



Stable oxygen and hydrogen isotopic composition of bentonites from Cabo de Gata (Almería, Spain)

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ABSTRACT

The aim of this study is to investigate the nature of the solutions and the temperature during the bentonite formation by using $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and the relationship between chemical and isotopic composition of smectites from Cabo de Gata region. Therefore, 36 bentonite samples had been selected. For analyses the $< 2 \mu\text{m}$ fraction were separated. Most of the samples contain smectite above 90 wt%. The stable oxygen and hydrogen isotopic composition of the analysed smectites is close to the "montmorillonite line". However, from isotopic composition two types of bentonite can be distinguished. The Sierra de Gata (SG) and Serrata de Nijar (SN) types show $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values above and below this line, respectively. Temperatures obtained from geothermometer equation are similar to the temperatures values obtained from the equation of Savin and Lee (1988). Estimated formation temperatures of SG type are 25 and 49 °C higher compared to those of the SN type (6 and 25 °C).

Correlations between structural cations versus isotopic composition show no statistical significance concerning all samples. However, separating the samples of SG (Sierra de Gata) from SN (Serrata de Nijar) a statistical significance for the individual areas is obtained. In both cases the effect is similar for ^{18}O and for ^2H . This could be due to the different composition of the solutions forming these bentonites.

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1. Introduction

The isotopic composition of a naturally occurring clay depends on (a) the isotopic composition of the ambient water at the time the mineral formed; (b) the temperature of the environment when the mineral formed; (c) whether the clay formed in isotopic equilibrium with its environment, and if so, the magnitude of the isotopic fractionation factor at the temperature of formation; and (d) whether the mineral has retained its original isotopic composition, and if not, the environmental conditions of subsequent isotopic exchange and the degree to which the mineral has approached isotopic equilibrium with the new environment.

Application of stable isotope data to geological processes may involve "tracer" and isotopic fractionation approaches. Tracers can be used to identify the origin of a component if distinct isotopic compositions occur in a respective geologic setting.

Many authors used stable oxygen and hydrogen isotope data to estimate the conditions during clay mineral formation in sedimentary basins (Yeh and Savin, 1977; Yeh, 1980), at the sea floor (Cole, 1985; Schöps et al., 1993) and in bentonite deposits

(Leone et al., 1983; Kolarikova and Hanus, 2008). The aim of this study is to evaluate the *nature* of the solutions and the temperature during bentonite formation, using $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and chemical signals of smectites from Cabo de Gata region.

2. Geological setting

The Cabo de Gata volcanic outcrops are part of an extensive volcanic area mainly submerged beneath the Alboran Sea (Fig. 1). The origin of these volcanic rocks is associated with the geotectonic dynamics of the Western Mediterranean Sea during the Neogene. The continental collision prior to an extensional process occurring in several stages according to the different phases of magmatism is the one that best fits the data on regional geology, geophysics, palaeomagnetism and geochemistry (Fernández Soler, 1992). The volcanic rocks give K:Ar ages ranging from 15 to 7 Ma (Bellon et al., 1983; Di Battistini et al., 1987; Zeck et al., 1999). The volcanism is of the calc-alkaline type, with rocks predominating by andesites to rhyolites, andesites and dacites (López Ruiz and Rodríguez Badiola, 1980; Bordet, 1985; Fernández Soler, 1992). Two distinct calc-alkaline volcanic formations occur in this area: Sierra de Gata (SG) and Serrata de Nijar (SN; see Fig. 1).

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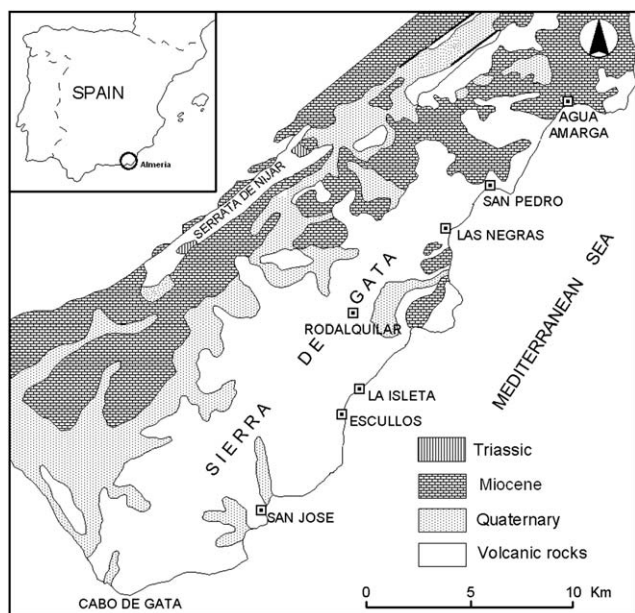


Fig. 1. Geological map of the study area (Cabo de Gata; SE of Spain) and sampling sites for bentonites (SN: Serrata de Nijar; SG: Sierra de Gata).

