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Invited Lectures

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Associação Portuguesa de Argilas

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The Associação Portuguesa de Argilas (APA) did organize the Second Mediterranean Clay Meeting held in Aveiro from 16th to 19th September, 1998. The meeting was attended by about 150 registered participants. Spain, Italy, France, Portugal, Israel and Tunisia were the countries more represented.

The master topic of the meeting was “Tradition and Innovation in Clay Science on the Turnover of the Millennium”. As a matter of fact, clay being the natural raw material having the most numerous and diversified applications is the matrix that links the constantly renewed aims, either fundamental or applied, of clay scientists. These knowing progressively more and better the crystallochemistry of clay minerals and their interactions with inorganic and organic compounds are able to do innovation on both structural and functional products based on clay.

Two publications were issued, one gathering the plenary lectures delivered by the eight invited lecturers, other gathering the seventy three extended abstracts submitted to be presented as posters.

On behalf of the Organizing Committee I wish to express our appreciation to all participants, to the Clay Groups involved (Associação Portuguesa de Argilas, Sociedad Española de Arcillas, Groupe Francais des Argiles and Gruppo Italino A.I.P.E.A.), as well as to the University of Aveiro for the contributions and facilities being provided, fundamental for the success of the meeting.

Celso Gomes
Chairman
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ISOTOPIC CONSTRAINTS TO THE ILLITIZATION PROCESS IN PROGRESSIVELY BURIED DIAGENETIC VOLCANO-SEDIMENTARY ROCKS

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Introduction

Illitization of smectite is a dominant process in the diagenetic evolution of sedimentary rocks, which has been extensively studied during several decades because of its impact on economic concentrations of hydrocarbons. However, consensus has not yet been reached as to the details of the mechanism of this process: solid state reaction (Weaver & Beck, 1971), closed-system reaction (Hower et al. 1976; Boles & Franks, 1986), process between a dissolution-precipitation reaction and a solid state transformation (Ahn & Peacor, 1986) are those mentioned the most often. The visible change monitoring this process is the increase in the amount of illite layers in the mixed layer illite/smectite, as a function of burial depth that is to say as a function of temperature increase. This progressive mineralogical and chemical trend has not been computed in different ways to provide information on how the amount of illite layers increases and to evaluate thermodynamically and kinetically formational models.

Discussion

Illitization of illite/smectite induces an increase in the potassium content of the particles, especially in buried shales of different sedimentary basins, despite differences in the provenance of the precursors, the age of deposition, the depths of burial and the tectonic history of the basins. $^{40}$Ar contents increase, suggesting the radiogenic $^{40}$Ar is retained (incorporated?) by the illite/smectite during the stage of most intense illitization (Fig. 1). Deeper in the sequences, the radiogenic $^{40}$Ar is released (Clauer & Chaudhuri, 1995) Illitization of illite/smectite in buried shales seems, therefore, to be controlled by a transformation process integrating the structure of the precursors and the occurrence (reuse?) of inherited radiogenic $^{40}$Ar. This behaviour of incorporation
(retention) of radiogenic $^{40}$Ar seems also to occur for $^{87}$Sr, but it has been less documented. Mineralogical studies of the illitization process in associated shales and sandstones has shown that the X-ray evolution patterns of the illite/smectite in both lithologies, may be identical relative to depth. However, the K-Ar and $\delta^{18}$O data are clearly different for the illite/smectite of the two lithologies, with more significant changes in the contents of radiogenic $^{40}$Ar and in the $\delta^{18}$O values of the clay particles of the sandstones than in those of the shales (Fig. 2). Distinctly different mechanisms are required for interpretation of these differences: a continuous transformation process for the illite/smectite in the shales, as proposed earlier, and a stepwise dissolution-precipitation process for those of the sandstones.

![Age vs Depth and Ar*](image)

**Fig. 1.** Relationships between depth, amounts of radiogenic $^{40}$Ar and K-Ar apparent ages of the <0.1 $\mu$m fractions from shale sediments in the Gulf Coast basin (after Aronson & Hower, 1976, in Clauer & Chaudhuri, 1995). The figure outlines clearly the fact that the age decrease between 2500 and 4000 m is related to K$_2$O uptake, as the radiogenic $^{40}$Ar increases in the same interval of intense illitization.

IIIlrite/smectite fundamental particles representing the smallest separable particles (<0.03 $\mu$m) from buried bentonites, yield K-Ar ages that can be related to the diagenetic
history of these volcano-sedimentary rocks. The K-Ar ages of the fundamental illite/smectite particles relate clearly to the periods of maximum temperature affecting the units, during either burial history or hydrothermal activity, and which were set independently by computing the basinal evolution. In addition, it can be shown that the spatial distribution of illite/smectite K-Ar ages in thick bentonite beds does not result from Ar diffusion or particle recrystallization, but from slow diffusion of K into and through the beds (Table 1; Clauer et al., 1997). Interestingly, the finest studied fundamental particles (<0.03 μm) yield sometimes older K-Ar ages than the thicker fundamental particles, implying that illitization proceeds along a crystal growth mechanism, although not necessarily of Ostwald ripening type. This means that the individual particles of diagenetically formed illite/smectite fundamental particles consist of illite layers having different ages.

![Graph showing K-Ar ages and δ¹⁸O values](image)

Fig. 2. Differential decrease, relative to depth, in the K-Ar ages of the <0.4 μm fractions from shales and sandstones in the Handil field, Mahakam Delta Basin. The distinct δ¹⁸O changes relative to depth are suggestive for different processes in the two lithologies, if one admits similar temperatures for both at the same overburden (after Clauer et al., in press).
Table 1: K-Ar data of illite fundamental particles from Montana and east Slovak bentonite units (after Clauer et al., 1977)

<table>
<thead>
<tr>
<th>Samples</th>
<th>K2O (μm)</th>
<th>Ar* (%)</th>
<th>40Ar* (10^-6 cm^3/g)</th>
<th>Age (Ma ± σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montana bentonite (center of the bed, Upper Cretaceous 88-85 Ma)</td>
<td>&lt;Y J.Lm 3.62</td>
<td>37.65</td>
<td>5.02</td>
<td>42.5 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>Y - X 5.50</td>
<td>45.42</td>
<td>7.61</td>
<td>42.4 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>X -0.1 5.07</td>
<td>41.99</td>
<td>6.78</td>
<td>41.1 ± 2.0</td>
</tr>
<tr>
<td>Montana bentonite (lower contact, Upper Cretaceous 88-85 Ma)</td>
<td>&lt;Y J.Lm 3.51</td>
<td>49.25</td>
<td>7.36</td>
<td>63.9 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>Y - X 6.15</td>
<td>55.09</td>
<td>10.16</td>
<td>50.5 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>X -0.1 6.43</td>
<td>66.20</td>
<td>10.53</td>
<td>50.1 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>0.1-0.3 6.49</td>
<td>63.09</td>
<td>12.41</td>
<td>58.4 ± 1.9</td>
</tr>
<tr>
<td>Zempleni bentonite (East Slovak Basin, hydrothermal evolution)</td>
<td>&lt;Y J.Lm 7.71</td>
<td>52.73</td>
<td>3.37</td>
<td>13.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>X -0.1 8.27</td>
<td>65.40</td>
<td>4.17</td>
<td>15.6 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.1 - 0.2 8.97</td>
<td>66.51</td>
<td>3.94</td>
<td>13.6 ± 0.4</td>
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<tr>
<td></td>
<td>0.2-0.3 9.62</td>
<td>61.67</td>
<td>4.46</td>
<td>14.3 ± 0.5</td>
</tr>
<tr>
<td>CIC1/20 bentonite unit (East Slovak Basin, diagenetic evolution Lower Sarmatian =13.5 Ma)</td>
<td>&lt;Y J.Lm 2.32</td>
<td>6.1</td>
<td>0.56</td>
<td>7.4 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>Y-X 4.18 6.0</td>
<td>0.52</td>
<td>3.8 ± 2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>X -0.1 3.88</td>
<td>7.01</td>
<td>0.47</td>
<td>3.7 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>0.1-0.3 4.07</td>
<td>8.19</td>
<td>0.67</td>
<td>5.1 ± 1.2</td>
</tr>
<tr>
<td>CIC 1/16 associated shale unit (East Slovak Basin, diagenetic evolution, Lower Sarmatian =13Ma)</td>
<td>0.01-0.02μm 4.68</td>
<td>41.44</td>
<td>5.95</td>
<td>39.0 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>0.02 0.05 5.25</td>
<td>62.80</td>
<td>11.75</td>
<td>68.2 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>0.05-0.1 3.53</td>
<td>62.11</td>
<td>12.51</td>
<td>68.9 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>0.1-0.3 4.66</td>
<td>76.72</td>
<td>16.84</td>
<td>108.8 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>0.3-2 2.73</td>
<td>12.43</td>
<td>4.67</td>
<td>52.3 ± 8.4</td>
</tr>
</tbody>
</table>

Ar* stands for radiogenic Ar and 40Ar* for radiogenic 40Ar; Ma stands for million years; the stratigraphic ages of the samples are given when available.
Consequently, their K-Ar data integrate longer or shorter periods of time. Punctuated diagenesis suggested by Morton (1985), on the basis of Rb-Sr data, as being a short lasting process, is only obtained for illite/smectite formed under hydrothermal conditions. Alternatively, the fines separable size fractions of shales associated with bentonites, systematically yield K-Ar dates that are dominated by inherited $^{40}\text{Ar}$ of detrital origin. It is still difficult yet to decide whether these high K-Ar dates record only partial recrystallization of detrital precursors during burial, or a closed-system behaviour inducing a reuse of the inherited radiogenic $^{40}\text{Ar}$ during illitization. It can, however, be stated that the low permeability of shales is probably not responsible for the excess of radiogenic $^{40}\text{Ar}$ in the illite/smectite material, as those from centre of thick bentonite beds do not yield abnormally high K-Ar dates relative to those from rims. The differences found among the K-Ar dates in shales and associated bentonites suggest that the transformation process of illite/smectite in low permeable sedimentary rocks, reuses most of the elements available in the immediate environment of the illite/smectite particles, for instance the radiogenic $^{40}\text{Ar}$ of the detrital precursors in the shales, which do not occur in bentonites devoid in detrital material.

Illitization is definitely dependent upon potassium availability. However, its completion depend on parameters such as the lithology of the host rocks. For shales, potassium could come from dissolved K-feldspars in the same volume of rock, suggesting its direct internal transfer from feldspar into the illite/smectite (Aronson & Hower, 1976). While, depending on local diffusion in bentonite beds, the amount of potassium available from alteration of K-feldspar in sandstones may be 20-25 times less than the amount needed to complete illitization in a given zone of the sedimentary sequence (Fig. 3), which implies a supply from outside by migration (Furlan et al., 1996). But temperature is also a driving parameter, as timing and duration of maximum temperature reached during the illitization process during burial-related diagenesis, can be evaluated in dating illite/smectite fundamental particles.
Fig. 3. Variations in the K-Ar dates, and K₂O (the adjacent value takes into account the dilutant components) and radiogenic ⁴⁰Ar contents of clay fractions (< 0.4 µm) and feldspar-enriched fractions (2-63 µm) in sandstones of the Handill field, Mahakan delta Basin (after Furlan et al., 1996). In the upper 2000 m, where the clays needed most of the K₂O during intense illitization, the feldspar ages remain constant or increase slightly, while the contents of radiogenic ⁴⁰Ar remain constant. In the lower 2500 to 4000 m, where the clays no longer need large supplies of K₂O, the ages of the feldspars decrease significantly indicating radiogenic ⁴⁰Ar and K₂O removals.
Conclusions

Following conclusions can be suggested, if one agrees that illitization of smectite -type precursors in volcano-sedimentary rocks is complete only when it provides isotopic ages that are reasonable in the context of the evolution of the formed minerals.

1- Illitization proceeds along a dissolution –precipitation process in sandstones and along a transformation process in bentonites and shales. In the latter, the picture is obscured by the behaviour of the inherited radiogenic $^{40}$Ar (and probably the radiogenic $^{87}$Sr) which seems to be reused during the process. Such a reuse may not to be induced by the physical properties of the rocks, but could result from difference between the rate of illitization and that of elemental diffusion.

2- Illitization integrates longer or shorter periods of reaction related to (or induced by) the intensity of the temperature, suggesting that the reaction is more thermally-than kinetically dependent.

3- Illitization protracts as a crystal-growth mechanism, as the finest fundamental particles yield K-Ar ages that are identical to or older than those of the thicker fundamental particles. However, it is not clear yet if the mechanism proceeds along the Ostwald ripening type.

References

LONGEVITY OF CLAY BARRIERS IN WASTE DISPOSAL.

Santiago Leguey.

Dpto. Q.A. Geología y Geoquímica Universidad Autónoma Madrid.

1. Introduction

The production of residual wastes in the last third of this century has become a social problem with repercussions on the quality of the environment of the population. Dangerous residuals with long period toxicity need to be isolated from the biosphere. The conditions of security must be for prolonged periods of time and so we require specific zones of the lithosphere that satisfy specific geological and mineralogical conditions.

The manipulation of residuals, the construction and the maintenance of the waste storage areas, as well as the rehabilitation of the occupied areas is today a multidisciplinary task that requires the application of adequate laws for its resolution.

The first attempts at controlling residual wastes were developed in England in 1876 where they constructed a plant for the incineration of the wastes. Later in 1898 in New York, the first plant for the recovery of wastes was constructed (MRS Material recovery Facility). In 1965 the US Congress passed the first law regarding residual wastes (Solid Waste Disposal Act). Until the 1970's no specific laws were passed in Europe to govern the protection of the Environment and management of wastes. Environmental studies were developed for the first time in 1975 at University centres following the lead of the Technical University of Berlin, one of the pioneering centres of these studies.

A large range of techniques have been developed or are being studied for the construction of waste storage areas. The majority of which are based on the use of natural materials to seal the waste deposit. In this paper we analyse the characteristics of clay materials that are being utilised or are being studied for this role in diverse types of waste storage areas and how different factors determine the function of the sealant material.

1.1. Production of Waste Material

The concept of a waste material as "a transportable object, lacking value that has been abandoned by its owner", shows a clear dependence between its production, with
the standard of living of different countries, shown by the major levels of production and the correspondence with the highest income levels. (fig 1)

The countries of the European Union (EU) produce annually $240 \times 10^6$ T of industrial wastes, $104 \times 10^6$ T of municipal wastes, more than $60 \times 10^6$ T of waste mud, the majority of which is deposited in landfills (65%), while 24% is incinerated and the rest partially recycled. It is estimated that there are between 60 000 and 120 000 landfills that occupy an area of between 800 and 1700 Km². The industrial wastes consist of $20 \times 10^6$ m³ of toxic and/or dangerous wastes and $80 000$ m³ of radioactive wastes of which $150m^3$ have high levels of radioactivity.

1.2. Management of Wastes

The management of wastes is the responsibility of different administrations (municipal, regional, national, etc.). the management implies the knowledge of the origin of the wastes, their treatment, recovery and/or reduction and the ultimate storage destination in conditions of maximum security (isolated) that prevents the dispersion in the biosphere with resulting contamination.

The management of the wastes has three fundamental objectives: a) reducing the production of wastes at the source; b) increment to the maximum the amount of recycling and/or exploitation of the wastes; c) guarantee the control of the waste during
their isolation in the storage facilities. Based on the nature and composition of the waste materials we can differentiate the following types of storage facilities,

1. Inert waste material dumps (household rubbish)
2. Non-dangerous waste material dumps (municipal solid wastes) (MSW)
3. Dangerous waste material dumps (industrial, medical, dangerous and toxic wastes, low activity nuclear)
4. Repository for medium and high level nuclear wastes (HLW)

Models of waste storage facilities

Security is the principal factor to take into account during the design and planning of the landfills, which depends fundamentally of the initial composition of the wastes and the leachates and contaminants produced during their storage. In Germany the standards established in June 1993 (Technical Guidance for Municipal Solid Waste - TG MSW), determined three categories of controlled waste deposits related to the composition and dangerousness of the leachates, Bilitewski et al. (1996).

A) Monofill consisting of residuals consisting of a single component such as plastics, tyres, packing material, etc with similar chemical reactivity that do not produce leached contaminant material.

B) Class I Landfill for wastes with a low organic content that produce low levels of leachate

C) Class II Landfill for wastes with a high content of organic material and corresponding higher leachate production.

i.3. Selection of Locations For The Storage Facilities

The solid wastes have been deposited for some time in natural surface depressions, in the excavated areas of abandoned mines and in open pits after the extraction of construction materials etc... These landfills are generally uncontrolled and have a high risk of danger, toxicity or the possible loss of contaminants.

The laws that regulate the management of the wastes specify that a series of standards for environmental protection must be fulfilled in the selection, construction and control of the landfill taking into account the risk of danger and/or toxicity, the duration of the activity and the volume of the material.

The selection and design of the sites have to take into account in the first place the sociological factors, so as to avoid any immediate or future danger to the health or security of the people, and also considering the protection of the flora and fauna. The growing sensitivity of the population to themes related to hygiene and environmental protection means that public opinion is one of the principal motivations taken into account by the environmental managers.
The inert wastes, municipal solid wastes (MSW), the toxic and dangerous wastes and the low activity radioactive wastes are usually deposited in surface zones where the technology is relatively simple and the costs are low to moderate, while the high activity radioactive wastes (RAA) it is predicted, will be stored in underground areas at depths of 500m with more sophisticated technologies and much higher costs.

The progressive increase of security measures in the isolation of wastes has given room for the development of diverse types of barriers, where the use of clay materials plays a predominant part: natural and artificial barriers for the isolation on the surface of less dangerous materials and engineering barriers for the geological isolation at depth of the highly dangerous materials.

II. Surface Isolation Barriers

The change in philosophy in the treatment and management of wastes has now accepted the use of sealing materials, it has now passed from a politically tolerant view of "dilute and disperse" the contaminants through "attenuate" or "retard" their effects to the opposite view of "contain and treat".

The concept of containing implies the increase and reinforcement of measures of isolation inside the landfill with the utilisation of natural and/or artificial barriers, together with the construction of systems of drainage and transmission to collect and later treat the leached materials and contaminants.

