

Crystallochemical Complexity of Magnesian Clays from the Tajo Basin

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INTRODUCTION

The Tajo Basin is an intracratonic basin located in the center of the Iberian Peninsula, filled along the Tertiary by materials coming from the erosion of the surrounding mountain ranges (Cordillera Ibérica, Sierra de Altomira, Sistema Central and Montes de Toledo). This basin is exceptionally rare (García - Romero, 2004), considering: 1) its richness in magnesian clays (sepiolite, palygorskite, saponite and stevensite), which need a high silica and magnesium activity to be formed, 2) the lack of potential source rocks with high contents in Mg to justify the formation of these clay minerals. In order to show the rareness of this basin as well as its wide differences, representative samples of the main deposits have been crystallochemically characterized.

MATERIALS AND METHODS

Eight samples from the main clay deposits located in the Miocene (Fig. 1) were chosen to show the complexity of the magnesian clays from the Intermediate Unit of the Tajo Basin.

- BAT1 was collected at Cerro de los Batallones (Madrid).
- E3, E10 and RESQ were collected in the proximity of the town of Esquivias (Toledo).
- CABP was collected at the town of Cabañas de la Sagra (Toledo).
- VER and ROS were collected at Cerro de Magán exploitation, which is located to the SE of the town of Cabañas de la Sagra (Toledo).
- SYU was collected near to the town of Yuncillos (Toledo).

The samples were characterized by X-Ray Diffraction (XRD), with the usual methodology for clay studies. A Siemens D-500 with CuK α radiation and a graphite monochromator was used.

Particle morphology and textural relationships were established using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM observations were performed using a PHILIPS XL-30 operating at 40kV, as well as a JEOL JSM-6330F operating at 10kV. Prior to the SEM observation, samples were air dried and Au-coated under vacuum in an Ar atmosphere. TEM observations were performed by depositing a drop of diluted suspension on a microscopic grid with collodion and coated with Au.

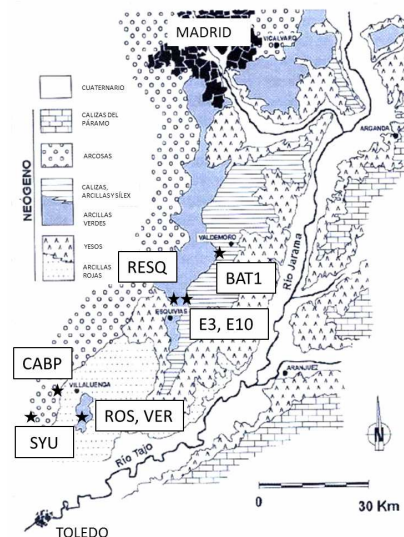


Fig 1. Localization of the samples. Map of the Madrid Basin, taken from Leguey and Doval, (1987).

The chemical composition was obtained using analytical electron microscopy (AEM) with TEM, in samples of great purity, using a JEOL 2000FX microscope equipped with a double-tilt sample holder at 200 kV. The microscope incorporates an OXFORD ISIS EDX spectrometer (136eV resolution at 5.39 keV) and has its own software for quantitative analysis. A PHILIPS CM-20 operating at 200 kV was also used.

Samples identified as smectite by XRD were treated in order to eliminate Mg located as interlayer cation. For this purpose 500 ml of a 1N CaCl₂ dissolution were added to 50 g of powder sample, stirred afterwards for 1h. The sample was washed until elimination of chlorides and recovered by centrifugation. The same procedure was done with KCl for the ROS sample.

RESULTS AND DISCUSSION

From the results obtained by the mineralogical characterization done by XRD, we can see that the samples correspond to sepiolites, palygorskites and smectites. This is confirmed by the structural formulae, which are estimated using the average of the analytical data obtained by AEM.

Palygorskite

Only the E10 sample diffracted as palygorskite with quartz as its only impurity. The d_{110} spacing is 10.8 Å, which is pretty high compared to its ideal spacing (10.4 Å). This is probably related to its high Mg content (Suárez et al., 2007) according to its intermediate composition in the sepiolite-palygorskite continuous polysomatic series (Suárez & García-Romero, 2013) which indicates the presence of sepiolite polysomes. Considering the point analysis obtained by AEM, we classify this sample as a magnesian palygorskite or as type III according to the classification of Suárez and García-Romero (2011).

This sample was also studied by García-Romero et al. (2014), noting that its fibres have an intermediate length comprised between 1 and 10 μ m, falling into group 2 of the size classification proposed by García-Romero & Suárez (2013). Fibres of this type are also

straight and might even look like rigid fibres.

