Biomarker Analysis of the Bentonites from Esquivias (Toledo)

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INTRODUCTION

The Tajo Basin is an intracratonic basin located in the center of Iberian Peninsula. It is filled by Tertiary materials formed during the erosion of the surrounding mountain ranges (Cordillera Ibérica, Sierra de Altomira, Sistema Central and Montes de Toledo). This basin is particularly rare (García-Romero, 2004) considering its richness in magnesic clays, which need high silica and magnesium contents to be formed, and the lack of potential source rocks with high Mg to justify the formation of these clay minerals.

In this work, we studied samples collected in a quarry in which magnesic bentonites are exploited. A mineralogical and biomarker analysis of these samples were conducted.

MATERIALS AND METHODS

28 samples were collected at a quarry in the proximities of the locality of Esquivias (Toledo) (Fig.1). They were collected at a vertical wall consisting of green clays, pink clays, carbonates and micaceous sands and labeled ESB1 to ESB28 from the bottom to the top.

All the samples were characterized by X-Ray Diffraction (XRD), with the typical methodology for clay studies that comprises the study of random powder of raw sample and the oriented aggregated of <2µm fraction (in normal ambience, after solvation with ethylene-glycol, and heated over 500ºC 2h). A Siemens D-500 diffractometer with CuKα radiation and a graphite monochromator was used. Semi-quantification of the samples was performed through the "reflective power method" (Martin Pozas, 1975),

For the analysis of biomarkers, dried samples were ground, and biomarkers extracted using accelerated solvent extraction (Dionex ASE 200). Free lipids were extracted with dichloromethane (DCM)/MeOH (2:1) at 1500 psi and 175ºC. The time of the heating phase was 8 min and the static extraction time 5 min. The extract was concentrated using rotary evaporation. Prior to analysis using gas chromatography–mass spectrometry (GC–MS), samples were methylated with trimethylsilyldiazomethane and silylated with a mixture of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine at 70ºC for 2 h. Samples were injected into an HP 6890 gas chromatograph equipped with a selective mass detector (HP 5973) and an ATM-5 column (25 m x 0.25 mm; 0.20 µm). It was the carrier gas and decafluorobiphenyl an internal standard. The oven temperature was programmed from 60 to 300ºC (held 20 min) at 6ºC/min, and the injector was maintained at 275ºC. Components were identified with the Data Analysis program and the Wiley Library. The identification and quantification of the n-alkanes was determined by the fragmentation ion m/z = 57, while the n-alkanoic acids were determined by the ion m/z = 74.

RESULTS AND DISCUSSION

X-Ray Diffraction.

The XRD characterization allowed us to identify the minerals present in the samples, being mainly quartz, calcite, potassium feldspar and plagioclase, along with phyllosilicates such as smectite, illite, chlorite and kaolinite (Fig.2). Smectites were trioctahedral according to the d-spacing of the 060 reflection at the most bentonitic levels, at the lower part of the column. Through the top of the section , the 060 reflection showed d-spacing values which corresponded to both tri- and dioctahedral character, due to the mixture of dioctahedral illite and trioctahedral smectite.

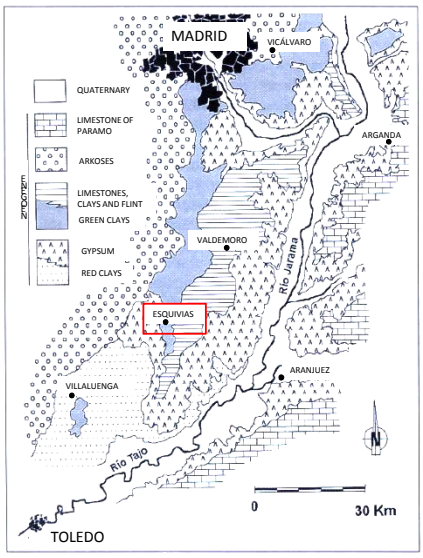

fig 1. *Localization of the samples. Map of the Madrid Basin, taken from Leguey and Doval, (1987).*

According to the content in the main minerals, we established 4 different mineralogical associations. All the minerals previously mentioned were included within the four groups, but in different proportions. Feldspar, chlorite, and kaolinite were always minority and the relative amounts of smectite, illite, quartz, and calcite determined the association:

- Bentonitic: >45% smectite (ESB1, ESB2, ESB3, ESB4, ESB5, ESB6, ESB8)
- Illitic: >35% illite and smectite < Illilte, (ESB10, ESB11, ESB12, ESB14,

palabras clave: Bentonitas, Biomarcadores, Cuenca del Tajo | ***key words:*** Bentonites, Biomarkers, Tajo basin.

