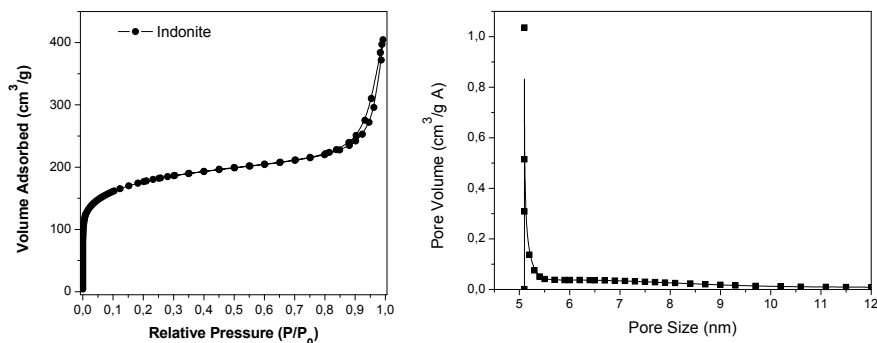


Figure 2.  $N_2$  adsorption-desorption isotherm at  $-196^\circ\text{C}$  and Horvath-Kawazoe pore size distribution of Indonite<sup>®</sup>.

## APPLICATION OF ULTRASOUNDS AND MICROWAVES TO OBTAIN MESOPOROUS HECTORITES

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The structural unit of hectorite consists of two tetrahedral silicate layers and is condensed to a central magnesium oxide octahedral layer. Cation exchange capacity arises from isomorphous substitutions of Li(I) for Mg(II). Hectorite ( $M^{n+}_{x/n} \cdot yH_2O[Mg_{6-x}Li_x](Si_8)O_{20}(OH.F)_4$ ) is a microporous compound with acid properties that could be interesting to be used as catalysts, however diffusion problems should be resolved. The aim of this work was the preparation of mesoporous hectorites using microwaves and ultrasounds to reduce synthesis time, save energy and studying the influence of several factors: the time of ultrasounds treatment, the salt quaternary used and the calcination conditions.

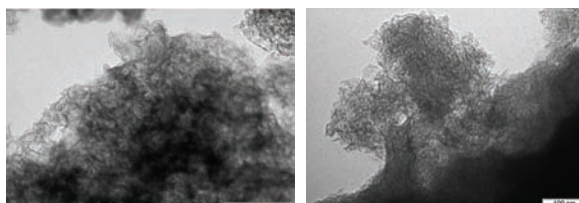
Experimental. Several mesoporous hectorites has been synthesized carry on the process described by Iwasaki et al<sup>[1]</sup>. The first group (MHC2(S<sub>1</sub>), MHC48(S<sub>1</sub>) and MH<sub>US/15</sub>C48(S<sub>1</sub>)) with a initial gel precipitated from an acid solution of Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>, MgCl<sub>2</sub> and LiF with LiOH at pH 12, this was homogenized by magnetic stirring for 1h in samples MHC2(S<sub>1</sub>), MHC48(S<sub>1</sub>) and for 15 min in an ultrasound bath for MH<sub>US/15</sub>C48(S<sub>1</sub>). This gel was mixed with dimethyldioctadecylammonium chloride (S<sub>1</sub>) the slurry was aged in a hydrothermal treatment at 453 K for 2 and 48h using a conventional oven (C). The second group (MH<sub>US/20</sub>C2(S<sub>2</sub>), MH<sub>US/40</sub>C2(S<sub>2</sub>) and MH<sub>US/20</sub>MW1(S<sub>2</sub>)) <sup>[2]</sup> were synthesized introducing some modifications: the quaternary salt used was dodeciltrimethylammonium chloride (S<sub>2</sub>), the ultrasound time was 20 and 40 min for MH<sub>US/20</sub>C2(S<sub>2</sub>), MH<sub>US/40</sub>C2(S<sub>2</sub>) respectively and in sample MH<sub>US/20</sub>MW1(S<sub>2</sub>) the age treatment was performed in a microwave oven during 1h. In order to obtain the final products the solids were calcined at 873 K until basic vapors were not obtained. Samples were characterized by XRD, N<sub>2</sub> physisorption, FRX, TEM and determination of C.E.C.

Results and discussion. TEM images of the first group showed the main presence of nano-sized sheets aggregated to make mesoporous, in the case to the hectorite with ultrasound (MH<sub>US</sub>C48(S<sub>1</sub>)) the size of the sheets is bigger than hectorites prepared without ultrasounds and consequently is more crystalline, the XRD confirm this fact and the Si/Mg ratio is closer to the theoretical value, however the BET analysis showed an increase of almost twice in the area and a certain CEC increase of this hectorite respect to MHC48(S<sub>1</sub>). The TEM images of the second group showed nano-sized sheets aggregated to make mesoporous with a smaller size than the first group.

