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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Insights into the longterm incorporation of multiple trivalent elements in hectorite: A polarized XAS study	**Experiment number**: EV-211
Beamline: BM30B	**Date of experiment**: from: 18-10-2016 to: 25-10-2016	**Date of report**: February 2017 *Received at ESRF:*
Shifts: 21	**Local contact(s)**: Isabelle Kieffer	

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Scientific background and aim

The magnesian smectite hectorite is one of the phases frequently detected during alteration of nuclear glass in the laboratory (e.g., [1]). Such secondary phases may sorb and thus delay the migration of radionuclides to the far field. Specifically, smectites have high affinity for metal ions in suspension and various retention modes can operate such as surface adsorption and structural incorporation. The uptake mechanism of lanthanides (used as surrogates for actinides) on hectorite has been well investigated (e.g. [2]). However, studies have tackled with only one single element at a time. Yet, the synthesis of hectorite in the presence of several lanthanides (La, Eu, Yb) shows that these elements can easily sorb simultaneously [3] and data on nanoparticulate hectorite containing these three elements suggested that size governs the extent of Ln(III) substitution for some Mg at hectorite octahedral site. However, no structural data (e.g., coordination number and interatomic distances) corroborating the simultaneous incorporation of various elements has been reported.

In the laboratory (e.g., [2,3]), hectorite can be synthesized within few days at high precipitation rates, and under these conditions, it is very likely that cations of size larger than that typically occurring at octahedral sites (e.g., Mg, Li, Fe) can be kinetically accommodated in the crystal structure. However, mineral phases in suspension for increased contact time can undergo dissolution-recrystallization (such as observed for e.g., magnetite), and thus possibly release large cations which then adsorb at the surface, thereby possibly altering the long-term immobilization. The chemical environment between surface-adsorbed and structurally incorporated cations is significantly different, at least in terms of number of neighboring atoms, and polarized EXAFS spectroscopy was used to discriminate these different binding modes (e.g. [2,4]).

Experiments and results

Hectorite containing simultaneously La, Eu and Yb was synthesized, and a highly oriented film has been prepared shortly after synthesis and stored under dry conditions to prevent further reaction. After aging for four years in suspension, a new textured sample was prepared from the same suspension. The local environment of the coprecipitated cations (La, Eu and Yb) was probed at the L_3-edge by polarized EXAFS spectroscopy at the BM30B beamline by considering various angles (α = 10°, 35°, 55°, 80°) between the electric field of the X-ray beam and the layer plane.

For Yb, the powder (α = 35°) EXAFS spectrum (Figure 1) of both samples clearly differs from that of the aqueous ions in position and amplitude of the oscillations maxima, indicating different environments. For the fresh sample, the amplitude of the EXAFS oscillations are similar to that for the aged sample, but the frequency slightly differs. Based on the oscillations, the bond distance to the first atomic shell decreased from the aqueous ions to the fresh sample, and slightly more upon aging. This decrease in bond length can be interpreted as an incorporation within a solid phase. For the fresh and the aged sample, polarized EXAFS spectra exhibit no angular dependence (Figure 2). This finding suggests that Yb may not be located in an anisotropic environment, i.e., at octahedral positon, contrary to Lu(III) [2]. Alternatively, Yb may be located in a suite of slightly differing structural environments and the recorded sums of all contributions do not exhibit any angular effect because of cancellation effects.

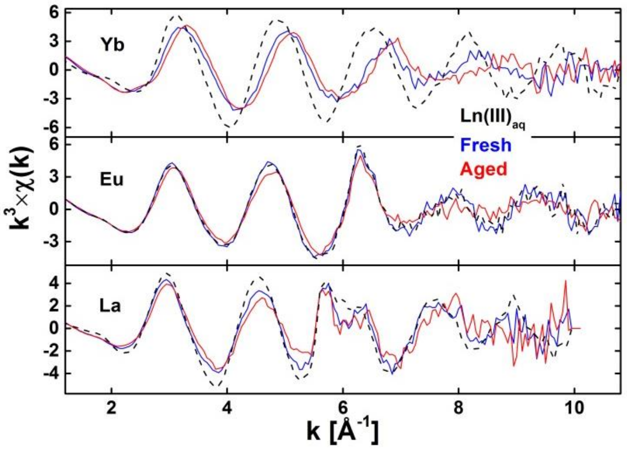

Figure 1. Powder EXAFS spectra at the La, Eu and Yb L_3-edge for hectorite containing simultaneously all three elements prepared after synthesis ("fresh") and after aging ("aged") in suspension for four years, together with data for the free aqueous ions ("Ln(III)$_{aq}$").

