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TRLFS characterization of Eu(III)-doped synthetic organo-hectorite

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ABSTRACT

Europium(III) was coprecipitated with the clay mineral hectorite, a magnesian smectite, following a multi-step synthesis procedure. Different Eu(III) species associated with the proceeding synthetic hectorite were characterized by selectively exciting the $^5D_0 \rightarrow ^7F_0$ transition at low temperature ($T < 20$ K). Fluorescence decay times indicated that Eu(III) ions may be incorporated in the octahedral layer of the brucite precursor as well as in the octahedral sheet of the clay mineral. The excitation spectra indicated that the substitution of the divalent Mg by the trivalent Eu induced local structural deformation.

This investigation implements the molecular-level understanding of the *f* element structural incorporation into the octahedral layer of sheet silicates by coprecipitation with clay minerals from salt solutions at 100 °C.

1. Introduction

Clay minerals may play an important role in a high-level nuclear waste (HLW) repository system. Clay-based materials can be used as a backfill or buffer, representing a geotechnical barrier within a multibarrier system (Mallants et al., 2001). Eventually, if the waste matrix gets into contact with groundwater, clay minerals may form as secondary phases upon alteration of the waste matrix in the course of the geological evolution of the repository system (Abdelouas et al., 1997; Luckscheiter et al., 2002). For example, the trioctahedral smectite hectorite has been identified in long-term corrosion experiments as one of the secondary phases forming in the alteration layer of HLW glass under near-field conditions (Zwicky et al., 1989).

Many fission products and in particular the actinides (or 5*f* elements) in the HLW have very long half-lives. Consequently, the long-term behaviour of a HLW repository system needs to be considered up to 10^6 years. In particular, the long-term radiotoxicity is solely dominated by the actinides (Salvatores, 2005).

Due to the structural characteristics of clay minerals, several molecular-level binding mechanisms can operate: outer- and inner-sphere surface complexation, cation exchange within the interlayer, and structural incorporation. In addition to adsorption reactions at the external clay mineral surface (including the interlayer), radionuclide (RN) binding by incorporation into the bulk structure of clay minerals may occur via coprecipitation. Trapped in structural sites, RN would be effectively "blocked" from further migration in the geosphere, in particular if a thermodynamically stable solid solution forms. A sound understanding of the molecular-level RN behaviour in the geosphere is required to assess the long-term safety of a HLW repository over geological time spans.

Structural substitution within the tetrahedral and octahedral sheets of various clay minerals in nature has been known for many decades (Brindley and Brown, 1980). In nature, the octahedral layer typically contains cations like Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Mn^{2+} or Ti^{4+} (see for example Dekov et al., 2007, and references therein). Here, we are concerned about the geochemical behaviour of actinides. Several concepts of HLW repository suggest that reducing conditions may prevail: the actinides Am, Cm, and some fractions of Pu may occur in their trivalent redox state. Considering the ionic radii (Shannon, 1976) of cations occupying regular tetrahedral (e.g. ^{IV}Si(IV) 0.26 Å) lattice sites in sheet silicates and the ionic radii of trivalent actinide Cm (^{VI}Cm(III) 0.97 Å) a tetrahedral cation substitution can be ruled out. A tetrahedral cation substitution can also be ruled out for the nonradioactive chemical homologue of Cm, the trivalent lanthanide (or 4*f* element) (Chapman and Smellie, 1986) Eu (^{VI}Eu(III) 0.95 Å). The incorporation of *f*

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elements may occur by substitution of ions in the octahedral lattice sites. From a crystal chemistry point of view, they could occupy a 6-fold oxygen coordinated lattice site (Pauling's first rule). However, compared to the size of cations (Shannon, 1976) which typically occur in octahedral sites in sheet silicates (e.g. ^{VI}Al(III) 0.54 Å, ^{VI}Mg(II) 0.72 Å, ^{VI}Li(I) 0.76 Å, ^{VI}Fe(II) 0.78 Å), substitution by trivalent actinides or lanthanides does not seem to be favourable due to the large strain, which would be induced by the substitution of such large cations (Allan et al., 2001).

The formation of sedimentary clay minerals is often deduced from the rare earth elements (REE: lanthanides, Sc and Y) content. The variation in REE concentrations reflects the composition of the fluids from which they precipitated and the structural compatibility for these ions (Severmann et al., 2004). For example, enrichment in heavy (smaller) REE was reported for a hydrothermally formed nontronite, a Fe-rich trioctahedral smectite, from the Trans-Atlantic Geotraverse (TAG) hydrothermal field on the Mid-Atlantic Ridge (Severmann et al., 2004), and from Eolo Seamount, Tyrrhenian Sea (Dekov et al., 2007). It was concluded that the REE uptake is controlled by crystal chemistry and that the REE occupy octahedral sites within the clay mineral structure. The Sr isotope data indicate that the clay minerals formed by direct precipitation from the solutions and that the REE were incorporated via coprecipitation. However, no spectroscopic technique was used to directly characterize the incorporated REE species.