**Table 1.** Hectorites characterization

| Materials                                  | BET Area | CEC meq/100g | Atomic relation (Si/Mg)· |
|--|----------|--------------|--------------------------|
| MHC2(S <sub>1</sub> )*                     | 564.1    | 47.9         | 4.1                      |
| MHC48(S <sub>1</sub> )*                    | 265.8    | 45.2         | 1.3                      |
| MH <sub>US/15</sub> C48(S <sub>1</sub> )*  | 494.0    | 57.4         | 1.4                      |
| MH <sub>US/20</sub> C2(S <sub>2</sub> )*   | 250.3    | 76.2         | 1.1                      |
| MH <sub>US/40</sub> C2(S <sub>2</sub> )**  | 611.6    | 131.3        | 1.5                      |
| MH <sub>US/20</sub> MW1(S <sub>2</sub> )** | 304.6    | 87.9         | 1.0                      |

\*calcination in an oven; \*\*calcination under air flowing, ·theoretical Si/Mg ratio= 1.53



**Figure 1.** TEM images of MHC2(S<sub>1</sub>) and MH<sub>US/40</sub>C2(S<sub>2</sub>) respectively.

The use of salt S2 improve CEC values and the increase of ultrasounds time together with a calcination under air flowing made possible to prepare MH<sub>US/40</sub>C2(S<sub>2</sub>), which presents higher cristalinity, BET area and CEC, together with the expected Si/Mg ratio. The microwave influence has been evaluated comparing MH<sub>US/20</sub>C2(S<sub>2</sub>) and MH<sub>US/20</sub>MW1(S<sub>2</sub>) samples, the use of microwave seems to improve the hectorite synthesis since in the half of time a material with similar characteristics has been obtained when microwaves are used.

Conclusions. The employed of ultrasounds in the synthesis process improve properties of the mesoporous hectorite obtained. The use of microwaves in the thermal treatment in the synthesis of mesoporous hectorite allows reduce the synthesis time.

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## RELEASE OF DRUGS IMMOBILISED ON LDHs SUPORTED ON BIOPOLYMER

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In the last years new materials such as biopolymers have been widely investigated to be used in the development of implants, to modulate the activation of tissues repair and the regeneration processes, and as bases of the healing process. Another important field of investigation of this kind of materials is the development of a precise and tuneable control of molecule release [1,2]. The possibility of local diffusion of a drug through biocompatible and reabsorbable matrixes offers the advantage of a drastic reduction of the administered dose, which in turn is related to development of side effects. A wide range of additives, organic and inorganic molecules, can be immobilised on the surface or the bulk of the biomaterial to incorporate directly this “active” molecules.

Hydrotalcite-like “anionic clays”, or layered double hydroxides (LDHs) are a class of ionic lamellar solids with positively charged layers, counterbalanced by exchangeable interlayer anions [3]. The capacity of the hydrotalcite to retain inorganic or organic anions in the interlayer allows to control their release so that they act in back processes like the controlled release of some drugs.

In the present work we have selected PLA (polylactic acid) as a reagent for encapsulation of LDHs due to its easy biodegradation, its biocompatibility and inertness [4]. A precise control of the degradation rate of the polymer has important effects on the release of the associated active molecule [5]. Actually, PLA plays a dual role, namely, as a film covering the nanocomposite particles, and as a biomaterial support for regeneration of human tissues.

Hybrid organic-inorganic hydrotalcites containing  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  in the brucite-like layers ( $\text{Zn}/\text{Al}$  molar ratio of 2:1) and Ketoprofen (Ket) or Chloramphenicol Succinate (Chlo) as counter-anions were synthesized by coprecipitation using drug/ $\text{Al}$  molar ratios of 2:1 to prepare the starting solutions. All samples have been characterised by element chemical analysis, powder X-ray diffraction, FT-IR spectroscopy, thermal analysis and morphology analysis (Scanning Electron Microscopy). Degradation of the solid in a saline solution was followed by UV spectroscopy to demonstrate the sustained release of the drugs from the nanohybrids.

The release studies evidence degradation of the composites in the serum medium and release of the drug molecules, in a larger extent for  $\text{Zn}/\text{Al}$ -Ket than for  $\text{Zn}/\text{Al}$ -Chlo. Degradation of the encapsulated samples is slower than that from PLA-



unsupported hydrotalcite, in such a way that degradation can be finely tuned by choosing the composite for optimum release processes in living organisms.

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## PHYSICAL, CHEMICAL AND GEOTECHNICAL PROPERTIES OF SPECIAL CLAYS DEPOSIT FROM TAMAME DE SAYAGO (ZAMORA, SPAIN)

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The special clays deposit of Tamame de Sayago (Zamora, Spain) is located on the south west border of the Duero river basin (i.e. central-west of the Iberian peninsula). The origin of this deposit is related to the weathering and hydrothermal alteration of a Palaeozoic granite. The special clays from Tamame de Sayago are formed by a mixture of kaolinite and smectite. Taking into account that kaolinite and smectite cannot separate by physical procedures, the commercial products obtained after separation of impurities (quartz, feldspart and micas) contain different percentages of the two minerals.

The aim of this work is to study mineralogical, physicochemical and geotechnical properties of commercial products, which are composed by different proportions of kaolinite and smectite mainly.

A complete characterization of the pure samples and four commercial products was made using XRD, TEM, SEM, and adsorption-desorption of N<sub>2</sub>. In addition the cation exchange capacity and the exchangeable cations were studied. Geotechnical properties studied include: Atterberg limits (AENOR, 1996: UNE 103103. 1994; UNE 103104: 1993), specific gravity of particles (AENOR, 1996: UNE 103302: 1994), expansivity in a Lambe device (AENOR, 1996: UNE 103600:1996), test of the free swelling in an oedometer (AENOR, 1996: UNE 103601: 1996) and test for calculating the swelling pressure in an oedometer (AENOR, 1996: UNE 103602: 1996).