The Cabo de Gata rocks have been exposed to marine and meteoric conditions throughout the geological history. The late volcanic activity also created hydrothermal systems with flow of marine and/or meteoric waters. Therefore, fluids with different chemical composition and different temperatures took part in the alteration processes of the volcanic materials. The alteration of volcanic rocks by acidic sulphate solutions produced mainly silica, alunite, jarosite and kaolinite (Friedrich, 1960; Lodder, 1966; Martín-Vivaldi et al., 1971; Puy et al., 1974). This process has been occasionally related to the gold deposits in the area (Sáanger-von Oepen et al., 1989, 1990; Rytuba et al., 1990; Arribas et al., 1995). On the other hand, neutral or slightly acidic or basic solutions would have caused the most important bentonite deposits in the area (Reyes, 1977; Linares, 1985, 1987; Caballero, 1985; Caballero et al., 1985).

Bentonite deposits of this area generally occur in relation to fractures, aligned mostly in a NE–SW direction. The altered materials are volcanic tuffs, agglomerates, ignimbrites. The hydrothermal alteration affected basic and acid rocks and produced deposits of variable form and thickness, from small pockets to massive deposits with several million tons of bentonite. Vestiges of the primary volcanic material of the deposition are occasionally preserved and reveal that the alteration took place *in situ*. Indications of transport and even some sedimentary structures are occasionally observed. The alteration affected material of different ages, but not all the pyroclastic materials were transformed. Mineralogical and geochemical studies have been carried out on these bentonites and the parent volcanic rocks of the Cabo de Gata region (see Caballero et al., 2005).

3. Materials and methods

36 bentonites samples were collected from Serrata de Nijar (SN-1 to SN-22) and Sierra de Gata (SG-1 to SG-14), with 97% dioctahedral smectitic component, quartz, plagioclase, amorphous silica and calcite as accessories. The surface area is 632 m²/g and the cation exchange capacity is 92 mEq/100 g (Cuadros and Linares, 1996).

The < 2 μm fraction were separated by ultrasonic dispersion and sedimentation in distilled water without using dispersing agents. The chemical analyses of major elements in the < 2 μm fraction was determined using X-ray fluorescence (XRF) in a Philips PW 1404/10 spectrometer.

The mineralogical analysis was determined by X-ray diffraction followed the standards of Wilson (1987) and Moore and Reynolds (1989), both for the bulk sample and for the oriented aggregate sample solvated with ethylene glycol. The equipment used was a Philips PW1712 diffractometer equipped with Cu-Kα radiation, graphite monochromator and automatic slit. The working conditions were as follows: tension 35 Kv, intensity 40 mA, goniometer speed 0.2°/s, integration time 0.4 s and scan interval between 3 and 70°2θ for the total powder sample and 3–50°2θ for oriented aggregates samples of the less than 20 μm fraction.

Oxygen isotopic compositions of the smectites (< 2 μm fraction) were determined by the method of Clayton and Mayeda (1963). After the removal of interlayer water by heating at 200 °C for 8 h under vacuum, the oxygen was extracted from the clay minerals by fluorination. It was then purified and converted to CO₂ using a vacuum line. For D/H measurements, structural water was extracted by heating the sample (previously degassed at 200 °C, in vacuo) at 1000 °C. The excess H₂ was oxidized to H₂O by reaction with CuO. The water was immediately removed by freezing in a glass trap cooled with liquid nitrogen. δ²H analyses were performed as described by Friedman (1953) and Coleman et al. (1982) by reduction with Zn at 450 °C. Isotope analyses of the samples studied show a standard deviation of replicate δ¹⁸O-values less than ± 0.2‰ and for δ D-values less than ± 2‰. All values reported are relative to VSMOW. CO₂ was measured in a Finnigan Mat 251 mass spectrometer with VSMOW as standard reference and analytical precision of ± 0.1‰.

4. Results and discussion

Table 1 shows the structural formulas for 1/2 unit cell, determined from the chemical analysis for each smectite in accord of Marshall (1949) method, which consists of supposing a network of oxygens and OH with a whole of 44 negative charges (O₂₀(OH)₄). To realize this calculation the sample must be a single mineral. The mineralogical impurities (~3%) present in the samples has been eliminated by stoichiometry.

The smectites have octahedral iron ranging from 0.014 to 0.30 atoms per half unit-cell; tetrahedral silica ranging from 3.65 to 3.97 atoms per half unit-cell and octahedral Mg ranging from 0.44 to 0.76 atoms per half unit-cell.

The δ¹⁸O and δ²H values for smectites from bentonites are given in Table 2 relative to VSMOW standard. In Sierra de Gata (SG-1 to SG-14), δ¹⁸O and δ²H values of the smectites vary from +16.3‰ to +25.8‰ and –85.7‰ to –29.7‰, respectively. The samples from Serrata de Nijar (SN-1 to SN-22) show δ¹⁸O and δ²H values from +24.3‰ to +30.5‰ and –82.5‰ to –33.8‰, respectively.

The isotopic composition (δ¹⁸O and δ²H) of smectites are plotted in Fig. 2, together with the Meteoric Water Line (MWL) (Craig, 1961) and with the “line for montmorillonite” obtained from isotope fractionation factors for montmorillonite–water at earth-surface temperature (Savin and Epstein, 1970). We can see that all data lies close to the “montmorillonite line”. Two types can be distinguished: the SG-type bentonite with δ¹⁸O and δ²H values above this line and the SN-type bentonite with δ¹⁸O and δ²H values below this line.

Clay minerals are usually produced in aqueous environments and their oxygen and hydrogen isotopic compositions may reflect

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