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Experimental evidence of the contrasting reactivity of external vs. interlayer adsorption sites on swelling clay minerals: The case of Sr^{2+} -for- Ca^{2+} exchange in vermiculite

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ABSTRACT

The potential contrasting reactivity of external (edge and basal) and interlayer adsorption sites is studied by investigating the Sr^{2+} -for- Ca^{2+} exchange in three different size fractions (0.1–0.2, 1–2, and 10–20 μm) of vermiculite. For a given equivalent fraction of Sr^{2+} in solution, the obtained experimental adsorption isotherms showed that the equivalent fraction of adsorbed Sr^{2+} on the solid decreased with decreasing particle size.

Using a combination of bulk chemistry, X-ray diffraction profile modeling of 00 ℓ reflections and morphological data, the interlayer site compositions were found to be independent of the vermiculite size fraction for a given chemical composition of the solution and without any preference between Ca^{2+} and Sr^{2+} cations. The lack of selectivity of both of these cations for interlayer adsorption sites [$\log K_{\text{int}}(\text{Ca}^{2+}/\text{Sr}^{2+}) = 0$] is supported by molecular simulation results indicating that Ca^{2+} and Sr^{2+} have similar interactions with the clay surface and water molecules in the interlayer space of vermiculite. In contrast, external adsorption sites exhibited a clear preference for Ca^{2+} cations [$-2.5 < \log K_{\text{ext}}(\text{Ca}^{2+}/\text{Sr}^{2+}) < -1.0$]. The two-site model (i.e., interlayer and external adsorption sites), which is constrained by the relative amounts of both types of sites derived from morphological analysis, is found to well interpret experimental ion-exchange experiments.

The two-site ion-exchange model derived from this study represents a morphology-constrained model with clear evidence of contrasting reactivity between external and interlayer adsorption sites. This model can be used to improve our understanding and prediction of the behavior of Sr^{2+} cations in contaminated soils with a wide range of particle sizes.

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1. Introduction

The cation exchange capacity (CEC) of clay minerals is an important aspect controlling inorganic element cycling in superficial environments, such as soils. This parameter is governed by crystal-chemistry and morphology of lamellar clay particles (Brigatti et al., 2013). The presence (or absence) of interlayer adsorption sites commonly separates clay mineral groups with relatively low (e.g., kaolinites, illites, micas, and chlorites) or high CEC values (e.g., smectites and vermiculites). The relative amounts of external adsorption sites, i.e., either located on the edges or on the (upper and bottom) flat basal surfaces of the particles, are mainly controlled by the morphology/shape of the particle, as its equivalent diameter and thickness. Considering a given mass of sample powder containing flat disk-shaped particles, the amount of external adsorption sites increases when the particle size decreases.

Several studies have considered different adsorption sites for interpreting the cation-exchange process of clay minerals. For instance, Bolt et al. (1963) considered three selectivity coefficients associated with “planar”, “edge”, and “interlattice” adsorption sites, respectively, to describe the cation exchange of K^+ with NH_4^+ , Ca^{2+} and Na^+ in illitic soil. In other studies, different types of adsorption sites were also considered when describing ion-exchange processes in illite and montmorillonite (e.g., Brouwer et al., 1983; Maes et al., 1985; Fletcher and Sposito, 1989; Poinssot et al., 1999; Bradbury and Baeyens, 2000; Zachara et al., 2002; Liu et al., 2004; Tournassat et al., 2004; Missana and García-Gutiérrez, 2007). In swelling clay minerals (i.e., vermiculite or smectites) with very fine particles, a noticeable amount of external adsorption sites may exist (Tournassat et al., 2003; Reinholdt et al., 2013). However, the assignment of a cation selectivity coefficient to specific external (edge + basal) adsorption sites is very complicated in the case of smectite. Indeed, due to the osmotic swelling of smectite particles dispersed in the aqueous phase, the number of layers per particle and the associated relative contributions of external vs. interlayer adsorption sites can vary as a function of chemical composition and

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ionic strength (Shainberg and Otoh, 1968; Fink et al., 1971; Tertre et al., 2011; Tournassat et al., 2011; Robin et al., 2015). In contrast, vermiculite clay minerals do not exhibit osmotic swelling of particles in solution (Lagaly and Dékány, 2013). Consequently, the integrity of the morphologies of vermiculite particles is preserved after immersion in water and thus the associated distribution of external vs. interlayer adsorption sites. This property makes vermiculite a good candidate for attempting to experimentally confirm the contrasting reactivity of external and interlayer adsorption sites.

An attempt to assign the contrasting reactivities of external and interlayer sites is performed in a case study of Sr²⁺-for-Ca²⁺ exchange on these three size fractions of vermiculite. The Ca²⁺ is one of the main cations that compensates for layer charge in swelling clay minerals in soils. In soils polluted due to nuclear power plant accidents, such as the Fukushima accident in 2011 or the Chernobyl accident in 1986, Ca²⁺ can be exchanged by strontium cations (i.e., Sr²⁺) in surrounding waters. Few authors tried to evidence a possible contrasted reactivity between Ca²⁺ and Sr²⁺ for both interlayer and external sites of smectites (Fletcher and Sposito, 1989; Missana and García-Gutiérrez, 2007). For instance, Fletcher and Sposito (1989) showed no preference between the two cations for both types of sites, whereas Missana and García-Gutiérrez (2007) reported no preference between the two cations only for interlayer sites. Indeed, these latter authors demonstrated a preference of Ca²⁺ over Sr²⁺ for edge sites. As far as vermiculite is concerned, Wild and Keay (1964) reported a preference of Ca²⁺ over Sr²⁺. However, in this latter study no attempt was done to assess a possible contrast of reactivity between the different types of site located in the particle. Then, the question concerning a possible contrast of reactivity for Ca²⁺-for-Sr²⁺ exchange for the different types of adsorption sites (i.e., interlayer and external) of swelling clay minerals remains.

