



XAFS investigations of the Ln(III) co-precipitation with clay minerals

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30-02-864

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Report:

Scientific background and aims of the study

Clay minerals are major sorbing solids in geological and engineer barriers of High-Level nuclear Waste (HLW) repositories. They may form as secondary phases, such as the smectite hectorite [1], upon alteration of the HLW matrix over geological time scales in the presence of ground water. The precipitation of such alteration phases represents a significant retention potential for radionuclides (RN), including actinides. Various binding mechanisms may account for this retention. Specifically, the incorporation of RN into the bulk structure of clay minerals may occur by co-precipitation, resulting in long-term optimal immobilization. However, the incorporation of actinides and their chemical surrogates, the lanthanides (Ln), in the octahedral lattice site of hectorite may be hindered by their large ionic radii (e.g. $^{VI}\text{Cm(III)} = 0.97 \text{ \AA}$), compared to those which typically occur in the octahedral sites of sheet silicates (e.g. Mg^{2+} , Fe^{2+} , Al^{3+} , Fe^{3+} ; $r \leq 0.75 \text{ \AA}$ [2]). Yet, Time-Resolved Laser Fluorescence Spectroscopy data collected for hectorite co-precipitated in the presence of the trivalent lanthanide Eu(III), suggested an Eu substitution for cations at octahedral sites [3].

Experimental part and results

Hectorite was co-precipitated in the presence of Lu(III) following a multi-step synthesis protocol [4]. The local chemical environment surrounding the lanthanide in the Lu(III)-containing precursor ((Mg/Lu) hydroxide) and in the Lu(III) co-precipitated hectorite was probed by EXAFS spectroscopy. Polarized EXAFS (P-EXAFS) experiments were carried out on these samples prepared as self-standing film by varying the angle α between the mineral layer plane and the electric field vector of the X-ray beam ($\alpha = 10, 35, 55, 80^\circ$).

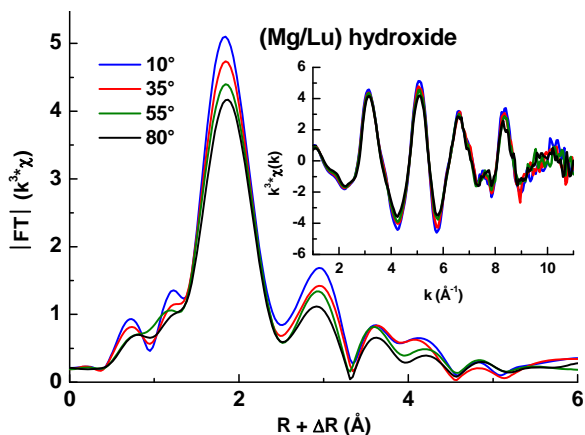


Figure 1. Dependence of the Fourier transform magnitude for the (Mg/Lu) hydroxide with the angle α between the brucite layer plane and the electric field vector of the X-ray beam. Inset shows the k^3 -weighted P-EXAFS spectra.

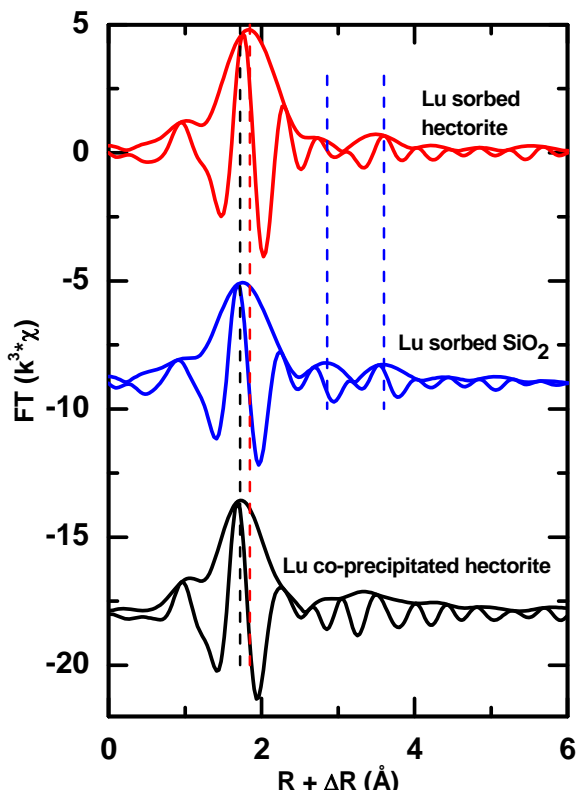


Figure 2. Comparison of Fourier transforms of EXAFS spectra for Lu(III) sorbed onto hectorite (87 $\mu\text{mol/L}$, pH 7) and onto SiO_2 (1.7 mmol/L, pH 7.5) and for Lu(III) co-precipitated with hectorite.

The angular dependence on the P-EXAFS spectra (Figure 1) collected for the precursor suggested an anisotropic environment around Lu(III). The data modeling indicated the presence of a neighboring oxygen shell at 2.27 \AA , pointing to a sixfold coordination by oxygen, as in a brucite octahedral site. An additional Mg shell was detected at 3.30 \AA . Finally, both the O and Mg coordination numbers decreased with increasing α values, supporting an Lu(III) incorporation in a flattened brucite layer.

The P-EXAFS data modeling for the Lu(III) co-precipitated hectorite indicated the presence of an oxygen shell at significantly short distance (2.19 \AA), as for the precursor. The data were well fitted considering Mg (3.12 \AA) and Si (3.36 \AA) as next nearest neighbors, with low coordination numbers. These data are consistent with Lu(III) located in a strained clay-like environment.

The comparison of the Fourier transforms (FT) of the data collected for Lu(III) sorbed onto hectorite and for

Lu(III) co-precipitated with hectorite reveals dissimilar crystallo-chemical environments (Figure 2). Current spectral simulations for surface-sorbed Lu(III) indicate a split of the oxygen shell in two subshells ($R = 2.23$ and 2.35 \AA), consistent with a Lu(III) binding to the clay particle with some bound water molecules, as was reported for Y sorbed onto hectorite [5]. The 5 atoms detected at 2.35 \AA match with the 4-5 water molecules usually found for the Ln(III) forming inner-sphere surface complexes [6]. Finally, powder EXAFS data were collected for Lu(III) sorbed onto silica. An O shell at 2.22 \AA was detected, together with two Si shells at ~ 3.0 and ~ 3.8 \AA , suggesting that Lu polyhedra share edges and corners with Si tetrahedra, respectively. The formation of such surface-sorbed species during the hectorite co-precipitation experiments may be ruled out.

Analysis of the EXAFS data collected for the Eu(III)-containing precursor and the Eu(III) co-precipitated hectorite will be realized in the next months. The results of this investigation will implement the molecular-level understanding of the retention reactions on clay minerals, which is essential to develop robust models for the migration behavior of RN out of nuclear waste repositories.

Acknowledgements

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References

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