



Research paper

Approach to the trace element geochemistry of non-marine sepiolite deposits: Influence of the sedimentary environment (Madrid Basin, Spain)

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ABSTRACT

The trace element geochemistry of sepiolite-rich beds from five lithological sections in the Neogene Madrid Basin was analysed. The samples were collected from representative deposits including alluvial fan (Vicálvaro, Cabañas de la Sagra), palustrine (Cerro de los Batallones) and mudflat (Esquivias, Magán) facies. The mineralogical composition of the samples point out the abundant content of sepiolite, commonly higher than 95%, with variable content of quartz, feldspars, calcite, palygorskite and/or Mg-smectite. The sepiolite occurs as laminated, massive and brecciated facies, often with intraclasts of similar sepiolite composition. The geochemical results indicate that all the trace elements analysed are mostly depleted with respect to the UCC standard (Upper Crust Composition), especially REE (<0.4). The higher depletion was observed in sepiolites from mudflat facies (V and U content are an exception). Cluster analysis of geochemical data corroborates the differences between mudflat sepiolites and those from palustrine and alluvial-related facies. The normalization of REE with chondrite allows clear differentiation between the sepiolites associated with alluvial fan facies from all the remaining samples. On the other hand, the La/Sc ratio against Th/Co ratio indicates provenance from felsic rocks. High content in F (>4000 µg/g) and low content of Li (20–180 µg/g) is remarkable, allowing to separate samples of sepiolite formed in alluvial fan environments from those of mudflat and palustrine deposits. The geochemical complexity observed in the sepiolites was closely related to the specific mechanisms of formation under different environmental conditions.

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1. Introduction

From a genetic point of view the formation of sepiolite takes place mainly in continental, non-marine environments (alluvial, lacustrine, palustrine) although occurrences in perimarine and hydrothermal conditions have been also reported (Calvo and Pozo, 2015; and references therein). Certainly, references to sepiolite formed in continental environments are abundant (Galán and Pozo, 2011, 2014; Pozo and Galán, 2015; and references therein). Scientific research on the genetic relationship between sepiolite and other Mg-clays is relatively scarce despite occurrence of fibrous and non-fibrous Mg-clays in a same deposit has been recognized (e.g. Chahi et al., 1997; Khoury et al., 1982; Post and Janke, 1984; Martín de Vidales et al., 1991; Hay et al., 1995; Pozo and Casas, 1999; Akbulut and Kadir, 2003; Pozo and Galán, 2015), thus suggesting a close genetic relationship between the Mg-clay minerals.

Sepiolite is a typical authigenic clay mineral (Calvo and Pozo, 2015) that usually precipitates from water bodies undergoing evaporation but it can precipitate also from interstitial fluids in sediments. Besides these

formation processes, sepiolite can originate from magnesian-silicate substrates or pre-existing minerals during diagenesis. The widest accepted mechanism for sepiolite formation is direct precipitation from solutions containing dissolved ionic species (silica and magnesium) (Trauth, 1977; Jones and Galán, 1988; Galán and Pozo, 2011).

The geochemistry of Mg-clays in relation to their formation pattern has been summarized by Tosca (2015). According to Tosca and Masterson (2014), sepiolite can be synthesized in the lab as a low crystallinity product at different pH, salinity and Mg/Si concentration than those required for kerolite or stevensite. At low salinity (NaCl_i = 0.00 mol/kg) sepiolite precipitation can form at pH between 8.7 and 9 depending on the Mg/Si concentration (whilst it forms at lower pH when Mg/Si concentration is high). At relative high salinity (NaCl_i = 0.46 mol/kg) and low Mg/Si concentration, pH rules the precipitation of sepiolite. These results indicate that Mg-clays formation can occur in a wide range of salinities controlled by the Mg/Si concentration and pH, thus supporting the results by Clauer et al. (2012) in the study of the crystallization conditions of kerolite–stevensite, saponite and sepiolite by means of isotopic analysis (δ¹⁸O, δ D).

Spain is the largest producer of sepiolite that accounted for about 95% of the world's annual production in the last decade (Murray et al., 2011). The sepiolite deposits under exploitation are mainly located in