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ESB17, ESB21, ESB22, ESB26, ESB27)

- Sandy: >50% quartz + k-feldspar + plagioclase (ESB15, ESB16, ESB18, ESB23, ESB24, ESB28)

- Carbonatic: >30% calcite (ESB7, ESB9, ESB13, ESB19, ESB20, ESB25)

It is remarkable that the bentonitic samples were the ones where smectite had a lower crystallinity, characterized by a higher FWHM with a Biscaye Index close to zero in the pink clays.

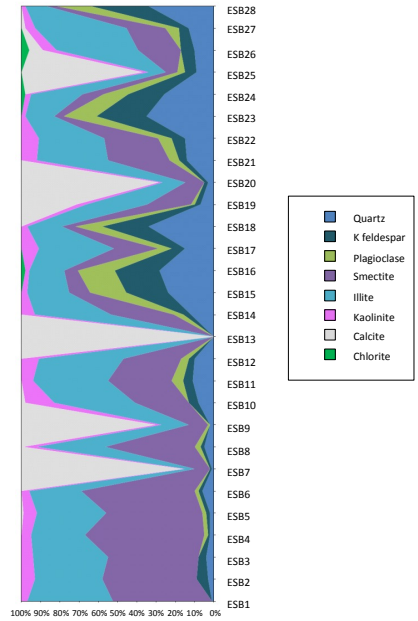

fig 2. *Variation in the mineral content.*

Biomarker Analysis.

We selected two types of biomarkers, *n*-alkanes and *n*-alkanoic acids. Some proxies were employed in this study, such as the Carbon Preference Index (CPI) (Bray and Evans, 1961), Predominant Chain Length, Average Chain Length (ACL) (Eglinton and Hamilton, 1967), P*aq* (Ficken *et al*., 2000) and the terrigenous / aquatic ratio (TAR_{HC}) (Silliman *et al*., 1996) for n-alkanes, and Predominant Chain Length and terrigenous / aquatic acid ratio (TAR_{FA}) (Bourbonniere and Meyers, 1996; Tenzer *et al*., 1999) in the case of the n-alkanoic acids.

Of note, both *n*-alkanes and *n*-alkanoic acids presented the highest concentration in the bentonitic samples, especially in the pink clays, probably due to their high specific surface. Performing a bivariate correlation matrix, it can be observed that these biomarkers only showed a positive significative correlation with smectite.

In the multivariate cluster analysis considering the mineral and the biomarker content, we observed that samples were perfectly grouped, except sample ESB19, according to their high content in phyllosilicates (Fig.3). Samples of the Carbonatic association separated from the others and, in the same way, samples of the Bentonitic, Illitic, and Sandy associations were separated from each other.

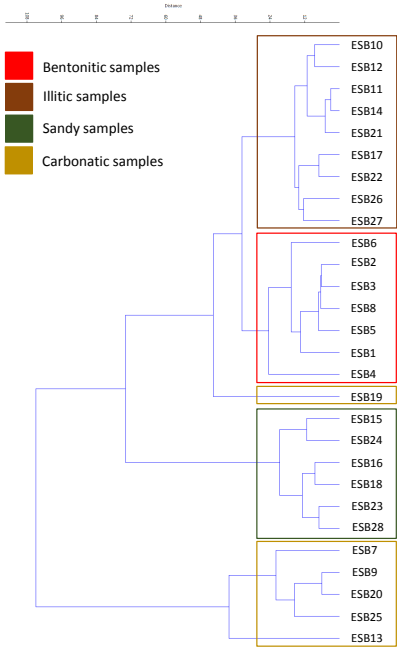

fig 3. *Multivariate cluster of mineralogy and biomarker content.*

The *n*-alkanes showed a distribution with odd over even chains predominance. In fact, the CPI values were superior to 2, indicating that the organic matter did not show an important maturity. Samples ESB13 and ESB16 were an exception, as CPI values were close to 1, which might be linked to microbial degradation or diagenetic processes (Hedges and Prahl, 1993).