The security of the landfill and storage of the wastes is based on a system of multi-barriers that impede the entry of waters (surface or sub-surface) and the leakage of leachate and contaminants into the biosphere. The system of multi-barriers has a different design depending on whether the landfill is at the surface or underground. During the construction and functioning of the waste site the following types of barriers should be considered,

BARRIER 1: **Processing of the waste** (making inert, physical-chemical treatment, separation of materials, etc), to immobilise the dangerous contaminants.

BARRIER 2: **Geological and hydrological** (preparation of the terrain, excavation, compaction, etc.), to reduce the possible risk of the fracturing of the artificial barriers and restrict the diffusion of contaminants.

BARRIER 3: **Design of the landfill** (dimensions of the cells, compaction of the wastes, and thickness of the fill, Physical-chemical and biological processes that will be put in place and their future affects on stability)

BARRIER 4: **Covering of the base and walls of the compartment** (landfills liner and walls), to avoid the loss of leachate and contaminants.

BARRIER 5: **Covering of the upper surface** (to avoid the entry of rainfall and the loss
of gases or strong odours).

BARRIER 6: Maintenance and monitoring of the systems of control of the waste site during a long time period.

II.1. Clay Barriers

The clay minerals satisfy the two basic functions required in the barriers, they reduce the porosity and so facilitate the retention of the contaminants. On the one hand, the small size of the crystals < 2µm and the possibility of incorporating molecules of water in some species closes the pores of the materials and makes it difficult for the passage of water due to its increased impermeability. On the other hand, the existence of surface properties and the exchange capacity favour the retention of certain contaminants.

The permeability values expressed as a function of the hydraulic conductivity depend on the grain size and grade of compaction of the materials, increasing with the predominance of fine fractions and the density. fig 2.

The physical-chemical properties of absorption and retention of contaminants are characteristic of the smectite group minerals that are known commercially under the name "bentonites". The parameters that determine these properties are the specific surface area and the Cation Exchange Capacity (C.E.C). The exchanged cation regulates the hydraulic behaviour of the Bentonite which when hydrated incorporates one or more molecules of water depending on the presence of divalent or monovalent ions.
The hydrated bentonite when compacted shows a noticeable reduction in hydraulic conductivity, also it is possible to modify the mechanical stability to increase in parallel the swelling pressure. fig 3.

![Swelling pressure versus clay dry density of montmorillonite-quartz mixtures (Villar & Rivas 1994)](image)

**Fig.3: Swelling pressure versus clay dry density of montmorillonite-quartz mixtures (Villar & Rivas 1994)**

### II.2. Natural Barriers

The geological barrier should satisfy the minimum conditions of low permeability and filtration capacity for toxic solutions. The most adequate terrain are sedimentary formations of stratified lutites with high contents of clay minerals, and a good cation exchange capacity, or the clay soils where the presence of small quantities of smectites improve the retention capacity. Nevertheless the percentage of smectite needs to be controlled, as an elevated content may generate negative effects such as shrinkage or instability in the presence of solutions with high quantities of electrolytes. In table II-A the minimum values of several parameters are shown to comply as a geological barrier.

### II.3. Artificial Barriers

These consist of clay materials and synthetic laminar materials of high resistance. The are provided as independent units or are manufactured as mixed products with properties of both materials.

#### II.3.1. Clay Materials

The construction of the clay base (clay liner) follows very strict security controls and should only use clays of high fine fraction content (< 2µm), whose minerals have a
high chemical resistance and retention properties. The clay materials once compacted should have a minimum hydraulic conductivity of $10^{-9}$ m/s$^{-1}$ and a thickness of between 0.5 and 2m depending on the standards of different countries (Bath, 1993). In table I-B the values used normally in Germany for clay barriers are shown,

Table I

<table>
<thead>
<tr>
<th>Barrier Parameters</th>
<th>A) GEOLOGICAL BARRIER</th>
<th>B) CLAY BARRIER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (m)</td>
<td>$&lt;3$</td>
<td>0.75</td>
</tr>
<tr>
<td>Permeability (m/s)</td>
<td>$&lt;10^{-7}$</td>
<td>$&lt;5 \times 10^{-10}$</td>
</tr>
<tr>
<td>Clay Fraction ($% &lt; 2\mu m$)</td>
<td>-</td>
<td>$&gt;20$</td>
</tr>
<tr>
<td>Clay mineral content ($)</td>
<td>-</td>
<td>$&gt;10$</td>
</tr>
<tr>
<td>Cation Exchange Capacity</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

The commercial products most commonly used in Germany and the United States have different compositions, in some Kaolinite predominates as the basic component, while in others bentonite. Sodium bentonite is used in a mixture with the soil to increase its impermeability, the bentonite content is about 8-10%. In table II the composition of some manufactured commercial products is shown, with kaolinite as the clay mineral used.

Table II

<table>
<thead>
<tr>
<th>Secursol 3301 *</th>
<th>Secursol 3060 *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay Fraction ($% &lt; 2\mu m$)</td>
<td>70-80</td>
</tr>
<tr>
<td>Clay Mineral Content ($)</td>
<td>50-60</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$&gt;65$</td>
</tr>
<tr>
<td>Illite</td>
<td>$&gt;30$</td>
</tr>
<tr>
<td>Smectite</td>
<td>$&gt;3$</td>
</tr>
<tr>
<td>C.E.C. (meq./100g)</td>
<td>$&gt;20$</td>
</tr>
<tr>
<td>Adsorption of water</td>
<td>75-85</td>
</tr>
</tbody>
</table>

- Fiebiger & Schellhorn, (1994)

II.3.2. Laminated Synthetic Materials

These materials are composed of layers of high density polyethylene (HDPE) that are known under the market name geomembranes. Their basic function consists of impeding the migration of leachate and therefore to contain them within the landfill for later treatment. Their permeability varies between $8.1$ and $6.8 \times 10^{-15}$ cm/s depending on the thickness. Proper installation and especially the sealing of the lateral joints of the lamina is necessary to guarantee the complete closure.

The geomembranes are protected against mechanical damage produced by the
wastes such as cuts, puncture and abrasion, etc. by the placement of filtering laminates known as geotextiles, they also impede the finer particles preventing them from accumulating in the drainage systems. The geotextiles are made of distinct types of fibres of polypropylene and polyester randomly oriented to avoid preferred directions of flow.

Other products known as geogrids are used to support long term tensile load.

II.3.3. Geosynthetic - Clay Liner

Also known as Geo-Clay (GCL), they consist of materials manufactured in the form of a sandwich, combining a layer of fine bentonite between two laminas of plastic or textile fibre. The upper layer should be permeable to permit the hydration and expansion of the hydrated bentonite, which leads to a more flexible but impermeable layer. The composition of the lower layer should be polypropylene without weave or high density polyurethane (HDPE), while the upper layer employs a woven layer of polyester or polypropylene. In table III the details characteristics of a typical geo-clay liner are given.

<table>
<thead>
<tr>
<th>Table III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower cover</td>
</tr>
<tr>
<td>Upper cover</td>
</tr>
<tr>
<td>Bentonite content</td>
</tr>
<tr>
<td>Particle size</td>
</tr>
<tr>
<td>Lamina thickness</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
</tr>
</tbody>
</table>

A geo-clay liner is manufactured with different levels of sophistication depending on its use. American Coloid makes a product which employs a layer of natural sodium bentonite (Volclay) between two layers of Geotextile of woven polypropylene (needlepunchure). During the weaving of the fibres they form micro cells which surround the bentonite, making it more difficult for the migration of the bentonite whether dry or hydrated, during transport, employment or when functioning. The initial permeability of this product with an average content of 5.8 K/m² of bentonite and a thickness of 6.4mm varies between $2.1 \times 10^{-11}$ and $6.6 \times 10^{-12}$ m/s with hydrostatic pressures comprising of 0.3 and 10.7 m respectively.

The physical and chemical stability of the bentonite may be modified in the presence of leachates containing sulphates or chlorides, reducing its capacity of hydration. These negative effects are compensated for by treating the bentonite with polymers such as polycrylamides that maintain the link between the hydrated particles.

A new product of geo-clay liner incorporates high density sodium bentonite (HDB) pre-hydrated with a minimum density of 1.36 g/cm³. This is made in laminas
with a content of 8K/m² of bentonite covered by geotextiles with different characteristics depending on the proposed application. The laminas have good flexibility and a hydraulic conductivity of $5.4 \times 10^{-14}$ m/s in water with a pressure of 450 KPa and of $4.6 \times 10^{-12}$ KPa after a contact period of 29 months.

II.4. Elements and Techniques of Sealing  
The isolation and sealing of a waste deposit requires an understanding of the normal techniques used for the basic components.  
Covering of the base (base linings)  
Covering of the surface (surface linings)  
Sealing of the walls  
Injected Barriers  
The techniques for the construction of the base and surface liners are similar, the utilise clay minerals, geomembranes and geotextiles as principal components for sealing materials. The sealing of the walls and the injected barriers utilise a cement and bentonite mud.

Covering of the Base  
In figure 4 the scheme followed for a geological barrier is shown, the various layers are in the following sequence,  
A □ □ > 0.75m of clay material, placed in three layers of 0.25m thickness.  
B □ □ > 2.5mm of high density polyethylene (HDPE) in a single lamina.  
C □ □ Protective layer  
D □ □ > 0.3m of drainage system with a drainage tube incorporated.  
E □ □ Waste.

![](image.png)  
Fig 4: Schematic diagram of base lining. (Fiebiger & Schellhorn, 1994)

Surface Covering  
In figure 5 the scheme for the different layers above the wastes with the thickness of each layer is shown,  
A □ □ > 0.5m compensation Layer. For the drainage of gases.  
B □ □ > 0.5m cover of clay materials, in two layers of 0.25m thickness.  
C □ □ > 2.5mm lamina of high density polyethylene (HDPE)
The standards of the EU for the design of the landfill that have been discussed in the European Parliament, considers the incorporation of different types of barriers as shown in figure 6.

II.5. Transport of Contaminants in the Barriers.

A knowledge of the types of transport of contaminants that may enter into contact with the saturated natural or artificial barriers, is essential to control them. The contaminants move initially by the process of advection within the flowing water and using diffusion between points of high and low chemical concentrations. Depending on
the chemical composition of the contaminating elements they may be dispersed, mixing with the underground water producing a dilution. In parallel, certain dispersed contaminants may be held by a process of sorption, displacing other cations of the exchange complex of the clays. Cations such as Na, Pb, Cd, Fe and Cu are retained on the surface of the clays and displace the other cations such as Ca or Mg what pass into solution, where they may attain high concentrations. The concentration of heavy metals due to this process of absorption (sorption) gives rise to the precipitation and the formation of a solid phase (Fleming 1996).

It is assumed in general that synthetic barriers and or mixtures have a limited lifetime and that in the medium term the isolation functions will depend fundamentally on the clay or geological barrier where they generate a plume of contamination. fig 7.

![Diagram](image)

**Fig.7**: The classic landfill problem showing generated leachate plume (Young 1996)

Normally in excavated landfill refilled with clay materials the mechanisms of transport are due to advection and diffusion, the first practically ceasing when groundwater level of the aquifer is reached (saturated zone), at this point the only method of transport is diffusion.

The movement of some leachates in some uncontrolled landfills, shows a process of general dispersion in the direction of sub-surface water flow and a possible process of adsorption (sorption) of certain elements such as NH$_3^+$ and K$^+$. the development of concentration isograds reaches a maximum distance of some 300m from the original focus.

The capacity of attenuation and dilution of contaminants in the geological barrier may be calculated based on the volume and composition of the potential contaminants to avoid that they reach the sub-surface waters. The type of porosity of the
rocks and their composition are important factors to take into account, given that the processes of absorption (sorption) require the existence of a clay matrix. Carbonate rich rocks such as marls or limestone neutralise the acidity of the waters and favour the precipitation of chalcophile metals. Active landfills that were started in the 1950's and controlled from 1976 onwards show that the plume of the leachate has been reduced when the residuals are covered and isolated from the rainwater.

II-6. Permeability of the Clay Barrier (Clay Liner).

The permeability of the compacted clay barrier should be very low, with the minimum requirement for hydraulic conductivity of \(10^{-9}\) m/s.

The plasticity of the clay materials is one of the diverse factors that control the behaviour of the permeability, with a noticeable increase when the plasticity index (P-I) is less than 12%. Values of the plasticity index greater than 65% may generate problems of stability, deformation and/or differential compaction. It is considered that the clay materials should have as a minimum 10% of fine particles smaller than 2μm to achieve
adequate values of permeability. The upper limit of fine particles depends on the proportion of the different clay minerals, whose liquid limit should be less than 90% and with an plasticity index value less than 65%, Murray et al. 1996.

The compaction of clay materials is required to achieve low levels of permeability. The content of water plays a fundamental role to allow the linking of particles to achieve the maximum density (Proctor density) fig 8.

The lowest values of permeability coincide with a water content between 18% and 24%, slightly greater than the water content for the highest values of the Proctor density. This difference could be due to the occupation of the pores when the material is saturated (Clark and Davies, 1996). The maintenance of the saturation conditions of the clay barrier is a fundamental guarantee of the impermeability.

II.7. Geochemistry Of The Clay Barrier.

The chemical stability of the clay barrier components depends on the volume and composition of the leachate, that experience significant variations with time. The average composition of the leachate after Cristianson et al. (1994) is shown in table IV.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.5 - 9</td>
</tr>
<tr>
<td>Spec. cond. (µS/cm)</td>
<td>2.500 - 25.000</td>
</tr>
<tr>
<td>Total solids</td>
<td>2.000 - 60.000</td>
</tr>
</tbody>
</table>

**ORGANIC MATTER**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total organic carbon (TOC)</td>
<td>30 - 27.700</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD₅)</td>
<td>20 - 57.000</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>140 - 90.000</td>
</tr>
<tr>
<td>(BOD₅)/COD (ratio)</td>
<td>0.02 - 0.80</td>
</tr>
<tr>
<td>Organic nitrogen</td>
<td>14 - 2.500</td>
</tr>
</tbody>
</table>

**INORGANIC MACROCOMPONENTS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total phosphorous</td>
<td>0.1 - 20</td>
</tr>
<tr>
<td>Chloride</td>
<td>150 - 4.500</td>
</tr>
<tr>
<td>Sulfate</td>
<td>8 - 7.750</td>
</tr>
<tr>
<td>Hydrogencarbonate</td>
<td>610 - 7.320</td>
</tr>
<tr>
<td>Sodium</td>
<td>70 - 7.700</td>
</tr>
<tr>
<td>Potassium</td>
<td>50 - 3.700</td>
</tr>
<tr>
<td>Ammonium-N</td>
<td>50 - 1.800</td>
</tr>
<tr>
<td>Calcium</td>
<td>10 - 7.200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>30 - 15.000</td>
</tr>
<tr>
<td>Iron</td>
<td>3 - 5.500</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.03 - 1.400</td>
</tr>
</tbody>
</table>

**HEAVY METALS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.01 - 1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.0001 - 0.4</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.02 - 1.5</td>
</tr>
</tbody>
</table>
The landfill of the municipal solid wastes (MSW) are characterised initially by the presence of oxygen and pH values between 7 and 8. The organic components play an important role in the reactions that produce the so-called “reactor landfills”, which regulate the evolution of the chemical elements (major, minor and trace), where the biochemical processes also have an elevated activity.

The chemical reactions commence with the decomposition of the organic material generating an “anaerobic acid phase” with the formation of organic acids. In this phase reducing conditions are produced and the pH descends below 5, with a notable increase in the concentration of organic substances in the leachate. After one or two years the chemical conditions of the landfill pass from the acid phase to the methanogenic phase with the generation of gases and a change in the pH to alkaline conditions. The change in pH is accompanied by an important decrease of the metal content of metals such as iron, manganese or zinc in the leachate. Table V. The formation of methane decreases considerably after 6 to 8 years the decomposition of the organic materials is accompanied by a generation of heat, that may cause an increase in temperature to 60 degrees C in some cases.

### Table V

**CHEMICAL DEVELOPMENTS IN REACTOR LANDFILL**

<table>
<thead>
<tr>
<th></th>
<th>ACIDOGENIC PHASE</th>
<th>METHANOGENIC PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.1</td>
<td>8</td>
</tr>
<tr>
<td>BOD₅ (mg/l)</td>
<td>13.000</td>
<td>180</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>22.000</td>
<td>3.000</td>
</tr>
<tr>
<td>Calcium (mg/l)</td>
<td>1.200</td>
<td>60</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>780</td>
<td>15</td>
</tr>
<tr>
<td>Manganese (mg/l)</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>Zinc (mg/l)</td>
<td>5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* (Förstner, 1996)
The acid conditions increase the permeability of the clay barrier, favouring the transport of contaminants, fig 9. Simultaneously it also produces the dissolution of the clay minerals, more obviously in smectites than in kaolinites that have a greater chemical stability.

![Diagram showing pH changes and hydraulic conductivity](image)

**Fig.9: Variation in hydraulic conductivity by acid. (Daniel & Shackelford 1989)**

There is very little experience regarding the evolution of the components of controlled landfill, were the oldest are just 25-30 years old. Nevertheless the mechanical degradation of the mass of the wastes produced by the initial pressure of the gases, transport of particles, transformation of the organic material, compaction, etc., one can assume may lead to a breach of the surface barriers and the penetration of rainfall.

The incorporation of oxygen in the rainfall oxidises the minerals reduced in the form of sulphates during the anaerobic acid phase and allows the mobilisation of trace elements. Tests of the metal mobility based on dredged material, shows a strong increase in the content of zinc and cadmium in the oxidised waters. Table VI. The progressive evolution of the oxidation from the surface to the base of the waste site, produces a continuous process of dissolution and re-precipitation, with the consequent concentration of the trace elements and the formation of sulphuric acid.
Table VI

METAL MOBILIZATION FROM DREDGED MATERIAL

<table>
<thead>
<tr>
<th></th>
<th>REDUCED WATER</th>
<th>OXIDIZED WATER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium</td>
<td>125 mg/l</td>
<td>&lt; 3 mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>80 mg/l</td>
<td>&lt; 3 mg/l</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt; 3 mg/l</td>
<td>120 mg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt; 10 µg/l</td>
<td>5.000 µg/l</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt; 0.5 µg/l</td>
<td>80 µg/l</td>
</tr>
</tbody>
</table>

The clay barriers using natural soils normally contain variable quantities of carbonate, the calcite reacts with the sulphuric acid precipitating gypsum. This reaction implies an important increase in volume, where the gypsum formed practically doubles the volume compared to the original calcite, producing expansive properties in the materials of the clay barrier. The decrease in density and the development of intercrystalline porosity negatively affect the mechanical stability and increase the permeability of the clay barrier.