As expected, the variability observed in the results obtained is related to the proportions of the two types of clay minerals in the sample, and results are conditioned by the low specific surface area of the smectite, which is related to its high crystallinity.

## ENHANCED TWO-PHOTON ABSORPTION CHARACTERISTICS OF POLY-CATIONIC DYES BY HYBRIDIZING WITH CLAY MINERALS

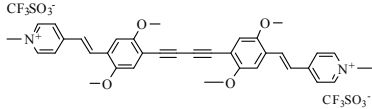
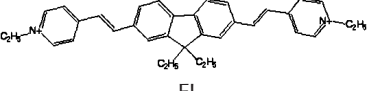
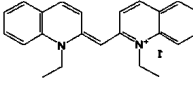
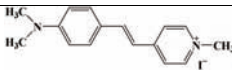
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Two-photon absorption (TPA) has attracted increasing attention in relation to various applications such as 3D-microfabrication, optical power limiting, optical data storage, two-photon-excited fluorescence imaging, and two-photon photodynamic therapy. For such applications, materials exhibiting a large TPA cross-sections ( $\sigma^{(2)}$ ) have strongly been desired. The  $\sigma^{(2)}$  of an organic dye, 1,4-bis(2,5-dimethoxy-4-[2-[4-(N-methyl)pyridinium]ethenyl]phenyl)butadiyne triflate (MPPBT) (Table.1), was found to be enhanced by hybridizing with a clay mineral (Smecton SA)[1]. Therefore, a dye-clay composite is a promising candidate of an efficient TPA material. However, the  $\sigma^{(2)}$  was not always enhanced when any cationic dyes were adsorbed onto the surface of clay minerals. Therefore, we have attempted to reveal a feature of the chemical structure of a dye of which  $\sigma^{(2)}$  is enhanced by hybridizing with a clay mineral.

We have measured the  $\sigma^{(2)}$  of several dye-clay composites in film state. The  $\sigma^{(2)}$  are summarized in Table 1 together with those of the dyes in solution state. The  $\sigma^{(2)}$  of dicationic dyes, MPPBT and FL, were considerably enhanced in composites compared to those in solution states. However, such enhancement of  $\sigma^{(2)}$  was not observed when monocationic dyes, PIC and HE, were employed. This observation suggests that the use of poly-cationic dyes is one of the important factor to enhance  $\sigma^{(2)}$  in composites.

Table 1. The  $\sigma^{(2)}$  of dyes in dye-clay composite films and in solution.

| Dye  | TPA cross-section (GM) |                | Number of cationic moiety |
|--|------------------------|----------------|---------------------------|
|  | Solution               | Composite film |                           |
| <br>MPPBT | 770                    | 3900           | 2                         |
| <br>FL    | 730                    | 4000           | 2                         |
| <br>PIC   | 400                    | 340            | 1                         |
| <br>HE    | 250                    | 150            | 1                         |

FL: 1,1-diethyl-4,4'-(9,9-diethyl-2,7-fluorenediyl-2,1-ethenediyl)dipyridinium perchlorate, PIC: 1,1'-diethyl-2,2'-cyanine, HE: 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide

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## TWO-PHOTON ABSORPTION PROPERTIES OF CATIONIC PORPHYRIN-CLAY COMPOSITES

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Two-photon absorption (TPA) increases with the square of the light intensity. When a laser beam is focused by a lens, the light intensity at a focusing point is higher than that at a defocusing point. Therefore, if a TPA excitable medium is irradiated by a tightly focused laser beam, only at the focusing point in the medium can be excited. Owing to this three-dimensional selectivity of excitation, TPA offers various attractive applications. However, TPA cross-section ( $\sigma^{(2)}$ ; efficiency of TPA) of most of materials are very small. Therefore, in order to realize such applications, materials exhibiting large  $\sigma^{(2)}$  are needed to be developed. Especially, materials with large  $\sigma^{(2)}$  at a short wavelength region have strongly been desired. The  $\sigma^{(2)}$  of some organic dyes were found to be enhanced by hybridizing with clay minerals [1,2]. Therefore, a clay-dye composite is a promising candidate for an efficient TPA material. In previous studies, rod-like dyes possessing a considerably long (about 2 nm)  $\pi$ -electron systems were selected as the dye to be adsorbed onto the surface of a clay mineral. Because, dyes with large  $\pi$ -electron systems tend to exhibit large  $\sigma^{(2)}$ . However, such dyes have intense one-photon absorption (OPA) band at visible wavelength region. Therefore, the net absorption at visible wavelength region of composites previously studied was dominated by the contribution from the OPA process. In this study, we attempted to fabricate clay-dye composite by employing a dye possessing a relatively short  $\pi$ -electron system, in order to develop materials with large  $\sigma^{(2)}$  at a short wavelength region.

