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Mechanism of Nd, and Lu sorption on silicates and layered silicates by EXAFS spectroscopy

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Scientific background and Aims of the experiment

Operation of nuclear power plants generate large amounts of fission and activation products, such as transuranian radionuclides (RNs). The final disposal of these RNs in spent fuel or processed nuclear waste in deep geological repositories is now contemplated, but safety issues have yet to be resolved, such as the exposition of future populations to long-lived isotopes. To limit this threat, several countries have decided to line these underground repositories with geochemical and engineered barriers. These barriers are foreseen to delay RN migration in the geosphere, essentially by RN retention at the surface of these solids. However, a reliable assessment of this retention hinges on a thorough characterization of the molecular mechanisms of RN immobilization at mineral-water interfaces. Because of comparable electronic properties related to the presence of f-shells, lanthanides are considered good analogues of trivalent actinides such as Am(III) and Cm(III), and therefore are used to decipher the possible molecular-scale mechanism of actinide retention.

The mechanism of Nd and Lu adsorption by silica was probed to understand how silicate minerals such ad quartz (α-SiO_2) and opal (amorphous SiO_2) may influence the fate of these elements in the natural systems. Figure 1 shows that the amplitude and position of the Fourier transform (FT) modulations for Nd and Lu vary only slightly as pH increases from 6 to 9. This result indicates that the environment of sorbed elements is hardly affected by the change in pH. Also, the amplitude maxima and imaginary parts for Lu-sorbed silica are shifted toward lower apparent distances than for Nd, a decrease in line with the decrease in ionic radii from Nd(III) (r = 1.109Å) to Lu(III) (r = 0.977 Å) [1]. Current spectral simulations suggest that the EXAFS contributions of cationic shells at $R + \Delta R \sim 2.6$ and 3 Å may be modeled by assuming Si atoms only at distances of, e.g., ~ 3.0 and 3.2 Å from the Nd absorbing atom. Such short Nd-Si distances suggest that Nd binds to edges of Si tetrahedra, as observed in Nd silicate solids [2].

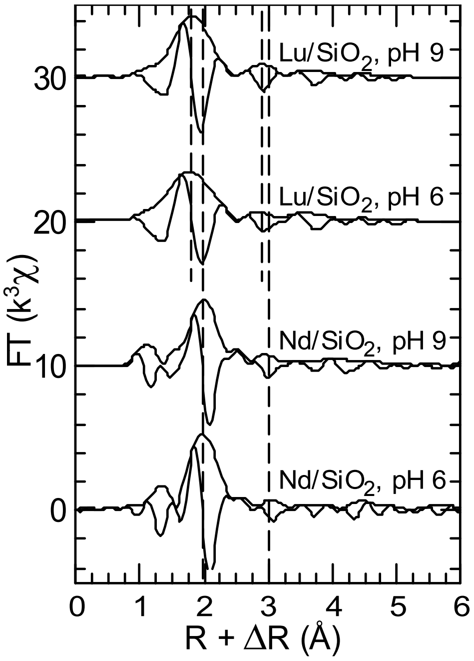

Figure 1. Fourier transform (FT) magnitude and imaginary parts for Nd and Lu (total concentration of 100 µM) sorbed by silica (2 g L^{-1}).

To determine the nature of lanthanide sorption on layered silicates, powder EXAFS spectra were collected for of Nd- and Lu-sorbed hectorite ($[Mg_{2.77}Li_{0.66}]Si_4O_{10}(OH)_2$) prepared at pH 6 and 0.5 M $NaClO_4$. Comparison of FTs for powder spectra reveals obvious spectral dissimilarities for Nd (Figure 2a) or Lu (Figure 2b) when adsorbed either by silica, or by the clay phase. For example, the FT maxima near 3 Å for the silica-sorbed samples are shifted toward much higher values (i.e., ~ 3.5 Å) for the hectorite-sorbed samples. These spectral variations reveal distinct crystallochemical environments, confirming that distinct sorption mechanisms operate for lanthanide sorption on silica or on clay minerals. The molecular mechanism of Nd and Lu retention was further investigated by polarized EXAFS (P-EXAFS) experiments on self-supported film of Nd- and Lu-sorbed hectorite. Figure 3 shows that the amplitude and, sometimes, the position of oscillation extrema of EXAFS spectra for Nd-sorbed hectorite significantly vary with the experimental α angle between the clay platelets and the electric field vector ε of the X-ray beam. A comparable angular dependence was observed for Lu, and this result indicates that the environments of sorbed lanthanides are anisotropic, as expected if the sorbed cations bond directly the clay structure [3-6]. Future structural interpretation of these spectral variations will take into account the occurrence, in the P-EXAFS formula for the L_{III} edge, of a cross-term generating and apparent dependence on α of both the number of neighbor atoms and the distance of backscattering shells [7]. The angular dependence will thus be resolved, and the crystallochemical environment of the sorbed lanthanide extensively characterized, by spectral simulations in the next months.