Sepiolites

The sepiolite samples are BAT1, CABP E3 and SYU. These samples are very pure, containing small amounts of quartz and calcite, as well as other clay minerals as smectite. It is remarkable that d_{110} spacings for the full rock diffractogram are higher than its theoretical one (Fig. 2).

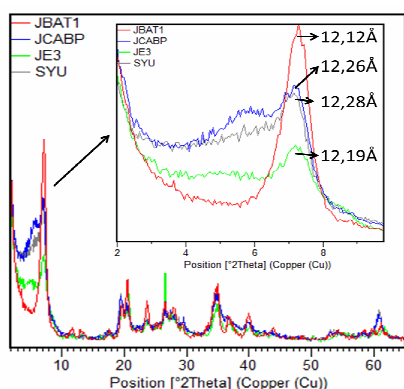


Fig 2. d_{110} different d -spacings for sepiolites shown by XRD.

In the ethylene glycol solvated oriented aggregate, the d_{110} spacing is even higher, as it is the case of sample BAT1, which has a value of 12.35 Å. Therefore, a small swelling took place. This, altogether, makes us think about a possible intergrowth of sepiolite and smectite. In a recently published article by Yeniol (2014), higher d_{110} spacings are interpreted as too poorly crystallized sepiolite.

Using the AEM data, we obtain the structural formulae, allowing the sample classification. According to the classification of Suárez and García-Romero (2011), samples BAT1 and E3 are classified as Al-sepiolite, which is an intermediate composition in the sepiolite-palygorskite polysomatic series.

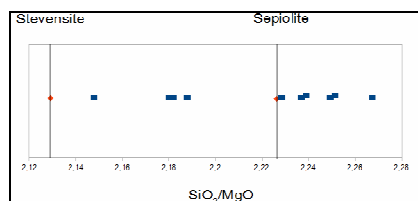


Fig 3. SiO_2/MgO relationship for particles of CABP.

The AEM analyses of fibrous particles of CABP sample show a very wide dispersion both for tetrahedral and

octahedral cations (Fig. 3) and they do not correspond to sepiolite. Some of them are intermediate between sepiolite and stevensite, while the others are closer to palygorskite. SYU also shows an intermediate composition between sepiolite and saponite (Fig. 4).

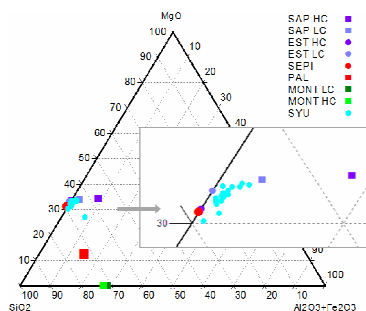


Fig 4. Compositional variation of the fibrous particles in the SYU sample. Theoretical compositions of clay minerals are also plotted for their comparison.

Smectites

The samples that diffract like smectites were RESQ, ROS and VER. These samples were also very pure, with small amounts of impurities such as quartz, calcite, as well as illite and chlorite in the case of VER. The XRD patterns for the RESQ and ROS samples show that they are strongly delaminated, as well as their clear trioctahedral character.

Regarding the crystallochemistry of these smectites, as for sepiolite and palygorskite, these minerals do not exactly fit to ordinary saponite and stevensite. In addition, the existence of Mg as interlayer cation adds a problem to the study of these samples. The AEM analysis of the natural RESQ and ROS samples fitted as 2:1 phyllosilicates, indicates that these samples result as talc, because the layer charge is close to zero. When RESQ and ROS samples treated with Ca and K are analyzed, these samples fit to saponite. Although these samples, ROS and RESQ, diffract as very pure and delaminated smectite, the presence of high amounts of fibres is observed by SEM.

The analytical data obtained from the VER sample show a wide variation of its mineralogy, going from saponite to illite and pure mica related to the presence of impurities in bentonite.

FINAL REMARKS

All the samples studied present a very

notable difference between their ideal formulae and the ones obtained from the data derived from the AEM analyses, as well as remarkable differences in the XRD patterns. These samples present a great dispersion regarding their chemical composition and sometimes the point analyses present intermediate compositions between sepiolite-palygorskite or sepiolite-saponite and they can even be adjusted for the two mineral phases. These XRD and AEM data suggest the existence of intergrowths, not only between sepiolite and palygorskite, but also between laminar and modulated phyllosilicates.

ACKNOWLEDGEMENTS

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