As for the cationic dye, 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin (TMPyP<sup>4+</sup>), shown in figure 1, was used. The distance between adjacent cationic sites within this molecule (1.1 nm) is almost half compared to that of the dyes treated in the previous studies. The dye was adsorbed onto a surface of synthetic saponite (Smecton SA, SSA Kunimine Ind. Co. Ltd, Japan) by ion-exchange reaction of a dilute aqueous dispersion of SSA with water solution of TMPyP<sup>4+</sup>. A film consisting of the TMPyP<sup>4+</sup>-SSA composites was prepared in a similar way as reported in the previous paper [2]. The aqueous dispersion of the composites was filtrated under suction through a mixed cellulose ester membrane filter (100 nm pore size, 25 nm diameter). The deposited film was placed on a fused-silica substrate for optical measurements.

The TPA spectra of the obtained TMPyP<sup>4+</sup>-SSA film and water solution of TMPyP<sup>4+</sup> measured by the open aperture Z-scan technique are shown in figure 2. As we have expected, significant enhancement of  $\sigma^{(2)}$  by hybridizing with clay was observed even from the present film consisting of a small dye. The maximum value of  $\sigma^{(2)}$  of

the film was 11260 GM ( $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ ), whereas the value of the solution was 1009 GM.

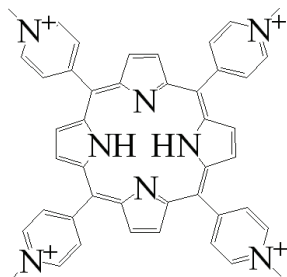


Figure 1. Chemical structure of TMPyP<sup>4+</sup>.

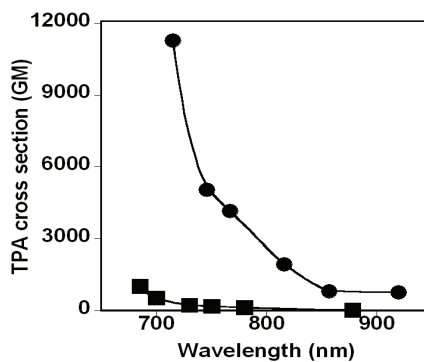


Figure 2. TPA spectra of film consisting of composites (●) and water solution of TMPyP<sup>4+</sup> (■).

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## COBALT CONTAINING SAPONITES PREPARED BY A MICROWAVE-HYDROTHERMAL METHOD

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Saponite is a natural smectite with theoretical formula  $[\text{Si}_{8-x}\text{Al}_x][\text{Mg}_6]\text{O}_{20}(\text{OH})_4[\text{M}_x] \cdot n\text{H}_2\text{O}$  ( $\text{M}$ = exchange cation). Natural clays are cheap and easily available, but they usually contain mineral impurities. Procedures to remove these impurities are time consuming and tedious, usually based on dispersion– decantation and they cannot lead to a final uniform product. For industrial applications the problems related to the presence of impurities can be avoided by the use of synthetic saponites. The synthesis of these materials leads to pure samples, with tailored chemical composition, cation exchange capacity, etc. Cobalt saponites are widely used in a great number of catalytic reactions such as oxidation, hydrodesulfuration or hydrocracking.

In this work we synthesise saponites by using hydrothermal treatment in a microwave furnace. The aim of this work is to obtain tailored cobalt saponites with pre-fixed composition and structural parameters.

Experimental. A water solution with the stoichiometric amounts of the cation salts was added to a sodium silicate solution containing NaOH and  $\text{NaHCO}_3$  for pH control. The gel formed was hydrothermally treated in a microwave furnace for 8 hours at 80 (sample SCo80) or 180 °C (sample SCo180). Samples have been characterised by element chemical analysis, PXRD, Vis-UV and FT-IR spectroscopies, thermal analysis (TGA, DTA, TPR) and surface area measurements.

Results and discussion. The X ray diffractograms of all the solids show diffraction maxima which positions coincide with those reported in the literature for natural saponites. The PXRD pattern of sample SCo80 shows weaker diffraction lines than that for sample SCo180. The (06,33) reflection is recorded at 1,53 Å for both samples, confirming the trioctahedral structure of the solids obtained, as expected for a saponite. The main difference lies in the intensity of the (001) reflection, corresponding to the separation between layers. This is very well defined for sample SCo180, suggesting a better stacking of the layers along the c axis. The FT-IR spectra are typical of solids with the saponite structure, displaying strong bands at ca. 1010, 660-695, and 456  $\text{cm}^{-1}$  that can be assigned to the Si-O-Si and  $\text{M}^{2+}$ -OH stretching and Si-O- $\text{M}^{2+}$  bending modes, respectively. While sample SCo80 is brown, sample SCo180 is purple. This difference can be explained from the Vis-Uv spectra. That for sample SCo80 shows typical bands of tetrahedrally coordinated  $\text{Co}^{2+}$  species, together with another band due to  $\text{Co}^{3+}$  species, whilst for sample SCo180 the predominant bands are those of octahedrally coordinated  $\text{Co}^{2+}$  cations. Specific

surface areas, as determined from the  $N_2$  adsorption-desorption isotherms recorded at  $-196^\circ\text{C}$ , were close to  $180\text{ m}^2\text{g}^{-1}$  in both cases. The t-plots evidenced that none of the samples are microporous.