In general, there was a predominance of alkanes with 25, 27, 29 and 31 carbon atoms (Fig.4), the last three indicating a terrestrial origin of the organic matter (Rieley *et al*., 1991). The predominance of C27 and C29 alkanes is linked to trees and woody plants (Cranwell, 1973). Some authors link the C27 alkane to a significant presence of deciduous trees (Engel and Macko, 1993). The C31 n-alkane is linked to herbaceous plants (Cranwell, 1987; Ficken *et al*, 1998). On the other hand, the only alkane that is linked to an aquatic origin is the C25 n-alkane, which is related to aquatic macrophytes (Ficken *et al*., 2000).

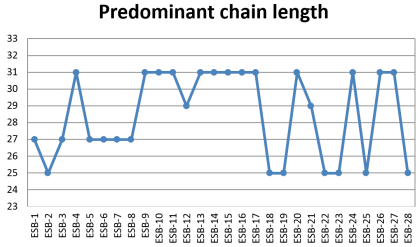

fig 4. *Predominant Chain Length of n-alkanes.*

Since we could observe a bimodal distribution at some samples, indicating a mixed origin, we used the ACL. This proxy is more trustworthy than the Predominant Chain Length when considering the possible origin of the organic matter. Samples ESB1, ESB2, ESB3, ESB6, ESB25 and ESB28 had lower ACL values (Fig.5), indicating a mixed origin of terrestrial vegetation and aquatic macrophytes or algae (Pancost *et al*., 2002). In the rest of the samples, the organic matter had a terrestrial origin, with certain influence of aquatic macrophytes. This is corroborated by the P*aq* index, with values between 0.1 and 0.6 (Ficken *et al*. 2000). Moreover, the TAR_{HC} values, together with those of ACL, showed that samples ESB1, ESB2, ESB3, ESB6 and ESB25 had a mixed input of terrestrial vegetation and algae (Silliman *et al*., 1996).

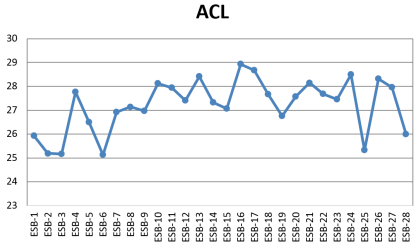

fig 5. *Average Chain Length (ACL) of n-alkanes.*

The *n*-alkanoic acids showed a unimodal distribution, being predominant the C16 homologue (Fig.6), indicating certain bacterial activity and degradation (Cranwell, 1974, 1976; Kawamura and Kaplan, 1987; Haddad *et al*., 1992; Ho and Meyers, 1994). Samples ESB3 – ESB8 showed a bimodal distribution, being the C24 and C28 homologues predominant in some of them.

Samples with a bimodal distribution,

present TAR_{FA} values higher than 1 (Fig.7). This fact indicated a major input of terrestrial organic matter with certain degradation, but less important than in the rest of the samples.

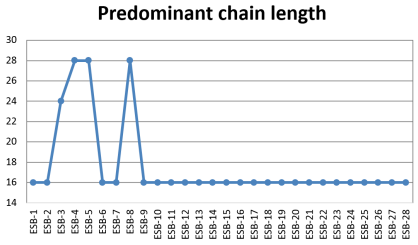

fig 6. *Predominant Chain Length of n-alkanoic acids.*

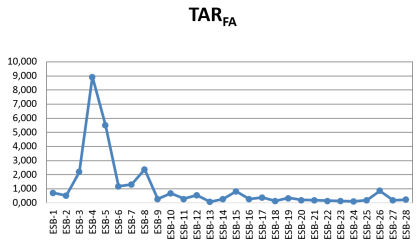

fig 7. *Terrigenous / aquatic acid ratio (TAR_{FA}) of n-alkanoic acids.*

CONCLUSIONS

Considering all the previous data exposed, we can conclude:

1. Smectite content is linked with the content of biomarkers.

2. Biomarkers, along with mineralogy, give excellent criteria to separate samples in different clusters.

3. Biomarkers are an important tool to identify diagenetic processes, such as the ones that took place at sample ESB13.

4. *n*-alkanes indicate that the organic matter input of these samples was aquatic, terrestrial, as well as a mixture of both of them.

5. Green clays present organic matter with a mixed origin, with influence of aquatic macrophytes or algae, while pink clays present mainly organic matter of terrestrial origin.

6. *n*-alkanoic acids indicate a notable degradation of organic matter in all the samples except in samples ESB3 – ESB8, whose degradation is less important.

ACKNOWLEDGMENTS

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