Research Paper

Stability of lanthanum-saturated montmorillonite under high pressure and high temperature conditions

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ABSTRACT

Smectite has been used to capture radioactive cations through adsorption in deep radioactive waste repositories in various parts of the world. Smectite is also important in the transport of water and some trace element cations such as rare earth elements (REE), which are captured in its structure, back to the mantle in subduction environments. Such captures are based on the ionic strength of the surrounding solution and the adsorption coefficient of smectite. However, captured cations can be released from the smectite structure once the ionic strength of the solution changes. In this work, the stability of a particular smectite (montmorillonite) structure saturated with lanthanum was verified at high pressures (up to 12 GPa) and room temperature and at high pressure and high temperature (HPHT) concomitantly. La^{3+}-montmorillonite remains stable up to 12 GPa at room temperature with a small variance in its vibrational mode. At HPHT, however, the structure becomes muscovite-like and rich in La^{3+}. When in contact with a Ca^{2+}-enriched solution, La^{3+} is partially replaced by Ca^{2+} in the new phase, returning to its original Ca^{2+}-montmorillonite phase, whereas another part remains La-muscovite-like. These results were confirmed by X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectroscopy.

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1. Introduction

Smectites are clay minerals with a tetrahedral:octahedral structural ratio of 2:1. Due to isomorphic substitutions in the octahedral and tetrahedral sheets, a net negative charge is established in the structure; this charge is balanced through cation adsorption, usually in the interlayer spaces, which results in a high cation exchange capacity (CEC) (Bergaya et al., 2006). In addition to the adsorption of mono- and divalent cations such as Na^+, K^+, and Ca^{2+}, smectite can also adsorb trivalent elements (e.g., trivalent rare earth elements (REE^{3+}) and trivalent actinides), as has been shown in several studies (Takahashi et al., 1998; Stumpf et al., 2001; Bradbury and Baeysns, 2002; Coppin et al., 2002; Stumpf et al., 2002; Coppin et al., 2003; Stumpf et al., 2004; Rabung et al., 2005; Brandt et al., 2007; Tan et al., 2010). Due to these and other features, smectites are used as geochemical barriers in different contexts including secondary barriers for deep nuclear waste disposal (Pusch, 1998), where smectites are employed to adsorb actinide trivalent cations. In the geologic environment, smectites can play an important role in oceanic subduction-related zones because they transport water in higher amounts compared to micas or kaolinites; thus, some elements such as K^+ and Na^+ along with very minor

quantities of incompatible elements such as REE^{3+} are transported back to the mantle, causing mantle refertilization.

The different reaction mechanisms between clay minerals and cations are as follows: outer-sphere interaction, inner-sphere interaction, cation exchange within the interlayer spaces, and structure incorporation in the octahedral layer (Takahashi et al., 1998; Strawn and Sparks, 1999; Stumpf et al., 2001; Bradbury and Baeysns, 2002; Coppin et al., 2002; Stumpf et al., 2002; Coppin et al., 2003; Stumpf et al., 2004; Rabung et al., 2005; Brandt et al., 2007; Tan et al., 2010). The different modes of clay mineral–cation interaction are highly dependent on the pH of the surrounding environment. At pH values equal to or lower than 5, the adsorption is outer-sphere; while at pH values higher than 5, adsorption becomes inner-sphere (Strawn and Sparks, 1999; Stumpf et al., 2001, 2002).

Several studies have shown that smectite stability is strongly dependent on temperature. Temperatures between 105 °C and 240 °C destabilize 40% of smectite, transforming it into illite in 3.4 million years (Kamel et al., 1990). At temperatures lower than 100 °C, the rate of transformation is 0.3% per million years (Chapman et al., 1984), while smectite remains unchanged for over 10^6 years at temperatures lower than 90 °C (Pusch and Karnland, 1988; Pusch et al., 1989).

The effect of temperature on the structure of La^{3+}-montmorillonite (La^{3+}-Mt) was studied by Mozas et al. (1980), who showed that La^{3+}-Mt loses all its interlayer water at 320 °C. In this condition,

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La^{3+}-Mt can be re-hydrated once temperature decreases. However, at temperatures higher than 500 °C, the re-hydration of La^{3+}-Mt no longer occurs (Alba et al., 1997).

Although some studies have investigated the temperature dependence of montmorillonite stability, few works have explored montmorillonite stability under high pressure conditions. When Ca^{2+}-montmorillonite (Ca^{2+}-Mt) is exposed to pressures up to 13 GPa at room temperature, the vibrational mode of the tetrahedral Si–O bond is affected without compromising the Ca^{2+}-Mt structure. Once pressure is released, Ca^{2+}-Mt returns to its original structural condition (Alabarse et al., 2011). Under high pressure and high temperature (HPHT) conditions such as 7.7 GPa and 250 °C, Ca^{2+}-Mt remains stable (Alabarse, 2009).

The goal of this work is to study the effect of pressure and temperature on the stability of La^{3+}-Mt. The results of this study will be used to understand the transportation of elements in subduction environments. In addition, we intend to transform La^{3+}-Mt into a new in La^{3+}-rich structure under HPHT and verify whether this new structure releases La^{3+} when in contact with an aqueous solution enriched in other elements. Lanthanum is analogous to actinide radionuclides due to their similar chemical properties (Krauskopf, 1986), and this experiment focuses on radioactive waste disposal. Future works will examine smectites saturated with different lanthanides (samarium, neodymium, gadolinium and lutetium).

2. Experimental methods

2.1. Starting material

Ca^{2+}-Mt was extracted from bentonite collected on the border of Brazil and Uruguay in the regions of Aceguá (Brazil) and Melo (Uruguay).