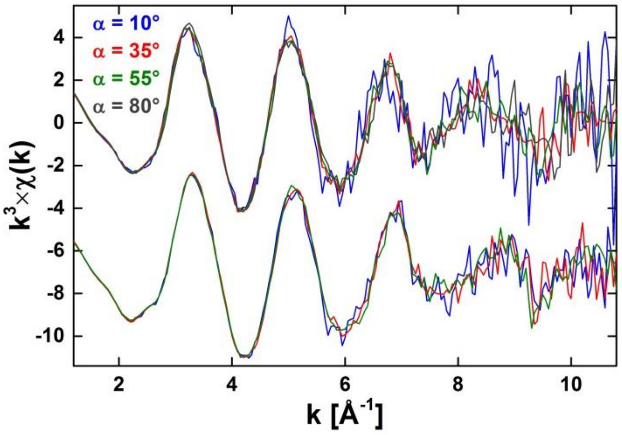

Figure 2. Polarized EXAFS spectra at the Yb L_3-edge for the hectorite containing simultaneously all three elements prepared after synthesis and after aging in suspension for four years.

For Eu, the spectrum of the aqueous ions is comparable to that of the fresh hectorite sample, and aging had no influence on the local chemical environment. The spectrum hints at the presence of a full hydration sphere meaning that this lanthanide is likely bound at the smectite surface and not occluded in any solid phase. The spectrum of the aged sample is also similar to that of the fresh sample, indicating that the structural binding did not change. Polarized EXAFS spectra (data not shown) for the fresh and the aged sample exhibit no angular dependence, very likely a consequence of Eu not present in an anisotropic environment.

The La L_3-edge spectra of both samples are very similar in terms of oscillation frequency, only the amplitude maxima slightly differs. This frequency is also comparable to that of the aqueous ions, meaning that the distance to the first shell are comparable in all samples. This result precludes La incorporation within hectorite structural sites. Polarized EXAFS spectra (data not shown) for the fresh and the aged sample exhibit no angular dependence, suggesting that La likely sorbs at various different positions at the surface.

La(III) (^{VI}La(III) = 1.03 Å) and Eu(III) (^{VI}Eu(III) = 0.95 Å) are both significantly larger [5] than cations typically present in hectorite octahedral sites (e.g., ^{VI}Mg(II) = 0.72 Å, ^{VI}Li(I) = 0.76 Å) and data suggest that this size mismatch hinders the incorporation of such species within octahedral sites. Data also suggest that a small portion of Yb(III) may be present at octahedral site, certainly a consequence of the lower size mismatch with Mg and/or Li. Fits to the EXAFS data will provide data on coordination numbers and bond distances that will allow to elucidate the immobilization mechanism. Because smectites occuring in nature [6] contain trace amounts of lanthanides, the results of this study also suggest either that the crystallization pathway used in the laboratory is not appropriate for the incorporation of lanthanides, or that lanthanides in these natural samples are present as both incorporated and adsorbed species.

Acknowledgements

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References

[1] Thien B., Godon N., Hubert F., Angeli F., Gin S., Ayral A. (2010) Appl. Clay Sci. 46, 135-141.
[2] Finck N., Schlegel M. L., Bosbach D. (2009) Environ. Sci. Technol. 43, 807-8812.
[3] Bouby M., Finck N., Geckeis H. (2015) Chromatography 2, 544-566.
[4] Schlegel M. L., Manceau A. et al. (2001) Geochim. Cosmochim. Acta 65, 4155-4170.
[5] Shannon R. D. (1976) Acta Cryst. A32, 751-767.
[6] Severmann S., Mills R.A., Palmer M.R., Fallick A.E. (2004) Geochim. Cosmochim. Acta 68, 73-88.