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## TEST AND CHARACTERIZATION OF RAW RESADIYE BENTONITE'S ORGANOPHILICALLY MODIFIED PRODUCTS

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Na- bentonites are being used widely in aqueous systems in order to adjust rheology due to their good thixotropy, swelling and forming gels after being dispersed in water. Replacement of Na cations with organic cations strongly enhances the hydrophobicity of the bentonite interlayers and consequently enables bentonites to swell in nonaqueous systems. These organophilic bentonites are employed in different technological areas such as paint, cosmetic industry, petrol and natural gas drilling. More recently organophilic bentonites are being used for obtaining a new class of materials called nanocomposites and also newly they are being used in environment and health fields; storing radioactive wastes, clarification of waste water which contains organic impurities, keeping organic volatiles, adsorption of paints in waste water and retention of boron.

In this study, by using one aliphatic and four aromatic Quaternary Ammonium Salts with varying ratios, natural Resadiye bentonite was modified to organophilic bentonite. Before modification, raw Resadiye bentonite had been enriched and its cation exchange capacity increased to 115 meq/100g from 65 meq/100 gr. After the modification, organophilic bentonite samples were characterized by TGA, FTIR and XRD. In order to determine rheological effect, 4% toluen-organophilic bentonite suspensions were prepared and viscosity values were measured. It was indicated that as the ratio of Quaternary Ammonium Salts increased, viscosity values raised until a certain ratio. It was also observed that organic cation type is effective in synthesis of organophilic bentonite. Finally all these results were compared with the results of the commercial product Bentone SD-1.

## POLYSACCHARIDE/LAPONITE NANOCOMPOSITES THROUGH PRE-FUNCTIONALIZATION WITH (3-AMINOPROPYL) TRIETHOXSILANE

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Polymer/clay composites have been studied for various uses such as engineering, agriculture, ceramics, surface coatings, absorbent materials, pharmaceuticals and catalysis, among others. Clays incorporated to polymeric materials can change the properties of the polymeric system, such as heat and mechanical resistance. The surface modification of clays with polymers can be considered one of the most effective methods for the formation of this type of materials. Polysaccharides, such as alginate and its acid derivatives, are biocompatible and biodegradable polymers effective in the production of adsorbent systems, or in the encapsulation and controlled release of active ingredients, such as drugs and fertilizers. On the other hand, laponite is a hectorite-like synthetic 2:1 phyllosilicate, with interesting physical properties for using in embedding in plastic systems. In this work, we report on the preparation of alginate/laponite composites.

Laponite was first functionalized with (3-aminopropyl)triethoxysilane (APTES), the solid obtained was then treated with alginate polysaccharide, or with alginic acid, in both cases dissolved in NaOH, using the proportion polysaccharide/clay 5:1. After the synthesis, the materials were washed and dried in an oven at 80 °C. The functionalization of the clay with APTES was confirmed in XRD by the displacement of the basal spacing from 14.8 to 19.0 Å, and permanence of this shift after formation of the composite. FTIR analysis also evidenced the functionalization by the signals characteristic of the silane molecules in the region of 1560-1330 cm<sup>-1</sup>, in addition to the characteristic bands of the polysaccharide. The thermal analysis showed the increased thermal resistance of the polymers in more than 300°C. The materials also showed considerable mechanical strength with formation of a one-piece material after drying, high-aggregation capacity of the polymer to the clay as the final composition is still close to the initial 5:1, and considerable adsorption capacity of the composite to metals.

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## APPLICATION POSSIBILITIES OF “BELCHATOW” CLAYS AS A RAW MATERIAL IN FLOODBANKS’ FIXING TECHNOLOGY

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Construction and renovation of hydrotechnical buildings such as floodbanks often required materials and technical operations which limiting water flow through them. Applied materials in this technology have to characterize very good hydro - isolation properties cooperated with low costs of producing.

Materials which comply with these conditions are clay-cement binders. As a raw material for these binders can be used polymineral clay “Belchatow” accompanying with brown coal deposits.

In the presented article clay-cement binders based on clay “Belchatow” have been shown. Their main technological parameters such as mechanical strength, filterability and rheological behavior have been presented. Flow curves, filterability factor “k” value and compresing strength depend on composition have been compared.

## CHITOSAN-CLAY BIONANOCOMPOSITES BASED ON MOROCCAN STEVENSITE

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Diverse nanostructured organic-inorganic materials are present in living entities, with amazing examples such as enamel in teeth or nacre in sea shells [1]. These materials usually have remarkable mechanic properties, which are attributed to the organic-inorganic alternating structure. Currently, polymer-layered silicates nanocomposites have attracted considerable attention because of their potential to produce materials with exceptional physical, thermal and mechanical properties than those of conventional composites. A key to several of the improvements is exfoliation/intercalation of the nano-clay to expose the large available surface area to the polymer and increase the effective aspect ratio of the nano-clay particles [2]. For this type of nanocomposites, several layered silicates have been studied. Recently, stevensites are attracting particular interest because their nanosized and quite transparent particles can be very useful for developing new materials, especially for applications related to specific adsorption, optical devices and improved nanocomposites.