The sodium bentonite used in geotextiles and soil/bentonite sealant products, may degrade in the presence of certain contaminants such as Ca, Mg, NH₄ or K during the hydrating phase or during the operational period. The displacement of the sodium from the exchange complex facilitates the flocculation of the clay, considerably increase the permeability. Tests of the permeability of commercial geotextiles pre-hydrated with water containing 1000 ppm of Cl₂Ca and later percolated with water containing 1% Cl₂Ca show a large increase in permeability within a few weeks, while a new product (CRC clay) of unknown composition, remains unaltered. fig 10. Kajita (1998).

Tests of the diffusion of Cd and Pb within the clay liner composed of marly loess with illite and smectite shows a major retention of the Pb compared to Cd within the clay, with coefficients of diffusion of 3.6 - 7.4 x 10⁻⁹ cm² and 4.9 - 6.7 x 10⁻⁸ cm² respectively. Roehl and Czurde, 1998.

The micro-organisms degrade the components of the synthetic barriers (geomebranes and geotextiles) at the same time the products segregate and react with metallic elements forming “biofilms”. These reactions produce colloids that favour the transport of elements which are less soluble in the form of complexes.
The multiple reactions of organic material degradation have a non-linear behaviour with a poorly defined development with time. The different mineralogical systems that develop are difficult to understand, the problem at the moment being the modelling of these processes to deduce some valid parameters for prediction purposes.

Recent data reveals how certain improvements introduced in the management of the landfill, such as the recovery of plastics and paper and the increase in the compaction of the wastes retard the development of the methanogenic phase and the production of bio-gas.

Tests for the prediction in the long term of the mobility of the inorganic contaminants of landfill, have been developed using the ash and slag from incineration plants (Kersten et al. 1995, In: Förster, 1986). The results show a rapid mobilisation of chlorides and sulphates, part of the calcium in the hydroxyl form, which transforms rapidly into carbonates, while the Fe and Al is transformed into hydroxides. It is expected with time that there is a progressive dissolution of the carbonates, modifying the pH from the initial values near 8 until the final values of the order of 5 or 6. This increase of acidity with time of the waters containing the leachate favours the dissolution and concentration of trace metallic elements. The calcium dissolved from the calcite is incorporated in the exchange complex of the clays.

The time required for the first stage, the complete migration of the chlorides and sulphates can be counted in tens of years, while the formation of oxides and carbonates can take hundreds of years. The final stabilisation of the major elements in the form of
hydroxides and oxides or incorporation in the structure of silicates will need some thousands of years.

III. High Activity Radioactive Wastes

The isolation of highly radioactive wastes requires their immobilisation for a prolonged period of time that can be between $10^4$ and $10^6$ years, which is the average time for the disintegration of the radionuclides, until concentrations similar to the regional geochemical background have been reached. During this period the wastes need to be stored in conditions of maximum security to prevent the radionuclides from reaching the biosphere and posing a threat to persons or the environment.

The design of the storage areas for highly radioactive wastes being considered requires burial of the wastes in excavated galleries in deep zones of the crust, at some 500m below the ground. The security requires a system of multiple barriers, where we can differentiate: the chemical barrier consisting of a matrix in which we vitrify the wastes, the physical barrier formed of a metal capsule into which we introduce the wastes, the engineering barrier formed of a fill between the capsule and the gallery rock walls and finally the geological barrier formed from the rock mass in which the storage area is located.

Actually the countries of the E.U. are considering three rock types that are the most suitable for the location of these storage areas, these are, salt diapirs, sedimentary clay formations and granite batholiths. In contrast, in the United States they are considering the possibility of placing the storage areas in volcanic ash situated in zones of minimum rainfall in the Nevada desert.

The design of the underground repository in granite rocks (fig 11) is expected to be based on the excavation of horizontal galleries of 2.40m in diameter, where they will deposit the capsules containing the wastes, each capsule will be 4.54m long and 0.9m in diameter with an approximate weight of about 12T. The engineering barrier surrounds the capsule and will have a thickness of 0.75m, this will be formed from blocks of compacted bentonite with an average density of 16T/m³.

The compacted bentonite plays a fundamental role in the system of isolation. When hydrated it develops expansive properties that seal the fissures and discontinuities of the terrain, impeding the access of sub-surface water to the capsule. The hydraulic conductivity of the compacted bentonite is of the order of 10-13 cm/s, the water can move solely using diffusion and requires about 200 years to reach the capsule, based on preliminary calculations made by Bucher and Muller-Vonmoos (1989). The capsule corrosion based on the same authors requires another 1000 years, in which time the radionuclides have only decreased in radioactive intensity by 1% from the initial values.
Simultaneously the bentonite may dissipate the residual heat that is generated by the wastes, which is of the order of 100°C at the contact between the capsule and the bentonite. When the physical barrier of the capsule is degraded, the properties of the absorption of the bentonite must retain and or retard the migration of the radionuclides to the geosphere.

III.1. Characteristics of the Radionuclides

The radionuclides present in the storage areas consist of the used combustible material from the nuclear cores and the contaminated materials during the functioning of the reactors, that have to be isolated at the end of their useful life. The radionuclides are classified based on security considerations in,

a) Critical radionuclides with the highest radiation rates.

b) Possibly critical radionuclides.

c) Non-critical radionuclides

The first group includes $^{14}$C, $^{99}$Tc, $^{127}$I, $^{135}$Cs and $^{237}$Np the second group includes $^{79}$Se, $^{107}$Pd and $^{93}$Zr and the diverse isotopes of the U, Pu, Am and Cm. The last three precursors of the radionuclides $^{237}$Np, $^{235}$U and $^{236}$U that have the longest half-life of disintegration.

The bentonite can retain or retard the migration of the radionuclides using diverse mechanisms:

a) Processes of filtration such as molecular and colloidal filtration

b) Surface processes of retention or exchange on the surface of the minerals

c) Processes of diffusion across the pores

d) Processes of precipitation if the water of the pores is supersaturated.

The transport of the radionuclides to the biosphere is principally using sub-surface waters, although some lighter elements such as carbon may be mobilised in the form of gas.

III.2. Tests of the Thermal Stability of Bentonite

Numerous tests have been made in recent times with different types of bentonites to predict their behaviour (changes in properties) during long time periods with elevated temperatures. The bentonites used for these tests correspond to those commonly used with commercial prototypes that are well defined, in which montmorillonite dominates but with different components in the exchange complex. The most common include Na Bentonite (MX-80, Wyoming USA), Ca Bentonite (Montigel, Bavaria, Germany), Ca-Mg Bentonite (Almeria, Spain) and K Bentonite (Kinnedule, Sweden). Also tested were Mg Bentonites of the Neogene basin of Madrid where saponites dominate the clay material.
III.2.1. Transformation Smectite-Illite

The transformation of smectite to illite by means of the formation of interstratified Illite-smectite has been recognized in natural environments (Velde, 1985, Huang et al. (1993), with others). Nevertheless in a recent revision of Meunier et al. (1998), they deduced that there are different reactions produced in hydrothermal tests using closed laboratory systems than in natural environments.

These authors using the Wyoming bentonite determined a first reaction where the montmorillonite of low charge $\Rightarrow$ high charge beidellite, saponite and quartz. This reaction takes place below 250°C, while that in natural environments appears in the interval 180°C-300°C. The beidellite of high charge, saponite and potassium is then converted into interstratified beidellite/mica, associated with quartz and chlorite.

This reaction is produced in tests at temperatures above 250°C with a reaction time of 40 days. The general confirmation of these intermediate reactions in the laboratory tests for the different types of bentonite modifies considerably the previous kinetic criteria that considered the existence of only a single reaction in the process of the illitization of the smectite.

The longevity of the properties of the bentonite has been investigated by Masden (1998), comparing the results obtained for the Bentonites MX-80 and Montigel with the K Bentonite of Kinnekule that contains approximately 50% of interstratified Illite/Smectite (Push and Madsen, 1995). The K Bentonite maintains values of the swelling pressure that are 55% of the Ca Bentonite of Montigel. The formation of the K Bentonite requires the gradual incorporation of potassium in a time-scale that has been calculated to be several hundred thousand years.

Cuadros and Altaner (1998) studying natural samples of interstratified Illite/Smectite of distinct geological formations with ages covering the periods from the Pliocene to the Ordovician (2-500 ma). The Al and Fe predominates in the octahedral layer with respect to other cations. As the amount of illite increases in the interstratified layers the proportion of Al in the octahedral layer is increased, the iron reduced while the Mg is stabilised with values of 0.5 for $O_{20}(OH)_4$.

III.2.2. Evolution of the Mineral Fabric

The differences in the mineralogical composition and properties of the bentonite (exchange capacity, specific surface area, swelling pressure, hydraulic conductivity, thermal conductivity, etc.) are maintained practically without change until temperatures of 90 to 100°C are reached. Only the dissolution of traces of carbonate and small variations in the exchange complex of the clay with a tendency to incorporate Ca and a
small increase in specific surface area are noticeable. In the hydrothermal alteration tests of the bentonite, from temperatures of 120°C it is possible to observe processes of dissolution-precipitation that rise gradually with the temperature and the duration of the tests. It depends also on the relationship water/solid and the chemistry of the water in the reaction. The increase in dissolved silica of the reaction waters is accompanied by a process of cementation of the solid material that fundamentally affects the fabric of the materials, cementing the particles and modifying the porosity (Güven, 1990; Leguey et al., 1996, Lineares et al., 1996, Push et al., 1996).

Tessier et al. (1998) studied the fabric of the clay of Fourges using a Transmission Electron Microscope (TEM), the clay was compacted at 60 MPa, hydrated afterwards and subjected for 330 days to temperatures of 90 to 145°C. The clay that contained 80% of interstratified smectite-kaolinite was activated with sodium carbonate for the tests. This clay was chosen by the Atomic Energy Commission of France for its good rheological properties. The observations with TEM revealed the presence of crystals of carbonate between the particles of smectite and kaolinite. At 90°C during the period of the test, the material subjected to an initial hydraulic pressure of 1 MPa reached a swelling pressure of 20 MPa. In parallel it produced a reorganisation of the clay crystals without significant changes in the dissolution of the solid phase. The same test at 145°C with alkaline pH and with an initial hydraulic pressure of 10 MPa produced a drastic change in the particles. It was observed that a high proportion of the clays dissolved with the formation of amorphous alumino-silicates, with a consequent decrease in the swelling pressure to 5 MPa.

### III.3 Tests at a Real Scale

The systems of storage have been reproduced "in situ", using an installation with two heaters that simulate the thermal environment, the weight and the dimension of the capsules of waste fuel. The project FEBEX (Full scale Engineered Barrier Experiment) is financed by the E.U., there are eight partners, seven European Union countries including France, Germany and Spain and one non-EU country Switzerland. The project is co-ordinated by ENRESA.

The project FEBEX is sited in Grimsel (Switzerland) where they make use of an old tunnel excavated in granites. Inside the tunnel they have drilled out a gallery of 70m in length and 2.28m in diameter, (fig 11). The project was started in 1994 and ends in 2001, they plan to complete the following objectives,

1. To demonstrate the possibility of constructing engineering barriers.
2. To study the thermal-hydro-mechanical processes (T.H.M) of the surrounding area.
To study the thermal-hydro-geochemical processes (T.H.G) of the surrounding area.

The project consists of four foundations, in the first the characterisation and selection of the Bentonite by groups from SCIC Zaidin (Granada), CIEMAT and the UPC. The Bentonite named FEBEX, comes from the deposits exploited by the company Minas de Gador (Almeria) which have been studied in the past by Linares et al. (1993).

The FEBEX Bentonite has a specific weight of 2.71, with a minimum content of montmorillonite of 88% and traces of quartz, plagioclase, K Feldspar, calcite and cristobalite. The grain size has a 90% fraction < 74μm and a 70% fraction < 2μm.

The engineering barrier is formed from 5331 blocks of compacted Bentonite of 1.75t/m3 with a humidity of 14%, a percentage of pores equal to 6.75% and a hydraulic conductivity of 5.9 x 10⁻¹⁴ m/s. Six hundred and twenty sensors have been installed for the control of 23 parameters. At the end of the installation they closed the gallery with a cover of concrete, and then started the testing, turning on the electric heaters on the 27th February 1997.

The project FEBEX is expected to encompass laboratory tests with actual size cells (models) to understand the processes of hydration of the clay barrier and in small-scale cells to analyse the mechanisms of transport of salts and the evolution of the mineral fabric.

The small-scale cells used for salt transport contain a pellet of compacted
bentonite with a density of 1.65 and 50mm diameter and 25mm thickness. In the test granitic water is injected with a pressure of 1 Mpa between the two extremes where they have established two thermal gradients, one low (35 to 60°C) and the other high (65 to 100°C).

Preliminary data (Martin et al. 1998) show that during the hydration of the bentonite a saline front is formed on the warmest side. This front is due to the Cl anion and small quantities of Mg, Ca and Sr, the front increasing in velocity as the temperature increases. In parallel there is a dissolution of anions, sulphates, arsenates and vanadates from the solid material, which pass slowly into the fluid phase. These tests are being complemented with others using saline water.

The pellets of bentonite of the transport tests are cut so as to study the fabric of the thin layers. The list of the components of the FEBEX bentonite without treatment is shown in the table VII.

Table VII

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FEBEX BENTONITE COMPOSITION *</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(THIN SECTION)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay Aggregates</td>
<td>69.30 %</td>
<td>Pyroxene/Amphib.</td>
<td>1.84 %</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.71 %</td>
<td>Calcite</td>
<td>0.48 %</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>3.53 %</td>
<td>Glass</td>
<td>3.36 %</td>
</tr>
<tr>
<td>Feldspar</td>
<td>1.05 %</td>
<td>Rock Fragments</td>
<td>0.19 %</td>
</tr>
<tr>
<td>Opaque</td>
<td>0.07 %</td>
<td>Matrix and Holes</td>
<td>19.36 %</td>
</tr>
<tr>
<td>Mica</td>
<td>0.11 %</td>
<td>* Cobeña et al. 1998</td>
<td></td>
</tr>
</tbody>
</table>

The majority of the clay aggregates have a size between 250 and 500μ when observed in polarised light. There are several types of aggregates isotropic, birefringent and oriented. These aggregates have distinct grades of re-crystallisation and paragenesis, therefore the isotropic aggregates are associated with dispersed oxides, the birefringent aggregates are frequently associated with the reaction aureoles in contact with the calcite remnants. The oriented aggregates are associated with the laminated original rock due to tectonic processes prior to the bentonization. In general all the differentiated phases show greater or lesser degree of reactivity.

IV. Conclusions.

Landfill failures are produced by landfill gas, surface and sub-surface water, slope and fire. There is very little data about the stability of the compacted clay liner. Only sporadic observations have been made of the top few centimetres of the altered material in the upper surface.
The diffusion tests within the clay barrier for the dangerous metals such as Pb or Cs suggest a very slow movement. Nevertheless certain important geochemical functions which affect retention such as variations in pH and redox potential have not been considered. Also the behaviour of the diffusion when the metals form part of organic-metal complexes is not known.

The control of the landfill and its apparent low environmental risk should not be allowed to mask the principal problem of the increasing amount of the land surface used for landfills.

The tests on the longevity of the bentonite in the engineering barriers shows that the bentonite does not experience appreciable changes in its composition or properties until a temperature of 90-100°C is reached.

The hydrothermal tests of bentonites under diverse conditions show that the initial mineralogical and textural changes take place at 120°C. There are some discrepancies over the illitization of montmorillonite or the appearance of other different mineral phases when compared to those in natural conditions.

The incorporation recently of the use of pressure in the hydrothermal tests of the bentonite, opens new perspectives about the kinetics of these reactions and the possible repercussions on the mineral properties.

V. References.


bentonita compactada sometida a procesos de calentamiento e hidratación. Congreso de Mineralogía y Petrología SEM98.


Linares, J., Barahona, E., Huertas, F., Caballero, E., Cuadros, J., Huertas, J,
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CHARACTERISTICS, USES AND BEHAVIOUR OF THE ILLITIC-CHLORITIC CLAYS FOR CERAMICS PRODUCTION

Bruno Fabbri

CNR, Research Institute for Ceramics Technology, Faenza, Italy

1. Clays in the Ceramics Industry

Ceramics industry utilizes clays of different types, depending on the product to be obtained. This aspect clearly comes out if one examines the single productive sectors which constitute the ceramics industry: tableware, sanitaryware, tiles and bricks (Table 1). Refractory sector was purposely not included in the list, because in this case clays are minority raw materials and they do not even play a secondary role in the body composition of different products.

In tableware sector, porcelain is the principal ceramic material, followed by earthenware. In both cases it deals with white bodies which mostly utilize kaolins and kaolinitic clays, which are practically free from iron impurities. On the contrary, totally different clays are used for majolica and cooking pottery. In this case it deals with coloured bodies which contain significant amounts of iron. These bodies are obtained using illitic-chloritic clays, with or without carbonate minerals.

In the sanitaryware sector, today iron-poor kaolinitic materials are almost exclusively used.

Table 1 – Types of clays used for the different ceramic materials produced in the various sectors of the ceramics industry

<table>
<thead>
<tr>
<th>TABLEWARE</th>
<th>Porcelain</th>
<th>Kaolins and kaolinitic clays</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Earthenware</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Majolica</td>
<td>Illitic-chloritic clays</td>
</tr>
<tr>
<td></td>
<td>Cooking-ware</td>
<td></td>
</tr>
<tr>
<td>SANITARYWARE</td>
<td>Vitreous-china</td>
<td>Kaolins and kaolinitic clays</td>
</tr>
<tr>
<td></td>
<td>Light single firing</td>
<td>Kaolins and kaolinitic clays</td>
</tr>
<tr>
<td></td>
<td>Red stoneware</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Red single firing</td>
<td>Illitic-chloritic clays</td>
</tr>
<tr>
<td>BRICKS</td>
<td>Porous single and double firing</td>
<td>Illitic-chloritic clays</td>
</tr>
<tr>
<td></td>
<td>Terracotta</td>
<td></td>
</tr>
</tbody>
</table>
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As grain size distribution is regarded, the Shepard classification diagram places these materials in the fields of silty clay and clayey silt (figure 3).
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As grain size distribution is regarded, the Shepard classification diagram places these materials in the fields of silty clay and clayey silt (figure 3).
Table 4 - Mineralogical composition of Italian illitic-chloritic clay raw materials for the production of floor and wall ceramic tiles (after Fabbri and Dondi, 1995b).