Clay minerals containing structurally substituted heavy metal ions have also been synthesized in the laboratory by coprecipitation and by ion exchange (Mn-hectorite: Higashi et al., 2007; Zn-hectorite: Nakakuki et al., 2004; Ni-hectorite: Nakakuki et al., 2005; Tb(III) ion exchange: Lezhnina et al., 2007). Spagnuolo et al. (2004) studied the coprecipitation of transition metal ions during the synthesis of hectorite from aqueous salt solution at 100 °C. Electron paramagnetic resonance (EPR) spectroscopy combined with EDTA extraction experiments indicated that Cu^{2+} (^{VI}Cu(II) 0.73 Å) and Zn^{2+} (^{VI}Zn(II) 0.74 Å) substitute for ions in the octahedral lattice sites more significantly than Cd^{2+} (^{VI}Cd(II) 0.95 Å) and Pb^{2+} (^{VI}Pb(II) 1.19 Å). More than 95% of the total Cu^{2+} and Zn^{2+} concentrations were present within the structure of the coprecipitate, whereas it was about 55 and 30% for Cd^{2+} and Pb^{2+}, respectively.

Tb(III) ion exchange experiments suggested that the lanthanide (^{VI}Tb(III) 0.92 Å; Shannon, 1976) can penetrate into the octahedral sheet of pre-existing hectorite (not coprecipitated), based on wet chemical analysis (Lezhnina et al., 2007). However, Miller et al. (1982, 1983) indicated that the migration into the octahedral sites may be relatively restricted for the lanthanides. From the dehydration of exchanged montmorillonite (Yb(III), Ho(III) and Eu(III)) it was concluded that the migration may occur only at relatively high temperatures.

However, the substitution of cations present in the octahedral layer for the trivalent REE may more likely occur by coprecipitation of clay minerals from solution. Recently, TRLFS investigations on Eu(III) coprecipitation with the magnesian smectite hectorite (Pieper et al., 2006) suggested a trivalent lanthanide incorporation into a solid phase: either in the clay octahedral layer, or in an amorphous silica phase. A TRLFS study on Cm(III) coprecipitation with hectorite strongly indicated an octahedral substitution mechanism (Brandt et al., 2007).

Based on this background, the system Eu(III)/hectorite is used as model system in this study to further investigate the uptake of trivalent REE by coprecipitation with clay minerals. The multi-step formation of organo-hectorite developed by Carrado et al. (1997a,b, 2000) allows to track the lanthanide through the clay mineral formation. Here we have used low temperature (T<20 K) site selective TRLFS measurements to characterize different Eu(III) species (i.e., a Eu(III) ion in a given chemical environment) during distinct reaction steps on the basis of excitation and emission data.

2. Experimental

2.1. Samples preparation and characterization

Eu(III)-containing organo-hectorite was synthesized at T≤100 °C following a multi-step synthesis procedure (Carrado et al., 1997a,b, 2000). First, a Eu(III)-containing $Mg(OH)_2$ precursor was freshly precipitated by dissolving $MgCl_2{\cdot}6H_2O$ (32 mmol, Merck®) in Milli-Q water (approximately 400 mL), adding 500 µL of a 1000 µg/mL (3.3×10^{-6} mol) europium solution (Alfa®) (Mg:Eu ~ 9700:1), and by adding a 2N NH_4OH solution under constant stirring. This brucitic precursor suspension was then centrifuged and washed with 4 volumes of Milli-Q water to remove excess ions.

In a 1 l round-bottom glass reactor, tetraethylammonium chloride (2.7 mmol, (TEACl), Fluka®) and lithium fluoride (8.5 mmol, Aldrich®) were dissolved in Milli-Q water (approximately 400 mL), and the precursor suspension was added. This mixture was constantly stirred using a suspended stirring bar, and brought to reflux in an oil bath. After about 30 min, Ludox HS-30 (48.8 mmol, Sigma-Aldrich®), a Na^+-stabilized 30% silica sol, was added drop wise (to reach pH 9–10). The total volume was approximately 500 mL and allowed to react for 8 days. The cooled suspension was centrifuged and the supernatant removed. The synthetic product was treated with HCl Suprapur (Merck®) at pH 3 and 25 °C in order to remove eventual traces from the remaining precursor, and was washed several times with Milli-Q water to reach the pH of distilled water. The suspension was filtrated using a 0.05 µm pore diameter filter, washed with Milli-Q water, and dried. To this synthesis procedure corresponds a Li:Mg:Si molar ratio of 0.27:1.00:1.52. Assuming a total incorporation of the trivalent lanthanide, this ratio yields the ideal hectorite composition: $Ex_{0.65945}[Li_{0.66}Mg_{5.33945}Eu_{0.00055}Si_8O_{20}(OH/F)_4]$. The corresponding europium content is 100 ppm, which is considered low enough to avoid any possible Eu–Eu quenching effect during the TRLFS experiments. However, half of the initially introduced lanthanide may be effectively incorporated, based on previous investigations on Cm(III) ($Mg:Cm = 2.3 \times 10^5:1$) coprecipitation experiments (Brandt et al., 2007).

Separately, a Eu(III)-containing precursor ((Mg/Eu) hydroxide) was prepared considering the same Mg:Eu ratio (Mg:Eu ~ 9700:1) as for the clay mineral. This synthesis was carried out under argon atmosphere (glove box) to exclude the formation of aqueous carbonate species. $MgCl_2{\cdot}6H_2O$ (37 mmol, Merck®) was dissolved in Milli-Q water (approximately 150 mL) and 580 µL of a 1000 µg/mL (3.8×10^{-6} mol) europium solution (Alfa®) was added. The hydrous compound was precipitated by adding a 2N NH_4OH solution under constant stirring. This suspension was decanted and the supernatant removed. Milli-Q water was added and the suspension was stirred; the supernatant was removed after decantation. This