In this work, we present the study of an abundant Moroccan stevensite, previously known as Rhassoul clay. The stevensite-rich clay used comes from a tertiary formation of Jbel Rhassoul located at the East of the middle-Atlas, in Morocco [3]. The chemical composition of purified clay is: 61.17% SiO<sub>2</sub>, 4.29% Al<sub>2</sub>O<sub>3</sub>, 2.18% Fe<sub>2</sub>O<sub>3</sub>, 2.21% CaO, 26.65% MgO, 1.23% K<sub>2</sub>O and 1.07% Na<sub>2</sub>O [4]. The chemical formula of stevensite is ((Na<sub>0.25</sub>K<sub>0.20</sub>)(Mg<sub>5.04</sub>Al<sub>0.37</sub>Fe<sub>0.20</sub>□<sub>0.21</sub>)<sub>5.61</sub>(Si<sub>7.76</sub>Al<sub>0.24</sub>)<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>). The surface area and the cation exchange capacity are 150m<sup>2</sup>/g and 60 mequiv./100 g, respectively.

Using purified stevensite, we prepared functional chitosan-stevensite bionanocomposites by intracrystalline adsorption of different amounts of polymer from solution. Amounts of chitosan exceeding the cation exchange capacity were incorporated as a double layer in the interlayer region of the clay as occurs in montmorillonite [5, 6]. The resulting materials were used as ionophore in the development of surface-modified sensors for the potentiometric determination of several ions, profiting from the functional groups in chitosan chains. Alternatively, the structural properties of chitosan-stevensite bionanocomposites were also evaluated. For this purpose, the bionanocomposites were prepared by dispersion of the clay particles in the chitosan matrix at a loading level of 1–5% (w/w), and processed as films by casting onto polyethylene slides and drying in air. The Young's modulus of

the chitosan/stevensite composite films was significantly improved by incorporation of clay.

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## **TOPIC 7**

### *Clays in Education Programs*





# *ORAL PRESENTATION*



## KEYNOTE

### INFRARED SPECTROSCOPY: PRINCIPLES AND APPLICATIONS IN THE STUDY OF CLAY-ORGANIC INTERACTIONS

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The vibrational spectrum of a molecule is considered to be a unique physical property characteristic of the molecule. As such, it can be used as a fingerprint for identification by comparing results with reference spectra. In the absence of a suitable reference database, it is possible to perform basic interpretation of the spectrum from first principles, leading to characterization, and possibly even identification of an unknown sample (Coates, 2000). IR spectrum can serve also as a fingerprint for mineral identification, and give unique information about the mineral structure: the family of minerals to which the specimen belongs, degree of regularity within the structure, nature of isomorphic substituents, the distinction of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities (Madejova and Komadel, 2001).

The infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds in a molecule (Coates, 2000). The basic model of a harmonic oscillator can explain the origin of many of the characteristic frequencies that can be assigned to particular combinations of atoms within a molecule. From Hooke's law we can express the vibrational frequency of a molecular ensemble. This simple equation provides a link between the strength of the chemical bond between two atoms (or molecular fragments), the mass of the interacting molecular fragments, and the frequency of vibration. Although very simple in concept, there is a reasonably good fit between the bond stretching vibrations predicted and the values observed for the fundamentals (Coates, 2000). Furthermore, changes in the bond strength due to influences of the molecules (for example- following its adsorption) or changes in the chemical composition as the adsorption influencing the mass of the molecular fragments- can change the energy needed for the vibration, thus- change the spectrum.

Several applications of IR spectroscopy in the study of clay organic interactions will be presented: (a) Recognition of clay minerals and adsorbed molecules by means of ATR-FTIR measurements, (b) Analysis of secondary structure of proteins, and

influence of adsorption on clay (Rytwo and Lang, 2010, *in preparation*), (c) Specific clay organic interactions (Rytwo et al., 2002; 2005), (d) Semi-quantitative analysis of adsorbed chemicals on clay minerals (Rytwo, Sandler and al., 2010, *in preparation*), (e) Orientation of adsorbed molecules on clay platelets (Rytwo et al., 1995; 1996) and (f) changes in the chemical composition: catalysis and degradation (Rytwo et al., 2009).

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## *POSTER PRESENTATIONS*



## CHARACTERIZATION OF EARTH BUILDING MATERIALS FROM ARCHAEOLOGICAL SITES ON LA RIOJA AND AND CATAMARCA (ARGENTINA)

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The use of earthen architecture had been widespread across the world in almost all continents since ancient times. In South America it has a long tradition, beginning in pre Columbian cultures, but it survives until the present. The use of sediments for the construction of Earthen buildings was a common prehistoric technique, widely employed in arid and semi-arid lands, where other construction materials were scarce. Earthen building techniques are varied, and they can be classified in three general types: monolithic systems (rammed earth), brickwork (adobe or mudbrick), and mixed systems (wattle and daub). Nevertheless, the recognition of archaeological evidence indicative of these kind of buildings is problematical, because this kind of architecture is vulnerable to destruction by weathering, especially by wind and water erosion. These processes frequently blur the evidence of earthen architecture, leaving fillings or mounds composed by loose and fine-grained material difficult to attribute to disaggregated earthen architecture. So, the presence of earthen architecture is often assumed rather than demonstrated.

