

# Feasibility of EXAFS experiments at the Np L-edge to investigate neptunium sorption on kaolinite

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**ABSTRACT.** We have investigated the feasibility of Np L-edge EXAFS measurements to study the sorption of neptunium onto the reference clay kaolinite KGa-1b.

Several collaborating groups selected the kaolinite KGa-1b from the Source Clays Repository as reference clay for a broad range of investigations dealing with the interaction of actinides in the system clay, humic substances, and aquifer. During recent EXAFS measurements of uranium(VI) sorption onto kaolinite KGa-1b, we found that this kaolinite contains traces of zirconium. The energy of the Zr K-edge equals 17998 eV. Therefore, we expected a distortion of the Np L<sub>3</sub>-edge (17610 eV) EXAFS signal at this energy or at  $k$  approximately equal to  $9.8 \text{ \AA}^{-1}$ . In our experiment we wanted to explore the possibilities for avoiding severe distortions in the Np EXAFS signal without limiting the useful  $k$  range to  $9.8 \text{ \AA}^{-1}$ .

**EXPERIMENTAL.** Two samples, 1 and 2, with different amounts of neptunium(V) sorbed on KGa-1b were prepared from a 1.8 mM Np(V) stock solution of Np-237 under the following conditions: 4 g kaolinite/L, pH 9.0,  $p(\text{CO}_2) = 10^{-3.5} \text{ atm}$ ,  $I = 0.1 \text{ M NaClO}_4$ . The total neptunium concentration for samples 1 and 2 was  $8 \cdot 10^{-6}$  and  $2 \cdot 10^{-5} \text{ mol/L}$ , respectively. The neptunium uptake of samples 1 and 2 as measured by  $\gamma$ -spectroscopy was 300 and 510 ppm, respectively. The solid residue was loaded without drying into the EXAFS sample holder. The neptunium EXAFS spectra were measured at ROBL (ESRF, BM20) [1] at room temperature in the fluorescence mode using a 13-element Ge solid-state detector.

The following measurements were performed on these samples:

- 1) The Np  $L\alpha_1$ -radiation at 13.9 keV was recorded as a function of photon energy across the Np L<sub>3</sub>-edge EXAFS region using single-channel analyzers (SCA's). The signal was corrected for detector dead time.
- 2) The EXAFS spectrum was measured at the Np L<sub>2</sub>-edge (21600 eV) by setting the SCA's to 17.8 keV to record the Np  $L\beta_1$ -radiation. Dead time correction was performed as described above.

**RESULTS.** Figure 1 shows the Np EXAFS spectra and the corresponding Fourier transforms of sample 1 (300 ppm Np) measured at the L<sub>3</sub>- and L<sub>2</sub>-edges. Seven sweeps at the Np L<sub>2</sub>-edge and six sweeps at the L<sub>3</sub>-edge were averaged. The useful  $k$  range at the L<sub>3</sub>-edge was limited to  $k_{max}$  equal to  $9.4 \text{ \AA}^{-1}$  due to the Zr K-edge absorption. The Np L<sub>2</sub>-edge EXAFS signal could be recorded with good statistics up to  $k_{max}$  equal to  $11.4 \text{ \AA}^{-1}$ . To obtain a higher resolution in the Fourier transform, it is preferable to record the Np EXAFS signal of the kaolinite samples at the Np L<sub>2</sub>-edge instead of the L<sub>3</sub>-edge.

Table 1 summarizes the EXAFS structural parameters of sample 1 derived from the Np L<sub>3</sub>- and L<sub>2</sub>-edge  $k^3$ -weighted EXAFS spectra. The detected neptunium coordination numbers and bond distances are consistent with the formation of a neptunium(V) carbonato species at the

kaolinite surface. A similar result was obtained for sample 2 (510 ppm, not shown here).

In conclusion, these test experiments showed that it is possible to study the sorption of neptunium onto kaolinite KGa-1b successfully using Np L<sub>2</sub>-edge EXAFS spectroscopy. In future EXAFS experiments, it will be possible to study sorption samples with less than 300 ppm neptunium by collecting more than seven sweeps per sample.

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## REFERENCES

[1] Matz, W. *et al.* (1999) *J. Synchrotron Rad.* **6**, 1076-1085.

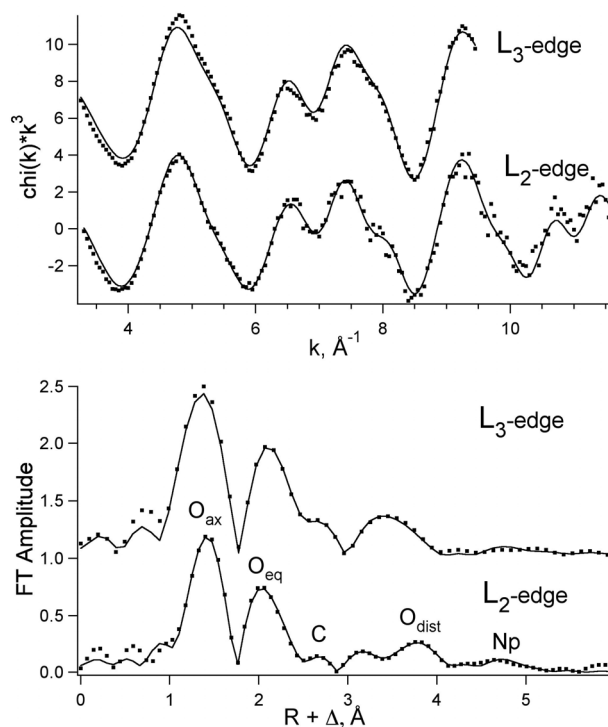


Fig. 1: Neptunium L-edge  $k^3$ -weighted EXAFS spectra (top) and corresponding Fourier transforms (bottom) of 300 ppm Np(V) sorbed onto kaolinite at pH 9.0 under ambient conditions. Dots – raw experimental data, solid line – best theoretical fit to the data.

Tab. 1: EXAFS structural parameters for 300 ppm Np(V) sorbed onto kaolinite at pH 9.0 under ambient conditions. Multiple-scattering paths are not listed. Coordination numbers were held constant during the final fit according to the result of previous fits.

Shell	Np L <sub>2</sub> -edge		Np L <sub>3</sub> -edge	
	R(Å)	$\sigma^2(\text{Å}^2)$	R(Å)	$\sigma^2(\text{Å}^2)$
2 x O <sub>ax</sub>	1.85	0.0021	1.84	0.0010
4 x O <sub>eq</sub>	2.55	0.0051	2.55	0.0054
2 x C	2.94	0.0060	2.95	0.0027
2 x O <sub>dist</sub>	4.24	0.0040	4.25	0.0044
1 x Np	4.86	0.0023	4.89	0.0050