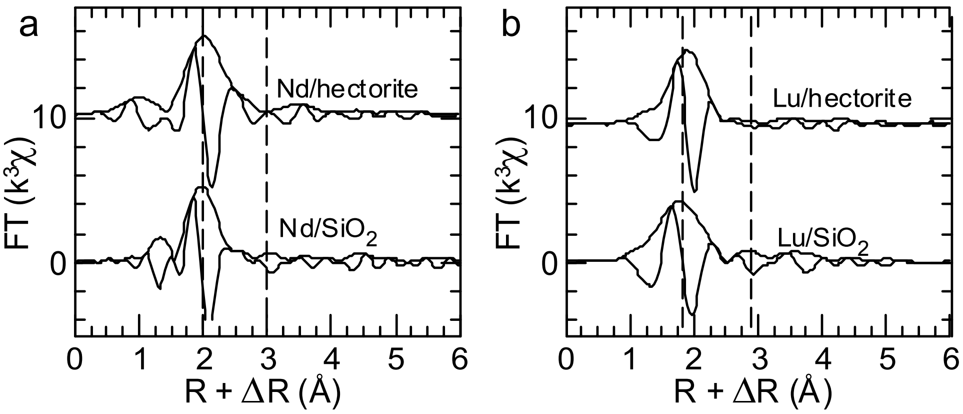

Figure 2. Comparison of Fourier transforms of powder EXAFS spectra for (a) Nd and (b) Lu sorbed on silica (100 µM L^{-1}, pH 6) and hectorite (100 µM L^{-1}, pH 6).

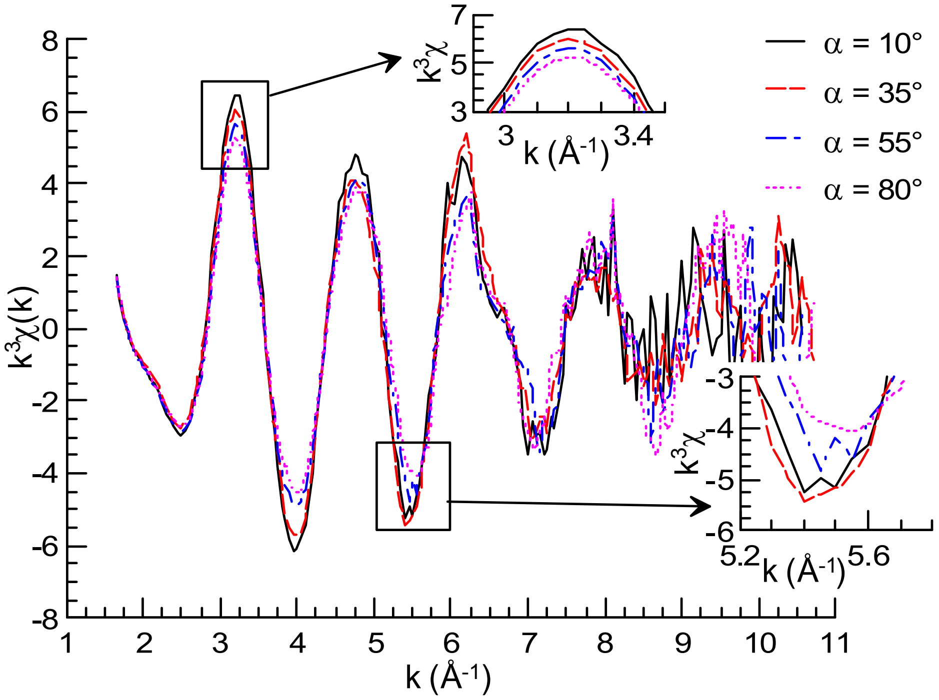

Figure 3. dependence of polarized EXAFS spectra for Nd-sorbed hectorite (pH 6) with the angle α between the hectorite self-supporting film and the electric field vector of the X-ray beam. Inserts magnify amplitude angular variations.

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