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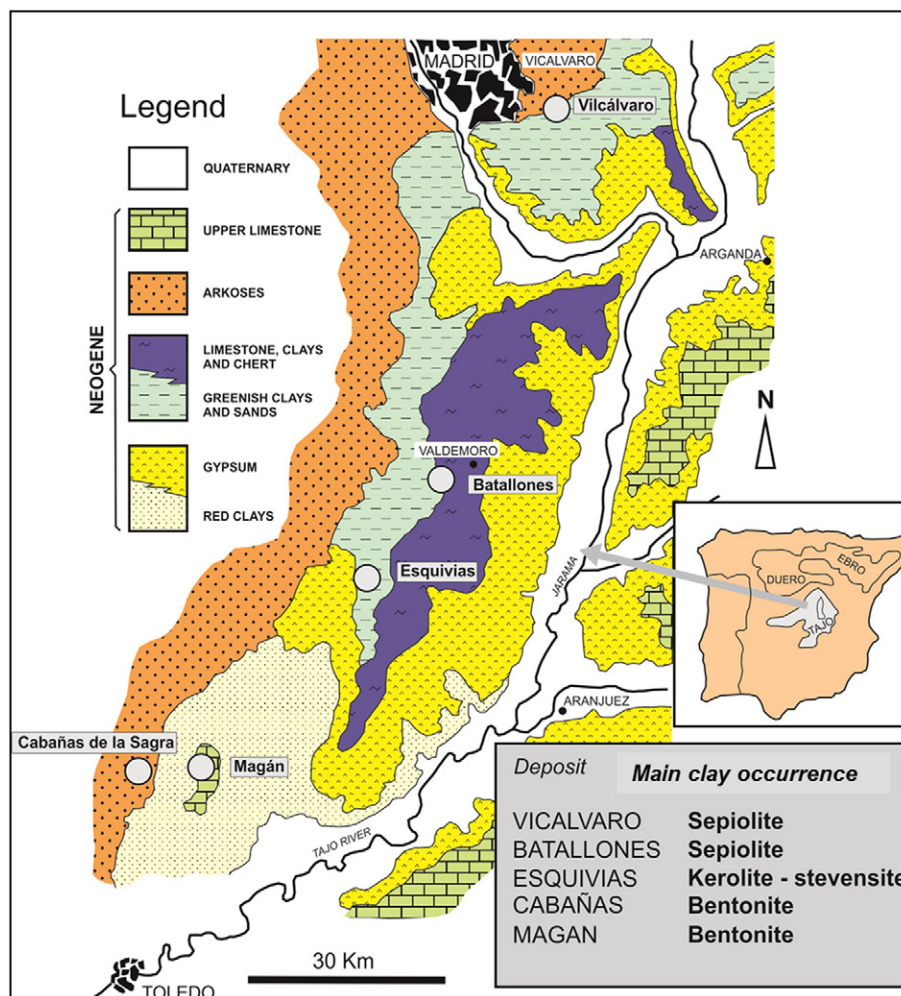


Fig. 1. Geological sketch of the Madrid Basin showing location of the sampled deposits. Modified from Clauer et al. (2012).

the Madrid Basin, central Spain (Galán and Castillo, 1984; Galán and Pozo, 2011; Galán and Pozo, 2014; Pozo and Galán, 2015).

The Madrid Basin is located in central Spain (Fig. 1). The basin formed as a result of intense Cenozoic Alpine deformation within the Iberian microplate driven by the Africa–Eurasia collision (De Vicente et al., 2011). During most of the Neogene, the basin was occupied by lacustrine and palustrine sedimentary deposits fringed by alluvial fan and fluvial distributary facies forming a centripetal drainage system (Calvo et al., 1995). The sedimentological analysis of the lacustrine deposits and their lateral relationship with alluvial facies that fringe the basin margin suggests that the lake systems underwent significant changes through Miocene (Calvo et al., 1989).

The facies association bearing Mg-clays was named “Magnesian Unit” by Pozo and Casas (1999) dealing with the anomalous Mg content the claystone deposits show. This unit is actually a transition zone between alluvial and marginal lacustrine facies within the Miocene Intermediate Unit (Galán 1979; Ordoñez et al., 1991).

The sepiolite deposits occur in two main palaeogeographic situations, either associated with distal alluvial fan facies (e.g. Vicálvaro–Cabañas de la Sagra) (Calvo et al., 1986; Leguey et al., 1989; Castillo, 1991; Bustillo and Alonso-Zarza, 2007; Galán and Pozo, 2011) or related to palustrine and mud flat shallow lacustrine sedimentary sequences (e.g. Cerro de los Batallones, Esquivias, Magán).

The geochemical variability of the Mg-clays of the Madrid Basin was reported by Torres-Ruiz et al. (1994) and Pozo et al. (1999a). Meaningful differences between sepiolite and Mg-clays were observed, especially in the abundance of rare earth elements (REE), transition trace elements (TTE), F and Li.

The aim of this paper is to show the geochemical characteristics of the different sepiolite deposits of the Madrid Basin, and make comparison among the deposits according to the sedimentary environment in which they occur. Particular attention is given to the correlation between trace elements distribution and paleoenvironment provided its eventual relationship with the process of sepiolite formation.

2. Materials and methods

2.1. Lithological sections and sampling

Taking into account the different sedimentary environments in which sepiolite occurs in the Madrid Basin a total of sixteen samples were collected from alluvial-related facies (Vicálvaro and Cabañas), mudflat facies (Magán and Esquivias) and palustrine facies (Cerro de los Batallones) (Fig. 1; Table 1). The palaeoenvironmental scheme and lithological sections with indication of samples collected are shown in Fig. 2.

The southernmost sampled deposits occur near the town of Cabañas de la Sagra and Magán, about 55 km far from Madrid (Fig. 1). One sample of white sepiolite was collected in the Cabañas bentonite-sepiolite deposit (Table 1). The bentonite/sepiolite beds are commonly bounded by arkosic facies at the bottom and/or arkosic facies or silcrete at top (Pozo and Calvo, 2015). Regarding the Magán bentonite deposit, one sample of brecciated pinkish sepiolite was collected (Table 1). Sepiolite occurs at top of shallowing-upward sequences with green bentonites (Fig. 3A).

Around 20 km far from the Cabañas de la Sagra and Magán deposits, a kerolite–stevensite deposit is exposed nearby the town of Esquivias

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