<table>
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<tr>
<th>Mineral</th>
<th>Emilia-Romagna region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ranzano</td>
</tr>
<tr>
<td>Quartz</td>
<td>18 – 29</td>
</tr>
<tr>
<td>Feldspars</td>
<td>5 – 12</td>
</tr>
<tr>
<td>Calcite</td>
<td>0 – 23</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0 – 5</td>
</tr>
<tr>
<td>Illite</td>
<td>22 – 29</td>
</tr>
<tr>
<td>Chlorite</td>
<td>8 – 17</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0 – 4</td>
</tr>
<tr>
<td>Smectite</td>
<td>0 – 8</td>
</tr>
<tr>
<td>Iron oxides</td>
<td>4 – 5</td>
</tr>
</tbody>
</table>

So, they are mixed together with carbonate-poor clays in order to obtain a mixture with a carbonate content as high as 15% approximately. It could seem interesting to have at disposal natural clays with the more suitable carbonate content, but that is not important from an industrial point of view, because industry always prefers to use mixtures of different clays instead of a single clay. In such a way, in fact, it is possible to optimize all the characteristics of the body and more constant characteristics are easily obtained because the natural variations of each raw material result very diluted.

Figure 4 - Ternary diagram based on mineralogical data of clays used for the production of non-porous floor tiles (after Fiori and Guarini, 1990)
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Much more characteristic is the composition of a clay for cooking-ware (table 5), because such an object must have very specific properties. Among these, the thermal shock resistance is the more important from a technological point of view.

3. Technological Properties of Dried Pieces

The properties of ceramic pieces depend not only on the used raw material but also on the adopted processing techniques. With reference to the characteristics of dried pieces,

<table>
<thead>
<tr>
<th>Carbonatic clay (CC)</th>
<th>Non carbonatic clay (NCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition (%)</td>
<td>Chemical composition (%)</td>
</tr>
<tr>
<td>SiO₂ 45.2</td>
<td>SiO₂ 71.5</td>
</tr>
<tr>
<td>Al₂O₃ 11.9</td>
<td>Al₂O₃ 12.9</td>
</tr>
<tr>
<td>TiO₂ 0.7</td>
<td>TiO₂ 0.6</td>
</tr>
<tr>
<td>Fe₂O₃ 5.1</td>
<td>Fe₂O₃ 4.7</td>
</tr>
<tr>
<td>MnO 0.1</td>
<td>MnO 0.1</td>
</tr>
<tr>
<td>MgO 2.9</td>
<td>MgO 1.5</td>
</tr>
<tr>
<td>CaO 14.9</td>
<td>CaO 0.9</td>
</tr>
<tr>
<td>Na₂O 0.8</td>
<td>Na₂O 1.0</td>
</tr>
<tr>
<td>K₂O 2.3</td>
<td>K₂O 2.0</td>
</tr>
<tr>
<td>P₂O₅ 0.1</td>
<td>P₂O₅ 0.1</td>
</tr>
<tr>
<td>I.L. 16.3</td>
<td>I.L. 5.1</td>
</tr>
<tr>
<td>&lt; 4 µm 65.0</td>
<td>&lt; 4 µm 31.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th>CC</th>
<th>NCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing water (%)</td>
<td>22.4</td>
<td>20.1</td>
</tr>
<tr>
<td>Linear shrinkage (%)</td>
<td>6.8</td>
<td>5.3</td>
</tr>
<tr>
<td>Bending strength (kg/cm²)</td>
<td>84</td>
<td>53</td>
</tr>
<tr>
<td>Open porosity (%)</td>
<td>23.0</td>
<td>21.2</td>
</tr>
<tr>
<td>Mean diameter φ₅₀ (µm)</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Sorting index</td>
<td>0.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>
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Table 6 — Characteristics and drying properties of pieces made of carbonatic and non-carbonatic clays by extrusion

<table>
<thead>
<tr>
<th></th>
<th>Carbonatic clay (CC)</th>
<th>Non carbonatic clay (NCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition (%)</td>
<td>Mineralogical composition and grain size distribution (%)</td>
<td>Chemical composition (%)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>45.2</td>
<td>Quartz</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.9</td>
<td>Feldspars</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.7</td>
<td>Calcite</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.1</td>
<td>Illite</td>
</tr>
<tr>
<td>MnO</td>
<td>0.1</td>
<td>Chlorite</td>
</tr>
<tr>
<td>MgO</td>
<td>2.9</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>CaO</td>
<td>14.9</td>
<td>Smectite</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.8</td>
<td>Fe-oxide et al.</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.3</td>
<td>&gt; 100 \mu m</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.1</td>
<td>100-20 \mu m</td>
</tr>
<tr>
<td>L.L.</td>
<td>16.3</td>
<td>20-4 \mu m</td>
</tr>
<tr>
<td>&lt; 4 \mu m</td>
<td>65.0</td>
<td>&lt; 4 \mu m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th>Processing water (%)</th>
<th>Linear shrinkage (%)</th>
<th>Bending strength (kg/cm²)</th>
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<th>Mean diameter φ₅₀ (μm)</th>
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</tr>
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<tr>
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<td>0.1</td>
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<td>5.3</td>
<td>53</td>
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<td>0.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>
5. Microstructural Characteristics of Fired Bodies

Some microstructural characteristics of the fired bodies are reported in table 8. They are derived from the cumulative curves obtained by mercury intrusion porosimeter. Open porosity in the carbonatic body (33.5%) is very higher than the non-carbonatic body (23.9%). Such a difference is a consequence of the reaction during firing, because the porosity after drying was practically the same (approximately 22 and 20% respectively. In other words, firing of non-carbonatic bodies has a very small consequence as open porosity is regarded. On the contrary, the presence of a large quantity of carbonate minerals favours a conspicuous increase of porosity depending on the volatilization of water and carbon dioxide and the subsequent formation of calcium silicate minerals.

<table>
<thead>
<tr>
<th>Microstructural Characteristic</th>
<th>CC</th>
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<tbody>
<tr>
<td>Open porosity (%)</td>
<td>33.5</td>
<td>23.9</td>
</tr>
<tr>
<td>Mean pore diameter (μm)</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
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<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The above process also produces an enlargement of the pore dimensions. In fact, mean pore diameter ($\phi_{50}$) was 0.1 μm after drying and 0.5 μm after firing. The same type of variation can be observed for the non-carbonatic clay, whose mean pore diameter varies from 0.4 μm to 1.4 μm. The change of the pore dimensions is due to a reassessment of the microstructure, that means a combination of the previous cavities and so forming new bigger pores.

The pore enlargement implies a decrease of the pore sorting, leading to practically the same sorting index ($\log_{10}(\phi_{90}/\phi_{10})$, $\phi$ in amstrong) for both types of clay. Of course, the microstructural rearrangement is favoured by the “matter mobility” during firing, when a molten phase develops. In the case under examination, the mobility should be greater in the carbonatic body, because it is finer and contained a higher amount of clay minerals.
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Table 8 – Microstructural and technological properties of fired bodies

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due to firing (from dried to fired) is high in both cases, but the variation is from 53 to 99 kg/cm² for NCC and from 84 to 305 kg/cm² for CC. This last value is very close to the empirical limit of mechanical resistance obtainable for illitic-chloritic clay based ceramics (Fabbri and Dondi, 1995c).

Speaking in general terms, the increase of mechanical resistance during firing is due to the union of the particles which constitute the raw material. This process occurs in a very greater measure in the carbonatic clay, so the observed trends are clearly explained.

Table 9 - Technological properties and frost resistance of fired bodies

<table>
<thead>
<tr>
<th>Technological properties</th>
<th>CC</th>
<th>NCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%)</td>
<td>17.3 ± 0.3</td>
<td>14.7 ± 0.1</td>
</tr>
<tr>
<td>Linear shrinkage (%)</td>
<td>9.0 ± 0.8</td>
<td>6.2 ± 0.2</td>
</tr>
<tr>
<td>Bending strength (kg/cm²)</td>
<td>305 ± 52</td>
<td>99 ± 11</td>
</tr>
<tr>
<td>Critical diameter (μm)</td>
<td>0.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Maage’s durability factor</td>
<td>26</td>
<td>97</td>
</tr>
</tbody>
</table>

7. Frost Resistance

A very particular property to be taken into account is frost resistance. It can be indirectly forecast by considering two parameters that can be obtained from the pore size distribution: pore critical diameter (ϕ₉₀) and Maage’s durability factor (table 9).

According to the first method, the products are defined frost resistant when ϕ₉₀>1.8 μm and not frost resistant if ϕ₉₀<0.5 μm.

According to the Maage’s method, the products can be retained frost resistant or not frost resistant when the durability factor is higher or lower than 70 respectively (Winslow et al., 1988). The Maage’s durability factor is calculated by the equation DF = 3.2/PV + 2.4P3, where PV is the specific pore volume (cm³/g) and P3 the percentage of pores larger than 3 μm.

In our case, both critical diameter and durability factor indicate that the non-carbonatic body is frost resistant. As the carbonatic clay is regarded, DF indicates a not frost resistant product, while the critical diameter does not supply a reliable forecast, because the value is between 0.5 and 1.8 μm, that is an uncertainty interval of the method.
due to firing (from dried to fired) is high in both cases, but the variation is from 53 to 99 kg/cm² for NCC and from 84 to 305 kg/cm² for CC. This last value is very close to the empirical limit of mechanical resistance obtainable for illitic-chloritic clay based ceramics (Fabbri and Dondi, 1995c).

Speaking in general terms, the increase of mechanical resistance during firing is due to the union of the particles which constitute the raw material. This process occurs in a very greater measure in the carbonatic clay, so the observed trends are clearly explained.

Table 9 – Technological properties and frost resistance of fired bodies

<table>
<thead>
<tr>
<th>Technological properties</th>
<th>CC</th>
<th>NCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%)</td>
<td>17.3 ± 0.3</td>
<td>14.7 ± 0.1</td>
</tr>
<tr>
<td>Linear shrinkage (%)</td>
<td>9.0 ± 0.8</td>
<td>6.2 ± 0.2</td>
</tr>
<tr>
<td>Bending strength (kg/cm²)</td>
<td>305 ± 52</td>
<td>99 ± 11</td>
</tr>
<tr>
<td>Critical diameter (µm)</td>
<td>0.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Maage’s durability factor</td>
<td>26</td>
<td>97</td>
</tr>
</tbody>
</table>

7. Frost Resistance

A very particular property to be taken into account is frost resistance. It can be indirectly forecast by considering two parameters that can be obtained from the pore size distribution: pore critical diameter (φ₉₀) and Maage’s durability factor (table 9).

According to the first method, the products are defined frost resistant when φ₉₀>1.8 µm and not frost resistant if φ₉₀<0.5 µm.

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Experimental data from kaolinite synthesis and from soil kaolinite in a catchment (Sierra Nevada, Spain) provide times of kaolinite formation of the same order of magnitude.

1. Introducción

Las visiones que se poseen sobre algunos aspectos relacionados con los minerales de la arcilla son muy variables. En general, la que más se aparta de la realidad es la que se refiere al tiempo necesario para su formación. El hecho de identificar a algunas asociaciones arcillosas con su aparición en algunos períodos geológicos concretos puede hacer pensar en un tiempo de formación muy grande. En otras ocasiones, todo lo más que se llega es a conocer su ubicación en un entorno determinado terrestre y, en el mejor de los casos, su posible génesis. En otros casos más particulares, las arcillas se identifican como un mero producto químico comercial, sobre el que se realizan estudios concretos y no se tiene sobre ellas ninguna noción sobre su procedencia, ambiente en que se originaron y mucho menos sobre el tiempo necesario para su formación.

Desgraciadamente, en la bibliografía internacional existe un aparente desinterés por el tema del tiempo en los minerales, por lo que son muy pocos los trabajos que se ocupan directamente de este asunto.

El tema cobra hoy un especial interés, por un lado, en relación con la deseable capacidad de regeneración del suelo frente a la erosión hídrica y eólica, y por el efecto de lluvias ácidas. Los minerales de la arcilla, como componentes fundamentales de los suelos, deben tener una velocidad de formación superior a la de erosión o degradación química del suelo, pues si no los suelos se destruirían en poco tiempo.

Por otro lado, existen en el mundo muchos grandes yacimientos casi monominerálicos de algunos de los minerales de la arcilla. Estos suelen ser, fundamentalmente, de origen hidrotermal o sedimentario. A la hora de evaluar recursos y tener en cuenta las cantidades enormes que se extraen de las canteras es lógico que se piense en lugares donde puedan existir condiciones actuales de formación de esos yacimientos minerales para tener nuevas reservas. Para efectuar estas previsiones es
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El grado de desarrollo de un suelo depende de la intensidad de los procesos formadores, de la susceptibilidad de los materiales a su transformación y del tiempo de actuación de los procesos.

Puede definirse un "tiempo de formación" del suelo como el lapso transcurrido desde que una roca aflora en superficie hasta que se origina un "perfil" de suelo con sus horizontes característicos, mediante una serie de procesos geoquímicos, biológicos y edáficos. Este concepto implica un "tiempo cero" a partir del cual comienza a transcurrir la edad (Linares, 1995). Durante ese tiempo se ha debido formar una cierta cantidad de minerales secundarios, entre los que deberá haber seguramente minerales de la arcilla.

El suelo, sin embargo, es erosionado gradualmente. En la mayoría de los casos debe existir un cierto equilibrio entre velocidad de erosión y velocidad de formación. El suelo se hace inestable si la erosión supera a la formación.

Cada año, por ejemplo, se denuda una capa superficial de suelo y se forma otra, destruyéndose la roca infrayacente. De esta forma la superficie del suelo va descendiendo y las formas del terreno tienden hacia la penillanura. Debe existir un momento en que el descenso de la superficie del suelo alcance la profundidad inicial del perfil. En este momento, puede hablarse de renovación del suelo. El "tiempo de renovación" del suelo es aquel que tarda en denudarse un perfil completo, lo que equivale a decir que el perfil entero se ha renovado (Linares, 1995). En ese tiempo se han tenido que renovar también todos los minerales de la arcilla existentes en ese suelo.

El "tiempo de formación" y el "tiempo de renovación" no tienen por qué ser de igual duración. Un suelo "vivo" puede poseer unas condiciones algo más agresivas que una simple alteración geoquímica de una roca, pero también los minerales secundarios neoformados pueden recubrir a los primarios e impedir o disminuir su hidrólisis. Estos y otros condicionantes hacen que ambos tipos de tiempos puedan ser diferentes.

Con estos planteamientos la visión del suelo es, entonces, completamente dinámica y no tiene mucho sentido hablar de edad del suelo. En efecto, en principio, no deberían encontrarse materiales con edad superior al tiempo equivalente a un "tiempo de renovación", ya que todo el material precedente a este tiempo ha debido ser erosionado. Los materiales secundarios de un suelo en el momento de su estudio no pueden ser más
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cuenca por escorrentía. La diferencia entre ambas cantidades representa el resultado de los procesos de disolución e hidrólisis que ocurren en la cuenca. Se admite que, normalmente, la descarga hacia aguas subterráneas es despreciable frente a la escorrentía superficial. Por otra parte, se ha podido demostrar que los extractos acuosos del suelo poseen una composición similar a la de las aguas de drenaje y escorrentía superficial (Barahona et al. 1982; Delgado et al. 1982; White, 1995). En puntos convenientes se realizan medidas de flujo y de composición química y temperatura de las aguas. Las medidas deben hacerse durante largos espacios de tiempo. Asimismo, deben recogerse aportes hídricos y eólicos procedentes de la atmósfera. Estas cantidades deben sustraerse de las anteriores para realizar el balance global. En ocasiones conviene introducir datos del cambio de solutos debido a la biomasa y a las posibles reacciones de intercambio catiónico. De todas las cantidades mencionadas como aportes las procedentes de la atmósfera son las más importantes. Independientemente, se realiza el estudio tipológico y mineralógico de los suelos de la cuenca, y por comparación con los minerales primarios de las rocas se establecen todas las reacciones de meteorización lógicamente posibles. Los equilibrios químicos de estas reacciones tienen que estar de acuerdo con los solutos analizados procedentes de la escorrentía. El encaje entre ambas series de datos no es difícil y al final se calculan las cantidades de minerales primarios destruidos, por ejemplo, anualmente y las cantidades de minerales secundarios neoformados al año. De esta forma se cuantifica una cantidad máxima de minerales de la arcilla formados anualmente, ya que siempre cabe la posibilidad de que algunas de las especies en solución que proceden de los minerales primarios sean eliminadas por escorrentía antes de que puedan reaccionar entre sí y formar un nuevo mineral de la arcilla (Delgado et al. 1981; Velbel, 1986; Drever y Clow, 1995).

Otra posibilidad de obtener velocidades de meteorización de minerales primarios en suelos es el seguimiento de las marcas de disolución que se generan en su superficie. En los diferentes minerales primarios pueden observarse marcas de disolución, que normalmente están relacionadas con defectos, direcciones preferenciales de crecimiento, etc. La cantidad, densidad y profundidad de las marcas es una función de la duración del proceso de disolución. En algunos de los estudios realizados se muestra que la mayor parte de las marcas se producen dentro de los 7500 primeros años. Después, el avance de la disolución...
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Desde hace tiempo se viene resaltando el papel que puede desempeñar la materia orgánica en el aumento de la velocidad de disolución de los minerales primarios. La literatura es abundante y contradictoria en este tema. En la revisión reciente de Blum y Stillings (1995) se concluye que los datos existentes permiten afirmar que la materia orgánica, en realidad los ácidos orgánicos, solo incrementan la velocidad de hidrólisis de los minerales en un factor del orden de dos.