In this study, three different size fractions having the same crystal chemistry and similar particle aspect ratios but very contrasting external adsorption site relative abundances are used to study Sr²⁺-for-Ca²⁺ exchange. An analysis of the chemical compositions of interlayer and external sites is obtained using a multi-method approach involving bulk chemistry analysis, X-ray diffraction (XRD) modeling of 00 ℓ reflections, thermodynamic modeling, and molecular simulations. This combinational approach is used as evidence for the contrasting reactivity between external and interlayer adsorption sites and to build a two-site model of the cation exchange process.

2. Materials and methods

2.1. Sample preparation

Three distinct vermiculite particle size fractions (i.e., 10–20, 1–2, and 0.1–0.2 μm) were used in this study. These samples were obtained by a sonication procedure of vermiculite macro crystals (1–4 mm) immersed in water, followed by sequential particle size fractionation according to the same protocol as that described previously by Reinholdt et al. (2013). Raw vermiculite is from Santa Olalla in Spain, with a structural formula of $^{\text{inter}}[\text{Mg}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.04}]^{\text{oct}}[\text{Mg}_{4.92}\text{Fe}_{0.43}\text{Al}_{0.59}\text{Ti}_{0.04}]^{\text{tet}}[\text{Si}_{5.66}\text{Al}_{2.34}]\text{O}_{20}(\text{OH})_4$ (Marcos et al., 2003). The particles in these different fractions display the same crystal-chemistry and aspect ratio but contrasting proportions between

the external and interlayer adsorption sites (Table 1; Reinholdt et al., 2013).

The samples were first saturated with Ca²⁺ by placing an aliquot of the dispersed material in contact with the 1 mol/L CaCl₂ solution for 9 to 16 h. This procedure was repeated five times using successive solid and solution separation steps performed by centrifugation and the addition of fresh saline solutions. Next, the material was rinsed with ultrapure water until a silver nitrate test for Cl⁻ was negative. After Ca²⁺-saturation, the 10–20 and 1–2 μm size fractions were air dried, whereas the 0.1–0.2 μm fraction was maintained as a concentrated dispersion without drying. Such conditions for the 0.1–0.2 μm fraction were chosen to limit particle aggregation and favor their re-dispersion for cation exchange experiments.

2.2. Cation exchange experiments and thermodynamic modeling

Sr²⁺-for-Ca²⁺ isotherms were obtained for the different size fractions to derive information on the adsorption process as a function of particle size. For the two coarsest size fractions (i.e., 10–20 and 1–2 μm), 25 mg of air-dried Ca²⁺-saturated vermiculite were placed in contact with a given quantity of a 0.08 mol/L Ca(NO₃)₂ and 0.015 mol/L Sr(NO₃)₂ solution to obtain a total cation concentration of 10⁻² mol/L. The solutions were prepared using Milli-Q® pure water (18 M Ω ·cm). The solid/solution ratio used for experiments on these two fractions ranged from 3.5 to 3.6 g/L. For the 0.1–0.2 μm size fraction, experiments were performed using 100 mg of dispersion. The mass of the sample was then estimated at the end of the experiment by drying the dispersed material at room temperature on a glass slide. Due to the chosen protocol, the solid/solution ratio used for experiments performed on the finer fraction ranged from 1.8 to 4.4 g/L. Such variation resulted from the practical difficulty of working with a dispersed material with a clear tendency towards flocculation. The prepared samples were allowed to react for 3, 6 and 24 h for the 0.1–0.2, 1–2 and 10–20 μm size fractions, respectively. These durations were chosen based on preliminary results (not shown) devoted to kinetic studies and showed that these values were sufficient for achieving adsorption equilibrium while avoiding the detectable dissolution of the material, particularly for the finest size fraction. Next, the samples were centrifuged and the supernatant was removed to analyze the pH and aqueous Ca²⁺ and Sr²⁺ concentrations.

The pH measurements were performed in 1 mL of solution with a combined pH electrode (SCHOTT® Instruments) that was calibrated at 25 °C by using two pH buffer solutions. The aqueous Ca²⁺ and Sr²⁺ concentrations in an aliquot of the supernatant were measured using atomic absorption spectroscopy (AAS, Varian AA240FS). Sample aliquots were diluted in 2% HNO₃ to measure the aqueous concentrations between 0.5 and 5 mg/L, which corresponded with the linear ranges of the calibration curves. To account for possible interferences during measurements, samples and standards were prepared in 1 g/L LaCl₃ and 2 g/L KCl solutions (Lajunen and Peramaki, 2004). The total uncertainty estimated for all of the measured cation concentrations was $\pm 2\%$.

The experimental data of Sr²⁺-for-Ca²⁺ isotherms were plotted as an equivalent fraction of strontium in solution at equilibrium (noted {Sr²⁺}) as a function of an equivalent fraction of strontium adsorbed

Table 1
Theoretical cation exchange capacity (CEC) values relative to the different types of adsorption sites for the different vermiculite size fractions (derived from Reinholdt et al., 2013) and the CEC values measured in this study (in meq per 100 g of bihydrated Ca²⁺-vermiculite).

	Total theoretical CEC ^a	Interlayer theoretical CEC ^a	External theoretical CEC ^a	Theoretical external/total CEC (%)	Measured CEC
0.1–0.2 μm	217	158	59	27	218 \pm 15
1–2 μm	186	176	10	5	175 \pm 12
10–20 μm	180	180	0	<1	183 \pm 13

^a Derived from the work of Reinholdt et al. (2013) and adapted to a bihydrated Ca²⁺-vermiculite sample (considering a molar mass of 943.4 g/mol).

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