Recently, analytical studies of building materials have been enriched by different approaches, like geoarchaeology, archaeometry and conservation, together with advances in archaeology of architecture. Assuming the perspective of archaeometrical approaches, we have carried on several physical and chemical analytical tests in order to characterize archaeological building materials from La Rioja and Catamarca provinces (northwestern Argentina), attempting to define parameters for their determination in archaeological contexts. These materials have been recovered from different sites, belonging both to prehispanic and post-Hispanic times. Materials have been examined with regard to their chemical (organic carbon content by calcination and Walkley-Black, phosphate content by Kurtz and Bray<sup>1</sup>) and mineralogical composition (X-Ray diffraction analysis at bulk sample and in the < 2 µm sub-fraction, optical microscopy, SEM), but also to their physical (granulometric analysis, density, porosity ?) and mechanical properties, in order to investigate the nature of the raw materials used, the technology of manufacture and the potential use of specific recipes. In this contribution we present the preliminary results of the analytical tests performed.

XRD analyses indicate that the main components of all the samples are quartz and micas, with minor hematite. Building materials from Catamarca sometimes contain calcite, and less frequently heulandite and gypsum. La Rioja materials also contain potassium feldspar and calcite. The XRD study of  $<2\ \mu\text{m}$  sub-fractions indicates that Catamarca samples are composed of abundant illite-mica, smectite, subordinate chlorite and sometimes minor kaolinite. Samples from La Rioja contain higher proportion of illite-mica and variable smectite contents. The technological properties of earthen building materials should be mainly controlled by the proportion of clay- versus sand+silt-sized material, but also by the kind and relative proportion of expandible clays in raw material.



## PREPARATION OF LAYERED DOUBLE HYDROXIDE-ORGANIC INTERCALATION COMPOUNDS BY SOLID-SOLID REACTIONS

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The inorganic-organic intercalation compounds have been attracted increasing interests for advanced materials applications including optical, electronic, adsorptive, catalytic, and mechanical ones. The studies on the mechanism of the layered double hydroxide (LDH) formation and their structures, the introduction of guest species into the interlayer space of LDHs has been reported for such applications as catalysts, controlled photochemical reactions, electrodes, bioactive nanocomposites, polymer additives, and so on. The wide range of application of LDHs and their intercalates motivates researchers to develop a simple, economically viable synthetic method. For the introduction of guest species into the interlayer space of LDHs, three methods, i) coprecipitation from homogeneous solution containing the anions to occupy the interlayer space by pH adjustment and subsequent aging, ii) anion exchange of the pre-formed LDHs, and iii) so-called reconstruction, where calcined LDH (dehydroxylated and decarbonated form) was suspended in a solution containing the anion to occupy the interlayer space to restructure the layered structure, have been used. (J. He et al. (2006)) We have developed a simple synthetic method using magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite) as the inorganic sources for the synthesis of the Mg-Al LDH-deoxycholate intercalation compounds, where aqueous suspension of magnesium hydroxide, aluminum hydroxide and deoxycholate was hydrothermally treated in a closed vessel. The selectivity of bulky and monodentate deoxycholate anion as the interlayer anion of LDH was very low and other synthetic methods, conventional coprecipitation, anion exchange and reconstruction were not applicable. (M. Ogawa et al. (2000)) The method is an easy, environmentally friendly method potentially applicable to the preparation of a series of LDH with different structures and properties.

Recently, W. Tomgamp et al. (2008) reported the preparation of nitrate form-LDH by the solid-state reactions from magnesium hydroxide, aluminium hydroxide and magnesium nitrate. If compared with reported LDH syntheses mentioned above, the solid-state syntheses of LDH has such advantages as i) solid-liquid separation is not necessary, ii) carbonate contamination is less plausible. Accordingly, the solid-state formation of organic anion intercalated LDHs is worth investigating. Here we report the successful preparation of *p*-toluenesulfonate-LDH intercalation compound

by solid-solid reactions from brucite, gibbsite and *p*-toluenesulfonic acid. The reaction was conducted as follows; the mixture of brucite and gibbsite was milled for 1 hour, then guest species added to this mixture and subsequently milled for another 1 hour. This very simple synthesis is applicable to a variety of layered double hydroxides-organic intercalation compounds. In the present study, oxalate, malonate and some amino acids were investigated as guest species to form LDH intercalation compounds. This method has such advantages as no carbonate contamination and the adjustment of pH.

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## IMACS : AN INTERNATIONAL MASTER PROGRAMME ENTIRELY DEVOTED TO CLAYS

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Most existing Masters Courses dealing with clays focus on a single discipline or domain in which Clay Science does not necessarily constitute the main part of the course (Earth Sciences, Civil and Geotechnical Engineering, Materials Science, Environmental and Life Science, Chemistry and Chemical Engineering). However, Clay Science is a multidisciplinary endeavour, combining geology, mineralogy, crystallography, with physics, geotechnology, and soil mechanics together with inorganic, organic, physical and colloid chemistry and biochemistry. The IMACS (International Master in Advanced Clay Science) is the first multi-disciplinary programme that brings together the widely-distributed knowledge of clay science.

IMACS is an integrated 2 years master programme developed by five Universities: the University of Poitiers (France), the Technical University of Crete (Chania - Greece), the University of Aveiro (Portugal), the University of Ottawa (Canada) and the Federal University of Rio Grande Do Sul (Porto Alegre – Brazil), and is supported by the French Clay Group (GFA) and AIPEA which are associated members of IMACS.