La velocidad de formación de los minerales secundarios en cualquier ambiente geoquímico tiene que estar relacionada con la velocidad de destrucción de los minerales primarios, siempre que la solución en contacto no contenga elementos necesarios para las estructuras minerales secundarias en cantidades muy abundantes. En las alteraciones superficiales las concentraciones de las soluciones suelen ser muy próximas al agua de lluvia a excepción del contenido en $\text{CO}_2$ que puede ser mucho más elevado en los suelos. Por eso, es interesante considerar las velocidades de disolución de los minerales primarios, ya que ellas van a dar una indicación del tiempo requerido para formar los minerales secundarios de la arcilla, que es el objeto de nuestro comentario.

Desde hace mucho tiempo se conoce que unos minerales se alteran más rápidamente que otros. Se ha puesto de manifiesto que, en general, el orden de alterabilidad de los minerales es inverso al de la serie de Bowen (Goldich, 1938). La disolución de un mineral implica la ruptura de enlaces entre los átomos de un cristal, por lo que este proceso estará afectado por la fortaleza del enlace, el tipo de estructura cristalina y el quimismo del medio. En muchas ocasiones no se conoce bien el mecanismo del proceso de disolución. Actualmente, las técnicas de cálculo de "Modelización Molecular" (métodos "ab initio" y de Monte Carlo) están permitiendo conocer con cierto detalle los pasos por los que transcurre el proceso de disolución de algunos minerales. Uno de los temas que ha suscitado, y suscita aún, mayor interés es la presencia o ausencia de una capa de alteración sobre las superficies de los cristales. Este tema continúa abierto ya que se siguen presentando argumentos y datos a favor y en contra de la existencia de esta capa de alteración superficial, dependiendo de las condiciones de alteración.
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En el caso de las biotitas la alteración se inicia con la oxidación del Fe$^{3+}$ y una pérdida de potasio. Por ejemplo, la biotita puede pasar a interestratificados y finalmente a vermiculita o, incluso a caolinita. Se han encontrado crecimientos topotácticos de esmectitas sobre biotitas.

Piroxenas y anfíboles pueden mostrar "coherencia" con sus productos de alteración. Eggleton (1986) mostró que existía una concordancia perfecta entre parámetros de la red del silicato primario y la red trioctaédrica del talco secundario, al menos en las primeras etapas de la alteración. Después comienzan a aparecer oxihidróxidos de hierro que provocan deformaciones en los cristales incipientes de talco, aumentando entonces la velocidad de alteración.

Los olivinos son uno de los minerales menos resistentes a la meteorización. La disolución comienza a lo largo de grietas superficiales. Los productos de alteración son muy variados: saponita, serpentina, clorita, esmectita, goetita, hematites, etc. No se han observado fenómenos de "coherencia" entre el olivino y sus minerales secundarios. Al igual que en el caso de los piroxenas y anfíboles suele existir una cierta orientación de los cristales de mineral primario con los del secundario.

Estos resultados sugieren que en algunos casos la velocidad de disolución de los minerales primarios coincide, más o menos, con la velocidad de crecimiento o formación de los minerales de la arcilla secundarios. Esto es especialmente cierto en los casos en que la transformación se hace prácticamente en estado sólido, es decir, cuando se conservan parte de los componentes esenciales de las estructuras primitivas. El problema viene cuando los minerales primarios se disuelven. Los solutos ¿reaccionan inmediatamente para formar un mineral secundario? La respuesta es que, en general, sí. En el suelo y en otros ambientes superficiales, el aluminio y el hierro son muy poco móviles, al tender a precipitar a los valores de pH que existen en estas zonas (cercanas a la neutralidad). Debe ser muy normal que no viajen muy lejos del mineral primario y precipiten como oxihidróxidos o como silicatos, si existe sílice en solución. Este último caso es el más probable ya que siempre existen cantidades suficientes de sílice en las soluciones superficiales como para poder precipitar filosilicatos de la arcilla (Reyes et al. 1982a y b).
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5. Diferencias entre las velocidades naturales y experimentales

Las velocidades determinadas experimentalmente (cinética de disolución de minerales puros) son, normalmente, más rápidas que las determinadas para casos naturales (por balances geoquímicos en cuencas fluviales o por marcas de disolución). Existen varios problemas que impiden en algunas ocasiones comparar ambos tipos de velocidades. Uno de los problemas principales está en establecer el área superficial de los minerales primarios en los suelos, de forma individualizada. En el caso de los estudios de disolución en el laboratorio se suele usar el método BET para este fin, pero en las muestras naturales es prácticamente imposible obtener fracciones monomeronéricas de los distintos minerales. Hay que realizar estimaciones del área geométrica por medio de estudios microscópicos.

Existen algunas razones que explican la aparente controversia entre las velocidades obtenidas en el laboratorio y aquellas obtenidas en el medio natural (Drever y Clow, 1995):

a) Se ha observado el "envejecimiento" de las superficies de los cristales primarios. A medida que avanza su disolución van desapareciendo sus puntos débiles, lo que hace disminuir la velocidad de ataque. Además, es normal que se formen recubrimientos de minerales secundarios (arcillas u oxihidróxidos) que impiden un buen contacto de los cristales con el agua.

b) En otros casos se ha invocado la presencia de altas concentraciones de especies de aluminio que inhiben la disolución de los silicatos primarios.

c) Las concentraciones iónicas de la solución del suelo es en ocasiones muy próxima al equilibrio con los minerales primarios. De esta forma se retarda o minimiza su disolución.

d) En general, se supone que la solución de percolación del suelo tiene composición constante, lo que no es realista. Es conocido que en el suelo existe un sistema poroso muy complejo. Hay muchas razones para pensar que la solución del suelo en los microporos, por ejemplo, es muy diferente de la de los macroporos, que debe ser la normal de percolación.

6. Unos casos prácticos de cinética mineral

Para concretar algunas de las ideas expuestas se va a describir a continuación dos aproximaciones al tiempo de formación de caolinita en ambientes naturales. Por una parte,
5. Diferencias entre las velocidades naturales y experimentales

Las velocidades determinadas experimentalmente (cinética de disolución de minerales puros) son, normalmente, más rápidas que las determinadas para casos naturales (por balances geoquímicos en cuencas fluviales o por marcas de disolución). Existen varios problemas que impiden en algunas ocasiones comparar ambos tipos de velocidades. Uno de los problemas principales está en establecer el área superficial de los minerales primarios en los suelos, de forma individualizada. En el caso de los estudios de disolución en el laboratorio se suele usar el método BET para este fin, pero en las muestras naturales es prácticamente imposible obtener fracciones monomonerálicas de los distintos minerales. Hay que realizar estimaciones del área geométrica por medio de estudios microscópicos.

Existen algunas razones que explican la aparente controversia entre las velocidades obtenidas en el laboratorio y aquellas obtenidas en el medio natural (Drever y Clow, 1995):

a) Se ha observado el "envejecimiento" de las superficies de los cristales primarios. A medida que avanza su disolución van desapareciendo sus puntos débiles, lo que hace disminuir la velocidad de ataque. Además, es normal que se formen recubrimientos de minerales secundarios (arcillas u oxihidróxidos) que impiden un buen contacto de los cristales con el agua.

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cuenca de recepción fluvial de alta montaña con mínimas influencias antrópicas. Se determinó el balance de meteorización anual a partir de la composición de las aguas del río que drena el área y de las principales reacciones de meteorización de los diferentes minerales primarios. El ajuste numérico entre ambos tipos de datos fue muy aceptable. El resultado mostró que se pierden por disolución cantidades importantes de moscovita, paragonita, oligoclasa, hornblenda, dolomita, calcita y clorita, alcanzando un total de unas 400 ton anuales para un área de cuenca de 28.3 km², a una temperatura media anual de 8 °C.

Estos valores requieren un pequeño comentario. En principio, puede parecer que la cantidad destruida de minerales es excesiva. Sin embargo, puede demostrarse que para un espesor medio de los suelos de la zona de un metro y con una densidad aparente del material edáfico de 2 g/cm³, la pérdida de suelo alcanza el 0.007% cada año. Este valor es muy razonable y muestra que la meteorización en realidad es muy pequeña. Por eso, a escala humana el suelo se percibe como una imagen fotográfica, instantánea, estática. (No obstante, la pérdida de suelo al cabo de, por ejemplo, 10000 años es del 70 %).

La cantidad correspondiente de caolinita neoformada cada año es de 102068 kg para el total del área estudiada, lo que que representa 3.6 g/año.m² de suelo. Esta última cantidad parece muy aceptable y está de acuerdo con el balance global mineralógico efectuado también por los autores (Delgado et al., 1981).

Teniendo en cuenta estos datos, Barahona et al. (1987) han calculado el tiempo de formación de dichos suelos. El tiempo estimado es de unos 2500 años para el suelo medio de la zona (100 cm de profundidad), lo que también está de acuerdo con otros datos geomorfológicos de la región. Si se estima la profundidad a la que se encuentra caolinita en cantidad detectable por difracción de rayos X (258 cm), el tiempo estimado para la formación de todo ese sistema edáfico alcanza los 6600 años.

6.3. Comparación de ambos métodos

Se trata ahora de verificar si existe concordancia entre los datos de cinética de síntesis en el laboratorio y de neoformación natural de caolinita en suelos. Para ello podemos suponer que la transformación del material caolinitizable del suelo en caolinita tiene lugar a través de un proceso en dos etapas: 1) disolución de los minerales primarios
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disolución de los minerales secundarios, los resultados parecen muy aceptables como primera aproximación.

Se demuestra de esta manera cómo los ensayos de laboratorio son complementarios a los estudios de campo y ambos pueden llegar a conclusiones similares, por lo que se pueden considerar aproximaciones diferentes pero complementarias a un mismo problema.

Estos resultados permiten extraer una conclusión importante: la formación de minerales de la arcilla es relativamente rápida desde el punto de vista geológico, pero tiene una duración que excede con creces la magnitud de la vida humana.

7. Epílogo

La conclusión más importante de todo lo que se ha comentado es, precisamente, esa pequeña de la vida humana frente a los tiempos que marca la naturaleza y, concretamente, el tiempo necesario para formar, por ejemplo, una tonelada de un mineral de la arcilla particular.

Una consecuencia de eso es que los suelos, uno de los medios más idóneos para la

Figura 1. Estimación del contenido en caolinita en suelos de la cuenca alta del río Dílar (Sierra Bevada, Granada).
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ARCHAEOOMETRY OF ROMAN CERAMICS FROM SUASA (ITALY):
EVIDENCES OF LOCAL AND FOREIGN PRODUCTION

N. Morandi, M. C. Nannetti & C. Tampellini

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Abstract

Four distinct classes of ceramic, coming from the Roman city of Suasa (AN, Italy), and a large number of samples of clay and local ceramics were studied. Mineralogical analyses were performed optically on thin sections and by diffractometry (XRD). Chemical analyses were carried out using XRF to identify the principal oxides and 15 trace elements. Chemical data were processed using cluster analysis. Within each of the considered ceramic classes cases of uncertain or incorrect archaeological attribution, imitation and possible importation were easily identified and distinguished. The complete cluster of the entire population is a considerable help in distinguishing between locally produced and imported products. It was found that significant differentiation was not obtained if the cluster was limited to the principal oxides.

Introduction

As part of research carried out jointly between the Dipartimento di Archeologia and the Dipartimento di Scienze della Terra e Geologico-Ambientali (Bologna University) on ceramic material coming from the Roman city of Suasa (AN, Italy), the geochemical and mineralogical characterization of the finds were examined.

The study of four distinct classes of ceramics and a large number of samples of clay and local ceramics enabled cases of uncertain or incorrect archaeological attribution, imitation and possible importation to be identified and distinguished.

The objective of this research was to examine a large group of cases and verify the existence of a parameter or series of parameters useful in reconstructing the origin of raw materials or distinguishing between local and imported products.
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skilled local craftsmen. Eight samples stood out clearly in the cluster in Fig. 1 for the macroscopic differences in their chemical composition. The low level of kinship between them suggests that these are imported samples with extremely different origins (Morandi N. et al., 1998a).

The fragility of the pieces belonging to this class of ceramics prevented a sufficient number of samples from being examined in thin section to verify the type of temper commonly used. Diffractometric examination revealed the consistent presence of quartz and feldspars and a more sporadic presence of clinopyroxenes, micas, iron oxides and gehlenite.

2 - “Terra sigillata” (TS)

Fine ceramics used for serving plates and tableware (plates, bowls, goblets and vessels). The samples have a glossy surface (red, orange or dark grey). In some cases they are decorated, often smooth. The body is very fine and obtained from barely purified carbonated clays worked on a wheel (Pucci G., 1981).

Chemical characteristics: the most distinctive feature is the CaO% content which allowed three sub-groups to be identified: low content (~2%) (specimens imported from Africa), medium and high (~11%) (mid-Adriatic products). All the chemical variables taken together showed TS 5 and 6 samples to have values somewhere between those of the two types of product identified. As a result they are not easy to attribute. The cluster (Fig. 2) shows a clear distinction between the three groups described (Nannetti M.C. et al., 1996).

With regard to the characteristics of the framework fraction, various groups can be identified: mainly quartzous and abundant temper in the case of African imports while the mid-Adriatic terra sigillata group also includes several fragments of rock with less uniform dimensions than in the African specimens. XRD revealed the presence of quartz and feldspars with the sporadic presence of calcite, clinopyroxenes, gehlenite and hematite.

3 - “cooking ceramics” (CC)

This is crockery for kitchen use (plates and covers used with saucepans and casseroles, bowls and cooking pots) suitable for cooking over a flame or for serving
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polishing in bands or strips on the external or internal wall; glaze or engobe on the internal wall and more rarely on the external wall, coarse body and high temper content (Tortorella S., 1981).

The chemical characteristics show a low CaO content (2-3%) with some macroscopic exceptions in the case of a number of samples in which there is also an excess of Ba. In short, there is a close kinship between the various samples considered, although the considerable variations noted for individual factors prevent certain archaeological attribution (Mazzeo L. et al., 1997).

Mineralogical examination revealed a rich and diversified skeletal fraction. The granulometry is always coarse. In some cases, well formed crystals of sparry calcite were present in the temper. Quartz, feldspars, micas, amphiboles, garnet, zircon and epidotes (very frequently) were observed together with the occasional presence of calcite. Highly variable fragments of rock were consistently present. In addition to quartz, feldspars and calcite, XRD also revealed the presence of gehlenite and clinopyroxene, not always visible optically.

4 - “everyday ceramics” (COM)

These are unrefined pottery used for poor quality tableware (goblets, plates, jugs, bottles and jars). The body is uncoloured and consists of partially purified, relatively fine, clay (finer than the one used for cooking ceramics) (Tortorella S., 1981).

Among the chemical characteristics, the CaO values were the most distinctive. The majority of samples fluctuated around 12% and the more marked divergences were interpreted as incorrect attributions with reference also being made to their archaeological characteristics. The cluster (Fig. 3) grouping together cooking ceramics (CC) and everyday ceramics (COM) shows a distinction between the two populations (although this was not particularly marked), with three cases of imprecise attribution of everyday ceramics. It also identifies three samples which may not have been produced locally because of their lack of chemical kinship.

In these samples, optical and diffractometric examination showed phase variability in the temper similar to that of cooking ceramics. There is abundant temper; the granulometry is fine to medium; quartz, feldspars, mica, amphiboles,
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within the entire population of samples of ceramics from Suasa (Fig. 5) proved to be of interest. The distribution of points clearly shows a direct correlation between the two variables, enabling an ideal line to be drawn reflecting the geochemical coherence of Ca and Sr in the structure of the calcite which has reached equilibrium in the waters of the ocean. In addition to the group of well aligned points on this ideal line, there are also a number of samples located above and below it. The first can be attributed to the presence of additional Sr bearing minerals in the clay raw material. The second can be explained by considerable additions of sparry calcite (as a temper) coming from saccharoidal marble debris, known to be impoverished of Sr during the metamorphic process. All this demonstrates that the nature and possibly also the origin of the carbonate temper added can be known with a fair degree of accuracy.
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Conclusions

Examination of several Roman ceramics from Suasa shows that it is possible to distinguish cases of importation, imitation and uncertain or incorrect archaeological attribution. This can be made by the statistical processing of chemical data (principal and trace elements) together with optical and diffractometric analysis. It is also useful the comparison between the archaeological characteristics and the mineral-geochemical features of samples of local clay and kiln waste from local production. The complete cluster of the entire population is a considerable help in distinguishing between locally produced and imported products. Definition of the non-local production site is still entrusted to a much more extensive number of specimens including samples of the same age coming from places which although geographically distant are culturally linked to the population undergoing archaeometric definition. Finally, it was found that significant differentiation was not obtained if the cluster was limited to the principal oxides.

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DO MARINE CLAYS RECORD PALEOCLIMATES?

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Introduction

Scientist have for a long time been trying to interpret clay assemblages in marine series. Early studies often hesitated between inheritance from the continent and authigenesis within the basin. Many of them showed the predominance of inheritance in the distribution of recent marine clay minerals (Rivière & Visse, 1954; Weawer, 1958; Pinsak & Murray, 1960), whereas, smectites were often regarded as symptomatic of marine environments in ancient series (Millot, 1949; Lucas, 1962; Peterson, 1962). Furthermore, differential settling of the clay minerals during sedimentation processes were thought to explain the gradual illite and smectite enrichment of the clay minerals away from the major river months (Weawer, 1958; Whitehouse et al., 1960).

The debate has carried on ever since. During the sixties, numerous studies were devoted to clay minerals suites in recent sediments of the world oceans. Global maps of mineral distribution show that the basic zonation of clay minerals in the oceans is controlled by the contemporary climates on the continents (Griffin et al., 1968; Biscaye, 1976; Windom, 1976). It has therefore been inferred that marine clay minerals are in general directly inherited from the continents, and especially from their soils. Nevertheless, there are number of expections in the latitudinal zonation of clay minerals in the oceans, suggesting that the climate is not the only factor responsible for the distribution of terrigeneous clay minerals. For example, the clay minerals distribution in the Western Indian Ocean do not show any latitudinal distribution (Kolla et al., 1976, 1981). The suites are clearly controlled by terrigeneous inputs around the continents (Asia, India and Australia), but in the centre of the ocean there is an abundance of smectite which must be the result of the other processes. The most commonly proposed
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direct dating by radiometric methods, such as K-Ar applied to alunite, as well as to manganese oxide which contains potassium (cryptomelane and hollandite). Variations of stable isotopes ($^{13}$C, $^{18}$O, D) have also been used for "indirect" dating of regoliths based on the changing composition of the atmosphere, either globally or in response to climatic variations, or latitudinal drift.