The structural formula of the montmorillonite used in this work was determined by Calarge et al. (2003) from a bulk bentonite and is given by:

$$[Si_{3.87}Al_{0.13}]O_{10}\left(Al_{1.43}Fe_{0.08}^{3+}Mg_{0.53}Ti_{0.01}\right)(OH)_2 K_{0.01}^+ Ca_{0.2}^{2+}. \tag{1}$$
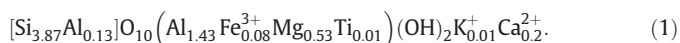
The material is montmorillonite with calcium as the main interlayer cation, and the calculated layer charge was 0.47 per $O_{10}(OH)_2$.

Ca^{2+}-Mt was separated from bentonite by particle decantation in order to concentrate particle sizes smaller than 2 μm (Day, 1965). First, the bentonite was gently ground, and 200 g of the sample was placed into 500-ml bottles (50 g of bentonite and 300 ml of distilled water per bottle) followed by shaking for 24 h. Subsequently, the solution was left in a beaker for 24 h and 30 min to allow particles smaller than 2 μm to separate according to Stoke's law.

2.2. Cation exchange process

Cation exchange was performed in order to produce La^{3+}-Mt from Ca^{2+}-Mt via the substitution of Ca^{2+} with La^{3+} using the saturation method. Ca^{2+}-Mt (0.1 g) was added to 25 ml of 1 mol/l $LaCl_3$ solution over 1 h. Subsequently, the solution was replaced with another 25 ml of 1 mol/l $LaCl_3$ solution and left for 24 h. The sample was then centrifuged and washed with ethyl alcohol until the AgCl test was negative for the presence of Cl in the final material. The pH was buffered at 5 during the entire procedure. The sample was dried at room temperature. Finally, the process was repeated in order to obtain a greater amount of sample.

2.3. High pressure and high temperature (HPHT) experiments

2.3.1. Toroidal chamber experiments

HPHT experiments were performed on a hydraulic press with a toroidal chamber. A detailed description of the equipment used is provided elsewhere (Khvostantsev, 1974; Sherman and Stadtmuller, 1987; Stefani, 2012). This apparatus can reach pressures of up to 7.7 GPa and temperatures up to 2000 °C. The pressure cell consists of a graphite heater (height of 12.0 mm, diameter of 8.0 mm, and wall thickness of 2.0 mm) and two small disks of pyrophyllite calcinated at 1000 °C (diameter of 4.0 mm and height of 1.5 mm). To apply isostatic pressure, the La^{3+}-Mt sample was placed inside a hexagonal boron nitride (hBN) capsule (2.0-mm internal diameter and height). Finally, the hBN capsule containing the sample was placed in between the two pyrophyllite disks. In all experiments, pressure was initially applied at room temperature and kept at the desired value for 15 min for pressure stabilization. The pressure calibration was performed using bismuth (Bi), which has phase transitions at 2.5 and 7.7 GPa (Sherman and Stadtmuller, 1987).

Heating was applied simultaneously to pressure by passing an electric current through the reaction cell, which heats according to Joule's first law. Temperature calibration was carried out with a platinum and platinum rhodium thermocouple (13% Type-R). The ratio of applied voltage and temperature is known from the literature (Bundy, 1988).

After the experimental run, the samples were ground in an agate mortar just before XRD analyses. The experiments performed in this apparatus have pressure and temperature accuracies of ±0.5 GPa and ±25 °C, respectively (Alabarse, 2009).

2.3.2. Diamond anvil cell experiments

A Piermari-Block diamond anvil cell (DAC) (Piermarini and Block, 1975) was used to reach pressures of up to 12 GPa at room temperature. A mixture of 1 mass% La^{3+}-Mt powder in KBr and a small ruby were placed in a 250-μm diameter hole drilled in a Waspaloy gasket pre-indented to a thickness of 80 μm (Piermarini et al., 1975). Pressure was determined using the ruby technique (Piermarini et al., 1975) with an accuracy of ±0.2 GPa.

2.4. Analytical techniques

The samples were analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

SEM-EDS was performed on a sample of natural montmorillonite (Ca^{2+}-Mt), La^{3+}-Mt and La^{3+}-Mt processed at 2.5 GPa and 700 °C for 8 h. The equipment used was a JEOL JSM 5800 with an acceleration voltage of 10 kV, which allows the detection of any element heavier than boron.

XRD analyses were conducted using a Siemens D500 XRD powder diffractometer equipped with a CuKα source and a graphite monochromatic in the secondary beam. The spectra of all samples were obtained from 3° to 65° with a step of 0.05° at 2 s/step and from 58° and 65° with a step of 0.02° at 4 s/step in order to investigate the b-parameter.

FTIR spectroscopy was performed on Ca^{2+}-Mt and La^{3+}-Mt samples. An in situ FTIR analysis was performed on La^{3+}-Mt under pressure in the DAC using a Bomem FTIR model MB100 equipped with a DTGS detector and a KBr beam splitter. The spectral range was 350 to 4000 cm^{-1}, and a total of 512 scans was performed with 4 cm^{-1} resolution.

3. Results and discussion

3.1. Ca^{2+}–La^{3+} exchange in montmorillonite

The compositions of the natural Ca^{2+}-Mt and La^{3+}-Mt obtained by SEM-EDS are shown in Table 1. The amount of calcium in Ca^{2+}-Mt is in agreement with the literature (Alabarse et al., 2011). The XRD analysis (Fig. 1) of Ca^{2+}-Mt suggested the presence of a minor amount of quartz, and Ca^{2+}-Mt is characterized by the presence of the (001) basal plane at a distance of 15.21 Å. The 001 basal plane changes to