The teaching language is English. During the first year, basic knowledge on clays is provided, followed by a four month master project, which completes the first year programme. The second year incorporates two elective specialization options in the following fields: 1) Environment, soil and geological systems, 2) Geomaterials and civil engineering – Assessment and processing, 3) Advanced clay – nanomaterials, and 4) Healing minerals. The master thesis (6 months) completes this second year and can be carried out at any of the partner research laboratories.

The completion of the curriculum is rewarded by a multiple Master Degree.

The IMACS programme was approved by the European Commission under a very competitive application scheme as an Erasmus Mundus Joint Master programme in July 2009 and it will open in September 2010. Erasmus Mundus is a cooperation and mobility programme in the field of higher education supported by the European

Commission. This programme offers financial support for high-quality joint master courses, attractive scholarships/fellowships for both Non European and European student candidates and short-term scholarships for Non European and European academics to carry out research or teaching assignments as part of the joint masters project.

Free language training in the local languages is offered by the five higher education institutions. Moreover, the programme makes available a range of services and facilities (e.g. visa request, accommodation, insurance, bank account opening, social and cultural activities among many others...) to the students.

This Masters Course is open to students holding a BSc (or a degree equivalent to 180 ECTS) or an academic equivalence based on professional experience (validation of acquired experience is required), and a fluent understanding of the English language.

IMACS website: [http:// www.master-imacs.org](http://www.master-imacs.org)



## CLAYS IN UNDERGRADUATION AND POSTGRADUATION PROGRAMS: THE CASE OF THE UNIVERSITY OF AVEIRO

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Aveiro is one of the most important ceramic industry regions of Portugal, being rich in clayey sedimentary geological formations, mainly from Upper Cretaceous and Pliocene ages, as well residual kaolinitic deposits. The oldest and more famous and prestigious Portuguese porcelain factory (Vista Alegre) is located here.

So, when the Aveiro University (UA) was created in the mid-70's, Natural and Environmental Sciences were naturally selected as priority areas to be developed. The so-called Interdisciplinary Environmental Studies Group (Physics, Chemistry, Biology and Geology) started education in these areas and created the Nucleus of Economy and Mineral Resources, with a very special attention to Geo-economics.

The development of the geology education and research came in the late 70's to translate itself in the creation of the Geosciences Department, the first in Portugal of its kind with a propose of integrating the various areas regarding Sciences of the Earth, including the Engineering Science as well as the Geophysical Science.

In the field of training activities, the first significant milestones were the launching of degrees in Teaching of Biology and Geology and Geological Engineering, in 1978/79 and 1980/81, respectively. Teaching of clays and clay minerals deserve, since the beginning, particular attention in the Geological Engineering graduation program.

Clay-related matters were taught within disciplines like Industrial Minerals, Ceramic Raw Materials and Crystallochemistry and Diffraction, but two very important steps were fulfilled first in 1986 with the inclusion, on the Geological Engineering graduation program, of a new discipline called Clays, entirely focused on clay science and technology, then in 1994 with the creation of the master degree in Industrial Minerals and Rocks (1994), also offering several clay-related disciplines, such as Geology of Industrial Minerals, Exploration and Exploitation, Industrial Applications, Technologies, Mineral Economy.

The training to the level of doctor has also been a constant concern in the Department and it is responsible for a PhD program in Geosciences, under which, along the last 15 years, about two dozen students submitted the dissertations focused on clay topics.

A large number of MSc and PhD thesis has been performed in close cooperation with industry as well as with national and foreigner research institutes, putting the UA in the front line of clay teaching and training, at national and international level.

This paramount position is well shown by the UA active participation on the recent creation of the IMACS (International Master in Advanced Clay Science), an integrated master programme designed by five universities: Poitiers (France), Technical University of Crete (Chania - Greece), Aveiro (Portugal), Ottawa (Canada) and Federal University of Rio Grande do Sul (Porto Alegre – Brazil), being the first European multi-disciplinary programme that brings together the scattered knowledge of clay science.

## **APPENDIX**

*Received after deadline*





## CONTACT PRESSURE EFFECTS ON VIBRATIONAL BANDS OF KAOLINITE DURING INFRARED SPECTROSCOPIC MEASUREMENTS IN A DIAMOND ATR CELL

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Over the last decades infrared spectroscopy has become a frequently used method to investigate the structure and bonding properties of clay minerals. Besides classic transmission techniques attenuated total reflection (ATR) spectroscopy was applied as a very fast and easy method. In this study we compared transmission spectra of kaolinite with ATR spectra obtained by a single reflection diamond ATR accessory (Golden Gate Mark II). The ATR spectra showed anomalous band positions which were obviously affected by the applied contact pressure of the sapphire anvil. Most of these vibrations can be assigned to basal Si–O bonds and all of them shifted their positions to lower wavenumbers. It is suggested, that these peak shifts are due to changes in the Si–O–Si bond angle. They are caused by distortions and rotations of SiO<sub>4</sub>-units within the tetrahedral sheet, due to shear forces perpendicular to the uniaxial pressure applied by the anvil. Furthermore, the intensity of a normally very weak transversal optical mode (TO-mode) of the inner surface hydroxyls (3684 cm<sup>-1</sup>) remarkably increased with increasing contact pressure, while the longitudinal optical mode (LO-mode) at 3694 cm<sup>-1</sup> strongly decreased its intensity. This possibly is determined by a strong alignment of the platy kaolinite particles along their ab-planes due to the applied pressure.



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