Distribution of bauxitic paleosurfaces in the present landscapes

Bauxite and thick kaolinitic profiles are especially well developed on the Cretaceous-Early Tertiary planation surfaces of the continents which result from the break-up of the Gondwana and still form extensive parts of present-day landscapes (Grandin & Thiry, 1983).

Large bauxite deposits of Late Mesozoic-Early Tertiary age are known in western and Equatorial Africa (Grandin; 1976; Michel, 1978; Boulangé, 1984; Schwarz, 1997), in East Africa (Bishop, 1966; Mutakyahwa & Valeton, 1995) and South Africa (Horn, 1983). In India, basalt plateaus of the Deccan Peninsula and the Kathiarwar block are covered by bauxite and laterite locally overlain by Tertiary sediments (Bardossy & Aleva, 1990; Valeton & Wilke, 1993). Extensive surfaces covered by laterite and bauxite of Late Cretaceous-Early Tertiary age are also described around the Guyana shield (Aleva, 1979) and in Brazil, where laterite and bauxite cover about 65% of the surface; ancient bauxite occurs especially in the eastern part of Central Brazil and the Atlantic shield (Melfi et al., 1988; Boulangé & Carvalho, 1989; Valeton et al. 1997). In Australia there are also large areas of ancient bauxite and related kaolinitic profiles (Daily et al., 1974; Loughnan & Sadleir, 1984; Anand et al., 1991). In North America, the Appalachian Piedmont supports several bauxite deposits (Gordon et al., 1958; Lukas et al., 1983) related to a deeply weathered paleosurface that forms a large part of the present-day piedmont (Fastovsky et al., 1989; Reinhardt & Sigleo, 1983).

Isotopic dating

The analysis of the oxygen-isotope composition of various regolith profiles and kaolinitic sediments across Australia has made it possible to distinguish profiles formed in the Late Paleozoic and Late Mesozoic-Early Tertiary from those formed during the Mid-Tertiary during the northward drift of the continent (Bird & Chivas, 1989, 1993). All these profiles are still cropping out and constitute a major part of the Australian continent.
direct dating by radiometric methods, such as K-Ar applied to alunite, as well as to manganese oxide which contains potassium (cryptomelane and hollandite). Variations of stable isotopes ($^{13}$C, $^{18}$O, D) have also been used for "indirect" dating of regoliths based on the changing composition of the atmosphere, either globally or in response to climatic variations, or latitudinal drift.

**Distribution of bauxitic paleosurfaces in the present landscapes**

Bauxite and thick kaolinitic profiles are especially well developed on the Cretaceous-Early Tertiary planation surfaces of the continents which result from the break-up of the Gondwana and still form extensive parts of present-day landscapes (Grandin & Thiry, 1983).

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heights (Simon-Coinçon, 1989). The first Alpine tectonic movements were perceptible during the Early Tertiary and the warm and humid climate of the Cretaceous became drier (Frakes et al., 1992). The instability of the relief, together with the climatic change, caused rheexistasy (Erhart, 1956): the alterite was eroded, causing the onset of the most important detrital discharge of the whole Tertiary in western Europe (Blanc-Valleron & Thiry, 1997). This "Siderolithic" discharge was not synchronous everywhere, but lasted at least from the Paleocene to the Middle Eocene, and led to large kaolinitic deposits in Germany and France. Kaolinite is also a major component of the Lower Tertiary marine deposits in the North Sea (Bjorkum et al. 1990; Pearson, 1990). This major kaolinite input to sedimentary basins occurred several Ma after its formation on the continent. At the time of its reworking the climate was no longer warm and wet, but had well marked dry seasons and the paleosols in the sedimentary deposits show mature calcrete, typical of a Mediterranean climate (Thiry, 1981; Simon-Coinçon et al., 1997; Colson et al., 1998). Moreover, kaolinite from this Cretaceous "stock" fed sedimentation locally all through the Tertiary, which is clearly visible in the terrigenous inputs in the Paris and Aquitaine Basins until the Upper Eocene and Oligocene (Trauth, 1977; Simon-Coinçon, 1989).

Scarcity of Smectitic Soils

Relative importance of smectitic soils

Smectite forms in a wide range of soils extending from dry tropical to temperate climates. Nevertheless, smectite formed in soils under temperate and Mediterranean climates contributes little to marine clays. Indeed, it seldom occurs on its own but is usually accompanied by other clay minerals like illite, vermiculite and various interstratified minerals. Thus, it is of no help in paleoclimatic interpretations of marine clays. Furthermore, from a quantitative point of view, these soils are shallow and only contribute small amounts to inherited materials during landscape erosion as unweathered bedrock and sediments are always reworked simultaneously.

Well developed smectitic soils are mostly restricted to dry tropical climates with an annual precipitation of 500-800 mm and a well marked dry season, coming with weak drained landscapes (Paquet, 1970; Bocquier, 1978; Boulet, 1978; Dudal &
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Most of the smectitic paleosols described in the literature consist of calcrete, with a low clay mineral content. Their potential contribution to the terrigenous budget of the marine deposits is therefore weak. True vertic paleosols are rarely reported: a few occurrences are described in flood plain deposits, among them Devonian vertic soils in the central Appalachians (Driese & Mora, 1993), Lower Triassic paleosols in Germany (Martins & Pfefferkorn, 1988) and Paleocene/Eocene vertic soils in the Paris Basin (Thiry, 1981).

Authigenesis of smectite in marine basins

Although the aim of this paper is not to discuss diagenetic processes that may occur in marine basins, it must be pointed out at this stage of the discussion that smectite very often develops within the basin, at the water/sediment interface during early diagenesis (Steinberg et al., 1987; Clauer et al., 1990). The development of authigenic smectite in marine basins during periods of high sea levels and/or low sedimentation rates may explain the often observed discrepancy between clay mineral assemblages in continental and shelf basins and in correlative oceanic deposits (Thiry and Jacquin, 1993). Authigenesis of smectite in marine basins explains the relative frequency and abundance of smectite in marine deposits as compared to its scarcity in soil profiles.

Weathering Rates, Reworking and Sedimentary Cycles

In order to be representative of climatic conditions, clay minerals must have reached a state close to equilibrium with their contemporaneous environment. Moreover, only in landscapes of relatively low relief, where erosion is moderate, is the eroded material derived predominantly from such soils. Low erosion rates permit soils to mature and to avoid the removal of clay minerals belonging to the substratum and irrelevant to their soil environment. If clay mineral distributions in marine/deep-sea sediments are to be interpreted in terms of changes in the clay mineralogy of the soils, the rate of soil formation must agree with that of the mineralogical changes recorded in the marine deposits. Knowledge of the weathering rates is of prime importance.

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Ancient environments

Note that geochemical weathering conditions may have changed considerably over geological times, especially because of the varying CO₂ composition of the atmosphere (Berner, 1994). Schmitt (1998) gives a striking example by modelling profiles formed respectively in a present-day environment and in a CO₂-rich atmosphere. He shows that the kaolinite assemblage in the weathering profiles is reached about three times faster (i.e., with three times less rainwater) when CO₂ abundance is increased 10 times (as predicted for the Mid-Cretaceous by the model by Berner). It means that with similar rainfall rates profiles would deepen three times faster than in present atmospheric conditions. The formation of smectite would be greatly reduced, but the increased pCO₂ has no direct effect on the appearance of gibbsite.

Time resolution of the sedimentary record

Reworking of soils will be sensitive in sedimentary deposits and indicative of climatic conditions only if the main part of the terrigenous input is directly inherited from mature soils. This can only occur if the landscape is covered with a substantial blanket of mature soils at equilibrium with the environment. Geochemical calculations, as well as geological and geomorphological occurrences of soils and paleosols, show that soil formation requires long-lasting landscape stability. A time span of at least 1 Ma seems to be necessary to form a landscape blanketed with thick kaolinitic or smectitic soils. Therefore, sequential changes in the sedimentary clay mineral assemblages with periods of less than 1Ma cannot be caused by climatic changes acting on soil mineralogy. Records of short-term changes in paleoclimates appear unrealistic; it is probable that only longer sequences are able to reflect paleoclimatic changes.

Sediment dispersal

Even if soil profiles are mature and at equilibrium with the prevailing climate, characteristic clay mineral assemblages must be eroded, transported and deposited for the climatic signal to be preserved in clastic sediments. Erosion and transport processes obviously cloud the signal to some extent, because horizons of different degrees of maturity and different soil types along regional catenas will be mixed, and frequently the bedrock will be eroded as well. A further complication may arise from the differential settling of clay minerals and the alteration of clay mineral assemblages in
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4) Soil formation rates are relatively slow. It may take one to several Ma to build
up a landscape with deep mature profiles. Terrigeneous materials are
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covered with such mature profiles. Under these conditions, only long-term
changes in the clay mineral assemblages of the sedimentary deposits may
possibly relate to paleoclimatic changes. Resolution of the paleoclimatic
record in marine clay may not be closer than 1 or 2 Ma.

5) For the climatic signal to be preserved in clastic sediments, characteristic soil
clay mineral assemblages must be eroded and transported. Erosion and
transport processes will obviously cloud the signal. Special attention has to be
paid to clay mineral transformations that may occur during successive
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basins. Transit through flood plains, where hydromorphic soils generally
prevail, may for instance seriously distort the original soil signal.

6) In every case, the arrival of the soil clay assemblages in the basin inevitably
occurs much later than their formation on the continent. In most cases, it is a
climatic change that leads to erosion reactivation and reworking of the soils
and thus introduces a discrepancy between the soil and sediment signals.

A clay particle has a long way to go from soil to marine sediment and
sedimentologists and paleoclimatologists should pay more attention to the difficulties of
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Some of the limitations can be overcome by a more critical evaluation of the data.
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MacFarlane 1981


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the montmorillonite TOT layer. For this type of interaction it is expected that some of the oxygen atoms of siloxane groups will serve as electron-pair donors, that is, their nonbonding hybridized orbitals, each with a lone pair electrons, will overlap with the antibonding orbitals of the aromatic \( \pi \) systems.

Cationic dyes, known also as basic dyes, are suitable reagents for the study of \( \pi \) interactions between aromatic cations and clay minerals. The chromogens of the cationic dyes are aromatic skeletons of several condensed benzene and heterocyclic rings or rings bound by a conjugated double bond system and the auxochromes are basic functional groups, the most important being \( \text{NH}_2, \text{NHR} \) and \( \text{NR}_2 \). They absorb light in the visible range due to \( \pi \rightarrow \pi^* \) transitions with very high extinction coefficients. In short range interactions, the location of the absorption maximum shifts according to the type of interaction (Robinson, 1994). Hence any change in the immediate environment of the dye can be detected.

During the last 30 years much work has been done in our laboratory on the adsorption of cationic dyes by different clay minerals. This includes visible and IR spectroscopy, X-ray diffraction, thermal analysis, calorimetric and electrokinetic study. In the present communication this work and some relevant work performed in other laboratories, will be reviewed. We shall discuss possible \( \pi \) interactions which may occur between the aromatic entities and the oxygen planes and possible aggregation of the dye cations in the interparticle space of flocculated clays. The contribution of these \( \pi \) interactions to the stability of adsorbed cationic radicals, which has been demonstrated for benzidine (Pinnavaia et al., 1974, Yariv et al. 1975) will not be discussed here. Possible \( \pi \) interactions between aromatic compounds and transition metals located in the sites of exchangeable cations (Mortland and Pinnavaia, 1971; Cloos et al. 1973 and 1979; Moreale et al. 1985) will also not be discussed here. The latter have been shown by several investigators to occur in the interlayer space of montmorillonite. These two types of \( \pi \) interactions should also be taken into consideration when the complete picture of adsorption of aromatic compounds by smectite minerals is considered.

**Metachromasy in aqueous solutions**

There are many cationic dyes which do not obey Beer's law in aqueous solutions; that is, the characteristic spectral features of their aqueous solutions change with concentration. For example, visible absorption spectra of metachromic dyes in different concentrations show one, two, or more maxima, the intensity of which depends on the dye concentration. The band of the dye at the longer wavelength is characteristic for a dilute solution and is usually called band \( \alpha \). Increasing dye concentration in the aqueous solution results in the gradual replacement of band
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TABLE 1: Absorption maxima (in nm) of cationic dyes in very dilute aqueous solutions (1.0-10.0 x 10^{-6} mol l^{-1}) and adsorbed by Na-montmorillonite (bentonite clay from Akli, Rajasthan). Data from Ghosal and Mukherjee (1972).

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The spectra of adsorbed SF and JG showed smaller shifts of approx. 15 nm, compared with their spectra in aqueous solutions. These were attributed to the high degree of steric hindrance in their molecular structures. The spectrum of adsorbed RB did not show any shift. Owing to structural non-planarity and the presence of projecting COOH group, steric hindrance of this dye is enhanced, so that it retains its non-aggregated form in the adsorbed state.

Recently, the effect of time on the adsorption of MB by montmorillonite up to 7 or 45 h has been studied by Breen et al. (1994 a and b) and by Gessner et al. (1994). They showed that in the first minute, metachromasy is obtained due to the rapid aggregation of the cationic dye on the external surface of the clay. A slower desorption process takes place, which tends to bring the dye inside the clay particles. At this stage the aggregated dye is transferred from one particle to another. Thus, with time, band β is replaced by band α or by a band which represents protonated MB. Schoonheydt and Heughebaert (1992) showed a similar phenomenon at a low loading of MB on Na-Laponite.

**Adsorption of metachromic dyes by smectite minerals**

The adsorption of the following metachromic dyes from aqueous solutions by different smectite minerals was investigated in our laboratory: methylene blue (MB), thionin (TH), acridine orange (AO), pyronin Y (PY), crystal violet (CV), ethyl violet (EV), cresyl violet acetate (CRV), rhodamine B (RB) and rhodamine 6G (R6G) (Appendix I). The smectites were montmorillonite, saponite, beidellite and Laponite saturated with different exchangeable cations. Smectite clay minerals reveal a high affinity for metachromic cationic dyes. When an
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appears even at a very low dye loading, e.g., less than 2 mmol CV or EV per 100 g clay. The appearance of band β indicates that the dye is involved in π interactions which may occur either between two or more dye cations, aggregated on the clay surface, as suggested by Gmann and O'Konskii (1963) or between oxygen planes of the TOT layers and monomeric dye cations, as suggested by Yariv (1988), or it is possible that the two interactions occur.

Fig. 1: Absorption spectra of CV (left) and EV (right), (a) an aqueous solution (4.0x10^-5 M) and of the same solution containing increasing amounts of montmorillonite. Degree of saturation are as follows: (b) 200; (c) 100; (d) 50 and (e) 5 mmol dye per 100 g montmorillonite (after Dobrogowska et al., 1991).

The visible spectra of AO adsorbed by vermiculite, montmorillonite, beidellite, saponite and Laponite were recently studied by Garfinkel-Shweky and Yariv (1997 a, b). The adsorption of this dye by the first four minerals resulted in metachromasy, which was not observed in their absence. In the presence of these minerals metachromasy appeared even at very low dye loadings (Fig. 2). Laponite, on the other hand, did not provoke metachromasy at this low loading but did it at a higher loading. This will be discussed later.

For the visible spectroscopy measurements, two parallel series of dye-clay suspensions were prepared. In one series the suspensions contained a constant amount of dye and increasing amounts of clay and in the other series they contained a constant amount of clay and increasing amounts of dye. In order to obtain reproducible spectra, the dye solutions were added into well-dispersed clay suspensions. Visible spectra of the dye-clay suspensions and of their supernatants
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![Absorption spectra of CV and EV](image-url)
became slightly colored and its spectrum showed the presence of a very dilute non adsorbed dye. This stage is defined for the titration as a “transition point” and for the clay as a “transition saturation”. In our first publications the terms “end point” and “saturation point” were used; but these terms are misleading because the clay continues to adsorb some of the dye which is added beyond this point. For the visible spectroscopy study the concentration of the clay in the suspensions was less than 0.1%. Under these conditions the monoionic smectites are well peptized. In general, the transition points, which were obtained by constant clay titration, were very close to those obtained by constant dye titration.

The point at which transition occurred, depended on the exchangeable inorganic cation initially saturating the smectite (Garfinkel-Shweky, 1996). Highest loadings were required for monovalent metallic cations, lower for divalent and the lowest for trivalent cations (see also Brindley and Thompson, 1970).

![Graph](image)

Fig. 3: The absorbance (in absorbance units) of bands α and β vs. dye loading (in mmol per 100 g clay) in the spectra of Na-saponite treated with AO. (A) constant dye concentration (4x10^-5 M); (B) constant clay (0.0166%) (after Garfinkel-Shweky and Yariv, 1997 b).

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Transition points in the titrations of different Na-smectites with the different dyes are summarized in Table 2. Those between the first and second region were determined from absorbance curves obtained with constant clay and those between the second and third region (maximum flocculation) were determined from absorbance curves obtained with constant dye.

The absorbance intensity of band $\beta$ relative to that of band $\alpha$ should give information on the extent of metachromasy, that is, on the ability of the clay to provoke metachromasy and on the affection of the dye to undergo this process. According to Fig. 2, band $\alpha$ is not observed in the spectrum of AO-beidellite. It is a weak shoulder in the montmorillonite spectrum, becomes a distinct band in the saponite spectrum and is the principal band in the spectrum of AO-Laponite in the first region of the titration. Thus, beidellite shows the highest ability to provoke metachromasy, and this ability decreases in the order montmorillonite, saponite and Laponite.

Absorbance ratio has not yet been determined from curve fittings and consequently, only trends of these properties were determined. With montmorillonite this trend depends on the dye. Band $\alpha$ was almost not detected in the spectra of AO treated montmorillonite but was relative intense in the spectra of TH-, MB-, CV-, EV- or PY-montmorillonite. However, even in these systems it was weak compared with band $\beta$, or appeared as a shoulder. Absorbance ratios of the two bands depended on the exchangeable metallic cation initially saturating the clay. For example, with Al-montmorillonite treated with MB band $\alpha$ was favored whereas with Na-montmorillonite band $\beta$ was favored.

Absorbance ratios also depended on the degree of saturation. Absorbance ratios of bands $\beta/\alpha$ in the titrations of Na-montmorillonite by CV and EV are shown in Fig. 4. These curves can be divided to three regions which are equivalent to those observed in the absorbance curves. The absorbance ratio is about 1 in the first region, it rises to about 1.5 in the second region and decreases to lower values in the third region. These changes support the idea that different types of $\pi$ interactions were obtained during the titration. In general band $\beta$ dominated the spectra of samples with a loading below the transition saturation. With higher saturations the intensity of band $\alpha$ increased and it became the dominant absorption band, in part due to the presence of free dye in the suspension.
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**Characteristic features of band $\alpha$**

The location of band $\alpha$ in the spectra of any of the dyes adsorbed by the smectites, depends on the degree of saturation. Representative wavelength curves are depicted in Fig. 4. The figure shows the location of band $\alpha$ in the spectra of CV and EV adsorbed by Na-montmorillonite, plotted against the degree of saturation. When the coverage was very low (e.g., below 1-2 mmol dye per 100 g clay), band $\alpha$ was located at the same wavelength as in the aqueous solution. With higher coverage, band $\alpha$ was bathochromically (red) shifted and was located at higher wavelengths (Table 3). So long as the added CV or EV were completely adsorbed by the clay, the maxima appeared at wavelengths above 600 nm. As soon as free CV or EV were present in the suspensions, the maxima of the $\alpha$ band shifted towards 590 and 595 nm, respectively. The first suspension to have a spectrum with an $\alpha$ band below 600 nm was considered to be that of a post transition point between the second and third regions. Therefore the transition saturation for the following titrations was regarded as the amount of dye in the last suspension to give an $\alpha$ at $>600$ nm. Similarly, degrees of transition saturation between the second and third regions were determined for treatment of montmorillonite with AO and PY and of saponite and beidellite with AO (Table 2).

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**Fig. 5:** Illustrations of the different types of dye-clay associations (after Garfinkel-Shweky and Yariv, 1997 b).
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Interlayer space exists only when there are tactoids with parallel TOT layers. Thus, the red shift, *inter alia*, proves that tactoids are present in the dye-clay aqueous system. The disappearance of band $\alpha$ before the transition saturation indicates that at this stage of the titration tactoids dissociate into separate platelets.

The acid strength of the interlayer space depends on the nature of the exchangeable metallic cation and consequently, the location of band $\alpha$ also depends on the acid strength of the cation. Small red shifts were observed with K-, Na- and Li-smectites, larger shifts with Ca- and Mg- and the largest were with Al-smectites.

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![Fig. 6: Wavelength curves of aqueous suspensions of Na smectites with different amounts of AO. The wavelength (in nm) of band $\beta$ is plotted vs. the degree of saturation (in mmol AO per 100 g clay). First region is obtained by clay-dye/clay spectroscopy. Second and third regions are obtained by normal spectroscopy. (After Garfinkel-Shweky and Yariv (1997 a).](image)
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interparticle space. Dye-clay associations that contain dimers and higher dye aggregates in the interparticle space of flocs are designated C and D, respectively. Possible models of associations of type C and D are shown in Fig. 5. The aggregation of the dye may occur in vacancies of card house or book house flocs (C1 or C2, respectively). Red shifted band α which is characteristic for tactoids, appears with the latter but not with the former.

From Table 3 it appears that the location of band β in the maximum flocculation point (minimum wavelength in the second region) is only slightly dependent on the smectite. It is therefore suggested that a similar π interaction between aggregated dye cations is responsible for the metachromasy in the second region of the titration of the other smectites by dyes.

X-ray diffraction data as evidence for π interactions between the oxygen planes of the TOT layers and the aromatic entity in the first region of the titrations

Basal spacings of dye-clay complexes containing various amounts of dye, were determined before and after thermal treatments. These basal spacings were dependent on the dye, the exchangeable metallic cation initially saturating the clay and on the degree of saturation. A thermal treatment of Na-montmorillonite, -beidellite and -Laponite at 300°C under vacuum resulted in a basal spacing of ≈1.0 nm, indicating dehydration of the clay. Na-saponite and -vermiculite required temperatures higher than 400°C for dehydration. Larger spacings were recorded after heating the dye-smectite samples at 300-400°C (1.14-1.38 nm) proving that the organic matter was located in the interlayer space. Simultaneous DTA-EGA study of several dyes adsorbed by Laponite and montmorillonite (Yariv et al., 1988 b, 1989 a, b, c and 1990 a) showed that air oxidation of the dye started slightly above 200°C with the evolution of H2O and CO2. At the same time charcoal was formed inside the interlayer space. The basal spacings of the thermal treated clays were those of clay complexes with interlayer charcoal. The formation of a charcoal layer inside the interlayer space may occur only if the precursor dye cation has been located in that site.

Three types of dye-H2O-clay associations were identified by XRD. The first type was characterized by a basal spacing smaller than 1.4 nm. It was obtained with small degrees of saturation. The second type, with larger basal spacings predominated when higher amounts of dye were used. The transition between the first and second type seems to occur at saturation between 30-40 mmol dye per 100 g clay which is equivalent to the transition between the first and second regions of the titration curves (absorbance or wavenumber curves). The third type, with smaller basal spacings (1.33-1.65 nm), was obtained in the presence of great excess of dye (third region). These samples were sedimented from the repetized system.
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orbital the electron density is high on one side of the O nucleus. Thus, it may essentially overlap orbitals of the acidic moiety whereas in a non-hybridized orbital the lone-pair electrons are equally distributed on both sides of the nucleus.

In covalent bonded oxygen $sp^3$ hybridization is expected on the O atom, giving rise to four equal hybridized-orbitals with a minimum repulsion between the electron pairs which fill the valence shell. This hybridization permits two nonbonding-hybridized orbitals with lone-pair electrons to serve as proton acceptors, in addition to the two $\sigma$ bonding orbitals. A $sp^3$ hybridization should result in an Si-O-Si angle slightly smaller than 109°, as is found in H$_2$O molecules. Determination of Si-O-Si angles in different silicates revealed that this angle ranges between 120-180°. In most silicates the value of 139-140° was determined (Liebau, 1985). An angle of 180 or 120° is an indication of $sp$ or $sp^2$ hybridization on the oxygen atom, respectively. If the angle ranges between these values it should be due to a resonance of two canonical structures, one with $sp$ and one with $sp^2$ hybridization on the O atom. The basic strength of the oxygen plane decreases with decreasing electron density in the nonbonding hybridized orbitals and consequently $sp^2$ hybridization on the O atom decreases basic strength compared with $sp^3$ whereas $sp$ hybridization leads to the abolition of the basic strength.

Some elements of the third row of the periodic table are involved in a $d_{\pi}-p_{\pi}$ bond in their overall bonding system (Cruickshank, 1961, 1985). In this bond which occurs between Si, P, S or Cl and N, O or F from the second row of the periodic table, $d$ orbitals overlap $p$ orbitals on the second atom to form $\pi$ bonds. In the formation of this bond in a siloxane group, the Si which has empty $d$ orbitals, serves as an acceptor of electron pairs and the O serves as the donor. This bonding is an addition to the $\sigma$ bonding and the Si-O bond is considered to have a partial double bond character. Siloxanes are unreactive. The strong bond between Si and O atoms and the partial $\pi$ interaction cause the oxygen to lose its basicity and to show extremely little tendency to donate an electron pair. Tetrahedral substitution of Si by Al leads to an increase in both types of surface acidity, the acceptance and donation of electron pairs. The increased acidic activity is due to the presence of additional exchangeable cations. In the following paragraph the increased basic strength of the Al substituted siloxane is explained according the Si-O bonding model of the VB treatment (Yariv, 1988 a, 1992).

The coordination number of Si in clay minerals is four, involving $sp^3$ hybridization. Three of the O atoms which coordinate the Si belong to the 'O-plane', whereas the fourth belongs to the 'O,OH-plane', which is common to the tetrahedral and octahedral sheets. The Si atom uses vacant $d$ orbitals to form $\pi$ bonds with O atoms. Oxygens from the O-plane are the major contributors to the $d_{\pi}-p_{\pi}$ bonding system. Each O atom requires one or two non-hybridized $p$
orbital the electron density is high on one side of the O nucleus. Thus, it may essentially overlap orbitals of the acidic moiety whereas in a non-hybridized orbital the lone-pair electrons are equally distributed on both sides of the nucleus.

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A π interaction between the O-plane and an aromatic ring is obtained as a result of the overlapping of hybridized nonbonding orbitals of oxygens and antibonding π orbitals of the aromatic ring. The antibonding π orbitals and the nonbonding hybridized orbital should be parallel to each other and perpendicular to the O-plane. This is demonstrated in Fig. 7 which shows that π overlapping may occur with $sp^2$ hybridization on the O, but cannot occur with $sp$ hybridization, due to the absence of a perpendicular nonbonding hybridized orbital. The figure also shows that O-planes of tetrahedrally substituted smectites, with no resonance between $sp$ and $sp^2$ hybridization, are better electron pair donors for π interactions compared with non-substituted smectites. Beidellite, saponite and to some extent also montmorillonite, possess tetrahedral substitution. Laponite, a synthetic hectorite, does not possess it. This model explains why metachromasy is observed only with tetrahedrally substituted smectites.

The basic strength of the O-plane and its ability to be involved in π interactions with aromatic entities depends on whether the clay is di- or trioctahedral. In a trioctahedral clay, the oxygen which bridges between the tetrahedral and octahedral sheets is coordinated by four atoms (one Si and three Mg). It is $sp^3$ hybridized and has no contribution to a $d_\pi-p_\pi$ bond with the Si. On the other hand, in a dioctahedral clay, where this bridging O is coordinated by three atoms (one Si and two Al), it is to some extent sp2 hybridized and has a small contribution to a $d_\pi-p_\pi$ bond with the Si. Consequently, the contribution of atoms of the O-plane to the π system of Si decreases, and the electron density at the nonbonding orbitals becomes higher, compared to their density at the nonbonding orbitals of trioctahedral clays. Thus the basic strength of the O-plane of dioctahedral clays is higher than that of trioctahedral clays. Recently, Garfinkel and Yariv (1997 a) showed that a sequence of surface basicity of the O-planes of several smectites can be determined from the spectra of an adsorbed metachromic dye, such as AO, as long as the dye clay association is of type B2. They assumed that the location of the metachromatic band in B2, depended on the strength of the π interaction between the clay and the dye and concluded that the basic strength decreased in the order: beidellite > vermiculite > montmorillonite > saponite > Laponite.

**Adsorption of R6G and RB by montmorillonite and Laponite**

The cationic dyes R6G and RB consist of a xanthene moiety which is responsible for their characteristic $\pi \rightarrow \pi^*$ absorption in the visible light. In addition to the xanthene group, these cations possess a phenyl ring, the plane of which is perpendicular to that of the three xanthene rings, and consequently, has only a small effect on the absorption of the $\pi \rightarrow \pi^*$ transition. These two dyes are metachromic, forming dimeric species in aqueous solutions. Due to steric
A π interaction between the O-plane and an aromatic ring is obtained as a result of the overlapping of hybridized nonbonding orbitals of oxygens and antibonding π orbitals of the aromatic ring. The antibonding π orbitals and the nonbonding hybridized orbital should be parallel to each other and perpendicular to the O-plane. This is demonstrated in Fig. 7 which shows that π overlapping may occur with $sp^2$ hybridization on the O, but cannot occur with $sp$ hybridization, due to the absence of a perpendicular nonbonding hybridized orbital. The figure also shows that O-planes of tetrahedrally substituted smectites, with no resonance between $sp$ and $sp^2$ hybridization, are better electron pair donors for π interactions compared with non-substituted smectites. Beidellite, saponite and to some extent also montmorillonite, posses tetrahedral substitution. Laponite, a synthetic hectorite, does not posses it. This model explains why metachromasy is observed only with tetrahedrally substituted smectites.

The basic strength of the O-plane and its ability to be involved in π interactions with aromatic entities depends on whether the clay is di- or trioctahedral. In a trioctahedral clay, the oxygen which bridges between the tetrahedral and octahedral sheets is coordinated by four atoms (one Si and three Mg). It is $sp^3$ hybridized and has no contribution to a $d_\pi-p_\pi$ bond with the Si. On the other hand, in a dioctahedral clay, where this bridging O is coordinated by three atoms (one Si and two Al), it is to some extent sp2 hybridized and has a small contribution to a $d_\pi-p_\pi$ bond with the Si. Consequently, the contribution of atoms of the O-plane to the π system of Si decreases, and the electron density at the nonbonding orbitals becomes higher, compared to their density at the nonbonding orbitals of triocathedral clays. Thus the basic strength of the O-plane of dioctahedral clays is higher than that of triocathedral clays. Recently, Garfinkel and Yariv (1997 a) showed that a sequence of surface basicity of the O-planes of several smectites can be determined from the spectra of an adsorbed metachromic dye, such as AO, as long as the dye clay association is of type B$_2$. They assumed that the location of the metachromic band in B$_2$, depended on the strength of the π interaction between the clay and the dye and concluded that the basic strength decreased in the order: beidellite > vermiculite > montmorillonite > saponite > Laponite.

**Adsorption of R6G and RB by montmorillonite and Laponite**

The cationic dyes R6G and RB consist of a xanthene moiety which is responsible for their characteristic $\pi \rightarrow \pi^*$ absorption in the visible light. In addition to the xanthene group, these cations possess a phenyl ring, the plane of which is perpendicular to that of the three xanthene rings, and consequently, has only a small effect on the absorption of the $\pi \rightarrow \pi^*$ transition. These two dyes are metachromic, forming dimeric species in aqueous solutions. Due to steric
Because of the absence of band \( \beta \) in the spectra of R6G-montmorillonite and -Laponite, their spectra are useful for studying the features of band \( \alpha \). A red shift from 525 nm (the maximum of band \( \alpha \) in an aqueous solution) was observed from the beginning of the titration of the clay by R6G. The red shift increased up to 60 and 45, respectively, mmol R6G per 100 g clay. On further titration of the clay, the wavelength of band \( \alpha \) gradually returned to the wavelength found in the spectrum of dilute aqueous solutions. The degree of saturation with the maximum wavelength was defined as a "transition saturation". From this stage onward the supernatant became slightly colored, absorbing at the wavelength characteristic for a dilute aqueous solution of the dye. The minimum absorbance (maximum flocculation) occurred at 70 and 60 mmol R6G per 100 g clay, respectively, between the degree of transition saturation and that where the location of band \( \alpha \) was at 525 nm (Tables 2 and 3).

The polarity in the interlayer space is higher than that of liquid water and consequently, the red shift observed at low coverage proves that the dye penetrates into the interlayer space. The red shift of band \( \alpha \) indicates a gradual increase in the polarity of the interlayer space. As more dye cations are adsorbed, they replace interlayer water and the hydrophobicity of the interlayer space increases. The increase in polarity is due to the fact that residual water is disordered and the degree of dissociation of non-structured water is higher than that of structured water. This type of dye-clay association was designated \( B_1 \). As was previously explained, the presence of a red shifted band \( \alpha \) proves the presence of tactoids in the system.

In addition to type \( B_1 \), another type of dye-clay association is represented by band \( \alpha \), with a maximum at the same location as that of a dilute aqueous solution and consequently, it should comprise monomeric cationic species located in an environment in which the polarity is very similar to that of the aqueous phase. This environment should be the liquid-solid interface, outside the interlayer space. This type of dye-clay association was designated \( A_1 \). It can be formed in the third stage of the titration, when the clay is repertized.

During the flocculation stage (the second region) there is also the possibility for the dye to be adsorbed into the interparticle space of the floc. This space is also more polar than liquid water and is responsible for a red shift.

The basal spacing of this complex gradually increased from 1.41 to 2.10 or from 1.59 to 2.01 nm with the loading from 8.4 to 84.0 mmol R6G per 100 g montmorillonite or Laponite, respectively. This spacing is not characteristic for association \( B_2 \). Samples from the repertized stage, with loadings above 100 mmol R6G per 100 g clay, gave spacings of about 1.6 nm.
Because of the absence of band β in the spectra of R6G-montmorillonite and -Laponite, their spectra are useful for studying the features of band α. A red shift from 525 nm (the maximum of band α in an aqueous solution) was observed from the beginning of the titration of the clay by R6G. The red shift increased up to 60 and 45, respectively, mmol R6G per 100 g clay. On further titration of the clay, the wavelength of band α gradually returned to the wavelength found in the spectrum of dilute aqueous solutions. The degree of saturation with the maximum wavelength was defined as a “transition saturation”. From this stage onward the supernatant became slightly colored, absorbing at the wavelength characteristic for a dilute aqueous solution of the dye. The minimum absorbance (maximum flocculation) occurred at 70 and 60 mmol R6G per 100 g clay, respectively, between the degree of transition saturation and that where the location of band α was at 525 nm (Tables 2 and 3).

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Molar enthalpies of adsorption of CV and EV by montmorillonite

Solution calorimetric measurements of CV and EV adsorption by several montmorillonites were carried out by Hepler et al. (1987) and Dobrogowska et al. (1991). Dye adsorption by montmorillonite are exothermic. The molar enthalpy of adsorption depended on the dye/clay ratio and on the exchangeable cation. In Fig. 4, molar enthalpies of adsorption of CV and EV by Na-montmorillonite are plotted vs. the degree of saturation. The figure shows a striking correlation between the enthalpies of adsorption and the spectroscopic results, especially the intensity ratios of bands $\beta/\alpha$. Also, these calorimetric results are consistent with the spectroscopic results, which show that metachromic effect in type B$_2$ is larger for CV than for EV in dye plus montmorillonite systems. In Na-montmorillonite associations of type C with dye aggregates in the interparticle space of flocs, release more energy than associations of type B$_2$ with dye monomers in the interlayer space. Association B$_2$ of other montmorillonites released higher molar enthalpies than type C. Associations of type A, with the dye adsorbed on the external surface of the clay, are expected to lead to the least exothermic (possibly even slightly endothermic) enthalpies of adsorption, because these associations appear only at high degrees of saturation, where the clays may carry positive charges. The figure shows that in the formation of associations A the molar enthalpies of adsorption become less exothermic as more dye is adsorbed.

Eletrokinetic study of adsorption of CV and EV by montmorillonite

A description of the electrophoretic mobility of montmorillonite during its titration by CV or EV, combined with visible spectroscopy (Schramm et al., 1997), is a good way to summarize this complicated study and to draw some conclusions. Fig. 9 demonstrates the effect of the degree of saturation of Li-montmorillonite by CV and EV on the following properties: (i) maximum wavelength of bands $\alpha$ and $\beta$, (ii) absorbance intensity corresponding to both bands and (iii) electrophoretic mobilities. The figure shows a striking correlation between the electrophoretic mobilities and the spectroscopic results. The first region exhibits an almost constant absorbance, indicating that at this stage the adsorption of the dye did not change the size of the original tactoids. Bonding of types B$_1$ (dye monomers in the interlayer space) and B$_2$ (monomers $\pi$-bonded to the O-plane) is formed from the very beginning of the titration of any of the monoionic montmorillonites with either CV or EV. An exchange takes place into the interlayer space with cations which are initially located inside the tactoid. Consequently, the electrophoretic mobility should not change during this stage. This was observed with polyvalent cations, which form large tactoids. Li has very small tactoids and some of the type B$_2$
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to the repeptization of the clay and the exposure of additional surfaces. Bondings of type A are the principal adsorption products that are formed at this stage of the titration. Spectroscopic measurements confirmed that the type A cations, monomers, dimers and higher aggregates, are attached to the external surfaces of peptized platelets or small tactoids (Fig. 5), contributing positive charge to the mobile particles. At well past the IEP there eventually is little surface area available for further adsorption and only small increases in electrokinetic potential result.

In conclusion, the different methods which were applied in the study of metachromic dye-smectite associations show that different associations are obtained by changing the mineral and the dye/smectite ratio.

References


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STATISTICAL ANALYSIS OF MINERALOGICAL AND GEOCHEMICAL PARAMETERS USED AS LITHOSTRATIGRAPHIC AND ENVIRONMENTAL MARKERS

Fernando Tavares Rocha

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Introduction

Clay minerals occur at the surface or near to the surface of the Earth’s crust, as a result of the interaction of earth’s crust with atmosphere, hydrosphere and biosphere, and they diminish as far as depth increases, as a consequence of the rock cycle. Clay minerals represent on the one hand reactive answers of the geological materials to the physico-chemical processes specific of certain environments and prevail during a certain time, and, on the other hand, after their formation, clay minerals constitute an active and characteristic part of the environment. This inter-active relationship existent between clay minerals and geological environments (Keller, 1970) allow the use of them as an important tool either for the study of the sedimentary series or for basin analysis.

Studying sedimentary series, the information made available by clay mineral associations can be of capital interest for the characterisation of the geologic formations and for the establishment of stratigraphic correlations, because, through the sedimentary sequences, clay mineral associations change in composition or in simple details of the crystallochemistry (for instance, crystallinity) of the respective clay mineral species.

The use of clay minerals as lithostratigraphical markers can be announced like this: like a fossil, a mineral or an association of minerals can characterise a layer and allow regional correlations (Pomerol, 1987). Clay minerals are the most ubiquitous components of sediments, from muds to desert or beach sands, to shales and marls, therefore being important components, in volume or in weight, of several kinds of sedimentary rocks, since the Proterozoic up to the Present.

One of the first applications of clay minerals in basin analysis consists of the utilization of selected minerals as lithostratigraphic markers allowing the definition of guide-layers in field sections or in borehole logs. These guide-layers were established on the basis of clear anisotropies found out in the lateral or vertical evolution of the selected
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successive sample mean values from a target specification, even minor, permanent, shifts in the mean will eventually lead to a sizable cumulative sum of deviations. Thus, this chart is particularly well-suited for detecting such small permanent shifts that may go undetected when using the X-bar chart.

The development registered in the last few years, for almost all the scientific disciplines, of the utilisation of geostatistical techniques, in particular the multivariate ones, is due to several causes, two of them deserving particular reference:

1. the need to gather enormous quantities of data requiring treatment, associated with the interest of simultaneous analysis of the relationships between two or more variables;
2. the availability of high stocking capacity, fast graphical processing and presentation of data, expressed by the evolution of informatic techniques, on the one hand through the permanent evolution of the software and on the other hand through hardware more powerful and of more accessible utilisation.

We may define a multivariate utilisation of data as an application of mathematical methods that treat carefully a large number of measurements, expressed by variables in a specific context in one or more simultaneous samples.

Such techniques may be divided in two large groups. One group deals with the association of two sets of variables, based on dependent criteria, represent the dependent methods; the other group, based on interdependent criteria, analyse the mutual association throw all the variables, without distinguishing their different nature. Of these two methods referred to, two application techniques are of quite spread use in the Geosciences disciplines: Principal Components Analysis and Cluster Analysis.

The statistical methods of multivariate analysis can be a good complement to other methods (microscopy, isotopic determinations and fluid inclusions...) used in mineralogical studies. Even though these techniques are generally classical and of common-use in what concerns to the mathematics involved, their use in mineralogy is quite recent and there is still no formal basis for their systematic application in mineralogenesis (Galan et al., 1995).

Obviously these methods constitute a powerful tool courtesy of the calculation facilities of computers, which must be directed, controlled and interpreted by mineralogists, who at all times will have, according to Galan et al. (1995) to:

- select the variables to be introduced;
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maximum of geometric conformity with them. The reduction of data spatial dimension requires the search of the group of lines called Principal Axes of Inertia or Factorial Axes better adjusted to the initial data clouds, concerning either the sample positions in \( \mathbb{R}^p \) space or the variable positions in \( \mathbb{R}^n \) space.

Therefore, among the methods of multivariate analysis, Principal Factor Analysis is of most interest in the application to the mineralogy since it takes into account a known population of samples and a group of variables of the same nature (e.g. chemical and mineralogical composition), and involves the variability of the system through a smaller number of new linearly independent variables (principal or common factors) chosen in descending order of their influence on the whole of the variables (Kaiser, 1958).

The first thing to take into account when this method is applied is the choice of variables, which should be sufficient to adequately explain the problem. In our case it is necessary to choose the minerals that play a role in the mineralogenetic problem and those fundamental chemical components of the relevant phases, or even significant trace elements which can support the genetic processes involved. Inspection of the multivariate correlation matrix of the original data, which at the same time constitute the base of the calculations in order to find the common factor loadings, can be a very useful tool in the selection of variables. These loadings explain the relations and assemblages within the original variables.

The common factors \( F_i \) (new variables) are abstract and it is necessary to interpret them in regards to the particular problem, taking into account their loadings for the original variables. In order to ease the understanding of what these factors actually represent, it is common to perform a new multidimensional transformation (e.g. Varimax rotation).

The graphical representation of this type of multivariate analysis comes about by taking the principal factors as references (\( F_2 \) vs \( F_1 \), \( F_3 \) vs \( F_1 \), \( F_3 \) vs \( F_2 \),...).

According to Lopez-Aguayo & Gonzalez Lopez (1995), the use of these statistical methods, as outlined by Imbrie and Van Andel (1964), Jöreskog et al. (1976), Davis (1986) and Reyment & Jöreskob (1993), allow us to perform a good characterization of the system data, reducing the complexity of the model to classify the variables and samples into natural groups (Mezzadri & Saccani, 1989).
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Overlying the sedimentary formations of the Mesocenozoic margin do occur Plio-Pleistocene and Holocene detrital deposits, represented by fluvial and fluvial-marine alluvium as well as beach and dune sands which would enabled, through the joining of successive sandy hooks, the beginning of the barrier structure formation around 550 d.C. This process continued up to the middle of the XVIII century, forming a large lagoon commonly, but improperly, known as “Ria de Aveiro” Vidinha et al. (1997) added to the textural analysis achieved by Vidinha (1995) relevant mineralogical data, in the same domains studied by that author (beach face, berm and dune), and tried a new statistical approach. More than 60 samples derived from 20 transversal profiles were studied.

Analysing the longshore trend of the more characteristic minerals, we found an uniform behaviour of quartz, unlike feldspars and clay minerals, which show an opposite disposition (Figs. 2 and 3).

In fact, analysing the relative contents of those minerals in the fine fraction, from north to south of the studied area, feldspars tend to decrease whereas clay minerals tend to increase their presence. This evolution may be the consequence of some pedogenetic processes, which are more intense in the southernmost dune areas. This fact is coherent with the higher stability in regards to coastal erosion shown by the southernmost dune areas, comparatively to the instability shown by the northernmost dune areas.

Figure 2 - Longshore evolution of feldspars contents of the fine fractions.
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The cluster analysis of the fine fractions mineralogical data (Figure 4) allows some interesting considerations to be made:

The definition of three clusters of mineralogical parameters: one formed by the association of the fine detrital minerals, kaolinite (Kt), chlorite (Chl) and illite (Ill); a second cluster formed by the association of the coarser detrital minerals, quartz (Qz), plagioclase (Plag) and K-feldspar (KFelds), with dolomite (Dol); and a third cluster formed by the association of the chemical minerals, calcite (Calc), anhydrite (Anid), opal C/CT (Op), halite (Hal) and zeolites (Zeol).

The association of the samples (on the basis of the same mineralogical parameters) in three clusters, of which two show a relatively good internal coherence, one formed essentially by samples belonging to the dune domain (samples x.1) and the other one formed by samples belonging to the beach face domain (samples x.3).
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Figure 5 - Multivariate factorial analysis of the fine fraction mineralogical data
Having in mind an attempt to establish a lithostratigraphic zonation in the sedimentary columns and to find out eventual lateral correlations, mineralogical parameters had been established in order to define guide-layers.

At an initial stage we applied the phyllosilicates/quartz+feldspars ratio, that means the fine detrital minerals/coarse detrital minerals ratio, submitted to statistical analysis, in particular Quality Control Analysis (vertical evolution of the parameter controlled by mean and standard deviation; vertical evolution of the cumulative sum of deviations). As a second parameter we applied the vertical evolution of the “factor scores” of the Principal Components Analysis of the mineralogical parameters being quantified (Figures 7 a, b and c show an example of these statistical analysis).

Analysing the vertical evolution of the studied parameters for the RGD 6 borehole (Figure 7) we can see three anisotropies (represented by samples 12, 29 and 39), all very clear in any of the three graphs of the Figure, but more evident in the one showing cumulative sum of deviations. The second anisotropy is slightly less clear, meaning a minor variation of the mineral composition. The strong anisotropy present at the base of the three graphs (samples 1 to 4) is related with the bedrock schist and its weathering mantle.
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Therefore, the geostatistical analysis being carried out allowed the definition, in each of the five studied boreholes, of three/four guide-layers (Table I), characterized by clear anisotropies put in evidence by the vertical evolution of the selected parameters.

<table>
<thead>
<tr>
<th>Units</th>
<th>Guide layers</th>
<th>Lithology</th>
<th>Mineralogy</th>
<th>Lithology</th>
<th>Mineralogy</th>
<th>Lithology</th>
<th>Mineralogy</th>
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<td>IKV</td>
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<td>IKV</td>
<td>Brownish medium sands</td>
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<tr>
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<td>K</td>
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<td>sandy silts</td>
<td>K</td>
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<td>medium sands</td>
<td>IKV</td>
<td>silty sands</td>
<td>VKI</td>
<td>medium/ fine sands</td>
<td>IKV</td>
<td>silty sands</td>
</tr>
<tr>
<td>C</td>
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<td>I</td>
<td>clayey silts</td>
<td>K</td>
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<td>brownish sands</td>
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<tr>
<td>III</td>
<td>silty sands with shells</td>
<td>IKV</td>
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<td>IKV</td>
<td>silty/ medium sands</td>
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<tr>
<td>B</td>
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<td>micaceous silts with ferruginous materials</td>
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<tr>
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</tr>
<tr>
<td>I</td>
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<td>IKV</td>
<td>Micaceous sands</td>
<td>KIV</td>
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Table I - Guide-layers, their lithologies and clay minerals composition

The utilization of selected lithostratigraphic markers allowed the definition of guide-layers in each of the five boreholes under study. These guide-layers were established on the basis of clear anisotropies found in the vertical evolution of certain mineralogical parameters. Four guide-layers (A, B, C e D) could be defined. Guide-layer A was defined in the lower section of the sedimentary columns, guide-layers B and C were defined in the intermediate sections whereas guide-layer D was defined in the upper section. All these four guide-layers are characterized by quantitative changes found in the kaolinite and/or vermiculite contents. So, we consider that the methodologies being adopted could be of great interest to discriminate situations where the classical parameters yield monotonous information.

Application example of application n° 3 - lithostratigraphical analysis and paleoenvironmental reconstruction (Cenozoic sediments)

Mineralogical analysis of a Cenozoic evaporitic formation in the Aveiro region (Portugal)

At the Aveiro basin a gap in the stratigraphic record do occur beyond upper Cretaceous. Eocene, Oligocene and Miocene formations have not been identified in the
Therefore, the geostatistical analysis being carried out allowed the definition, in each of the five studied boreholes, of three/four guide-layers (Table I), characterized by clear anisotropies put in evidence by the vertical evolution of the selected parameters.

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<th>Mineralogy</th>
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<td>brownish fine sands</td>
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<tr>
<td>D</td>
<td>clayey silts</td>
<td>clayey silts</td>
<td>sandy silts</td>
<td>medium sands</td>
<td>V</td>
<td>medium sands</td>
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<td>medium/ fine sands</td>
<td>SK</td>
<td>medium/ fine sands</td>
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<tr>
<td>C</td>
<td>muddy silts with shells</td>
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<td>medium sands</td>
<td>K</td>
<td>Silty medium sands</td>
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<td>Silty medium sands</td>
<td>K</td>
<td>Silty medium sands</td>
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<tr>
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<td>I</td>
<td>Silty medium sands</td>
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<td>Micaceous sand</td>
<td>K</td>
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Application example of application n° 3 - lithostratigraphical analysis and paleoenvironmental reconstruction (Cenozoic sediments)

Mineralogical analysis of a Cenozoic evaporitic formation in the Aveiro region (Portugal)

At the Aveiro basin a gap in the stratigraphic record do occur beyond upper Cretaceous. Eocene, Oligocene and Miocene formations have not been identified in the
From the application of R-mode factor analysis (Fig. 9) to the fine fractions mineralogical data, with redistribution of phyllosilicates contents by kaolinite, illite, chlorite, smectite and mixed-layers, some interesting considerations may be withdrawn:

- Factor 1 shows Psilom, Goe, Anat, Py, (C, Z) in opposition of Qz, FK, P, Kt, Ch, Sm.
- Factor 2 discriminates Op, Gy, Apat, Sulf, Sid.
- Factor 3 discriminates D, Ill, Inter.

Fig. 9 - R-mode factor analysis of the fine fraction mineralogical data.
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Once again, the cluster analysis (Fig. 12) confirms the associations observed in the Q-mode factor analysis.

There is a clear discrimination of sample number 13a, whereas the remainder samples could be grouped in three clusters, one comprising samples 17, 18, 19, 20 and 21, other comprising samples 13b, 14, 15 and 16, and one another comprising samples 10, 11 and 12. Sample 9 appears somehow isolated but linked with this last cluster.

The analysis of the data available allows the withdrawal of the following conclusions:
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The analysis of the data available allows the withdrawal of the following conclusions:
Samples of the Corvina 1 well were gathered as cuttings at every 5 m interval (some intervals are not represented as no sampling was made during drilling of the well). The most recent available data, based on faunal content (well logs and reports deposited at the Gabinete para a Pesquisa e Exploração de Petróleo, Lisbon), attributes the interval between depths 1838m and 2300m (462m) to the Upper Jurassic. The interval between 1800m and 2350m (550m), embracing the whole Upper Jurassic, was studied (a total of 103 samples were collected within the studied interval). This interval is represented by a succession of carbonates (limestones/dolomites and marls), claystones and, towards the top, some sandstone levels.

The mineralogical studies of the insoluble residues, particularly of their clay components, were based mainly on X-ray diffraction (XRD) determinations, carried out on non-orientated and orientated specimens. The Mn and Sr contents of the carbonate fraction were measured in each sample. Trace element analyses were carried out by atomic absorption spectrophotometry (AAS) following the method described by Renard & Blanc (1971, 1972) and Caetano (1993). All mineralogical and geochemical results were submitted to geostatistical analysis, in particular, to R-mode multivariate factor analysis.

Fig. 13 - Geographical location and geological setting of Corvina 1 well.
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The insoluble residue mineralogical content (Fig. 14) is clearly dominated by phyllosilicates throughout most of the studied interval although in the upper part, above depth 1930 m, quartz gains more importance. Plagioclase and gypsum are present in all studied samples. Other minerals such as K feldspars, opal and pyrite have almost continuous records; zeolites appear very discontinuously.

The obtained mineralogical data has also allowed the establishment of a vertical zonography being it able to distinguish six mineralogical zones based on their clay mineral content (Fig. 15).

![Fig. 15 - Clay mineral content and mineralogical zones of Corvina 1 well](image)

*Fig. 15 - Clay mineral content and mineralogical zones of Corvina 1 well (illite - I; kaolinite - K; smectite - S).*

Illite is predominant throughout the whole studied interval; the uphole evolution of the other clay minerals shows that kaolinite content has a tendency to firstly increase from the first to the second zones (depths 2350-2305 and 2305-2180 respectively). In the third and fourth zones (depths 2180-2045 and 2045-1930), a more smectite association is found and, finally, in the fifth and sixth zones (1930-1853 and 1835-1800)
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Factor 3 expresses a deposition environment of marine character, but more confined.

The vertical evolution of the Factor Scores (Fig. 17) is consistent with the zonography previously established.

The considerations postulated from the geostatistical factor analysis reflect, essentially, the influence of clastic influxes into the basin, enhancing, at the same time, different paleogeographical positionings of the studied stratigraphical units.

Figure 17 – Vertical evolution of Factor 1 Scores.
Factor 3 expresses a deposition environment of marine character, but more confined.

The vertical evolution of the Factor Scores (Fig. 17) is consistent with the zonography previously established.

![Figure 17 - Vertical evolution of Factor 1 Scores.](image)

The considerations postulated from the geostatistical factor analysis reflect, essentially, the influence of clastic influxes into the basin, enhancing, at the same time, different paleogeographical positionings of the studied stratigraphical units.


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