

Local structure of Th complexes on montmorillonite clay mineral determined by extended X-ray absorption fine structure (EXAFS) spectroscopy*

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Abstract

The research at the Waste Management Laboratory, PSI, concentrates on the understanding of safety relevant mechanisms and processes that govern the release of radionuclides from waste matrices, and their transport through engineered barrier systems and the surrounding geosphere. For this reason, detailed sorption studies of radionuclides in clay and cement systems are conducted. The studies are combined with extended X-ray absorption fine structure (EXAFS) spectroscopy measurements in order to understand the sorption mechanisms on an atomic level.

In this manuscript, a case study of Th(IV) uptake on montmorillonite is presented. EXAFS samples were prepared by incubating a montmorillonite suspension with Th for 7 days at pH = 5 ($Th_{initial}$: $4.3 \times 10^{-5} - 4 \times 10^{-4}$ M). The resulting Th loadings on the clay varied between 14 and 166 $\mu\text{mol/g}$. L_{III} -Th EXAFS spectra of Th treated montmorillonite were measured at the Rossendorf Beamline at the European Synchrotron Radiation Facility. Data analysis revealed the presence of two O shells at 2.27 Å and 2.45 Å in all samples. The spectra at low Th uptake suggest the presence of Si/Al and Th backscattering atoms at distances of 3.85 Å and 3.77 Å respectively. The presence of a Th-Si/Al backscattering pair suggests that Th is bound to Si tetrahedra by a double corner-sharing manner. At higher Th uptake, however, the spectrum shows a strong similarity with the spectrum of amorphous $Th(OH)_4$ and suggests that Th is predominately present as a newly formed $Th(OH)_4$ -like phase.

1. Introduction

Sorption on mineral surfaces strongly affects the fate and mobility of contaminants in the geosphere. Therefore, an atomic level understanding of sorption mechanisms of contaminants on mineral surface is of fundamental importance for maintaining environmental quality and assessing the long-term stability of waste repositories. On clay minerals several uptake mechanisms of divalent metal ions such as Ni(II), Co(II), and Zn(II) have been proposed: Sorption on edge sites, sorption on interlayer sites (Figure 1), and the formation of lamellar nucleation phases such as neoformed layer silicates and mixed layered double hydroxides (Scheidegger *et al.* 1997; Schlegel *et al.* 1999a; Schlegel *et al.* 1999b; Scheinost *et al.* 2000).

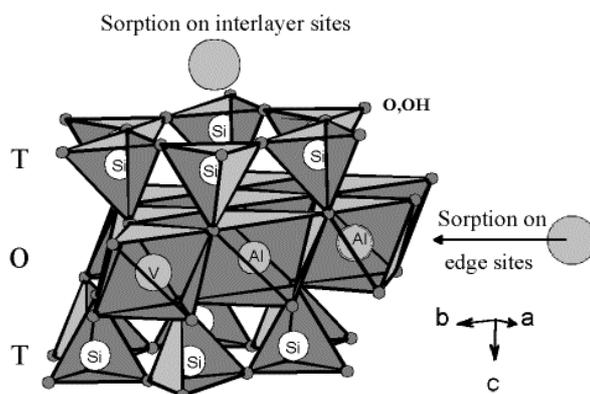


Fig. 1: Sorption modes on dioctahedral aluminous clays (V=vacancy) (Structure from Tshipursky *et al.* 1984).

In this study EXAFS was used to investigate the uptake process of Th(IV) on montmorillonite. Th has long been recognized as an important tracer element in natural waters, soils and sediments because of its accurately known source terms, long half-life and single redox state (Santschi *et al.* 1989). Thorium is, therefore, a suitable analogue for other tetravalent actinides. Furthermore, Th is of major concern in nuclear waste management and an important contaminant in fly ashes from lignite power plants (Savanonda *et al.* 1985). Th has been added to synthetic silicate glasses in order to study the structural environment of Th as a function of melt composition and polymerisation (Farges 1991). Long-term spontaneous radiation will make crystalline compounds (e.g. ZrSiO₄) to become aperiodic and also oxide glasses to nucleate (Lumpkin *et al.* 1986; Ewing *et al.* 1987). Dioctahedral aluminous clays are used as a backfill material in the Swiss concept for a high level radioactive waste repository and, therefore, metal sorption on montmorillonite has been investigated in our laboratory in great details (Baeyens *et al.* 1997).

2. Materials and methods

The montmorillonite STx-1 used in this study (Si₄Al_{1.67}(Fe²⁺,Mg)_{0.33}O₁₀(OH)₂(Me_{0.33},H₂O), where Me refers to a metal cation in the interlayer space between sheets) was purchased from the Source Clay Minerals Repository Project of the Clay Minerals Society.

The EXAFS samples were prepared by adding 11-100 ml of a Th stock solution (1·10⁻³ M (Th(NO₃)₄·5H₂O), pH 3.0, 0.001 M HNO₃) to 50 ml of a conditioned and purified montmorillonite suspension (ionic strength of 0.1 M (NaClO₄) to block cation exchange processes). The suspension was then filled up with a 0.1 M NaClO₄ solution to 250 ml resulting in a solid to liquid ratio of 2.4 g/L and an initial Th concentration of 4.3·10⁻⁵ – 4.0·10⁻⁴ M. The pH was adjusted and kept constant (pH = 5) and the samples were shaken end-over-end. The preparations were performed in a glove box under N₂ atmosphere (CO₂ and O₂ < 5 ppm). The reaction conditions were within the solubility limit of Th(OH)₄ (Ryan *et al.* 1987; Östhols *et al.* 1994; Neck *et al.* 2000). After 7 days of reaction time the suspensions were centrifuged and the wet pastes were filled into Plexiglas holders. The supernatant solutions were analysed by ICP-MS in order to determine the Th uptake on the Th/montmorillonite sorption system. Th L_{III}-edge EXAFS spectra were recorded at the Rossendorfer Beamline (ROBL) at the ESRF (Matz *et al.* 1999) using a Si (111) crystal monochromator and Pt coated mirrors. All sorption samples were measured at RT in fluorescence mode using a 4-element Ge solid-state detector.

Data reduction was carried out by using the WinXAS 97 1.3 software package (Ressler 1998). Radial structure functions (RSFs) were obtained by Fourier transforming k³-weighted $\chi(k)$ functions between 2.9 to 10 Å⁻¹ using a Bessel window function with a smoothing parameter of 4. Amplitude and phase shift functions were calculated with FEFF 8.0 (Rehr *et al.* 1991) using the structure of thorite (α-ThSiO₄) (Taylor *et al.* 1978) as reference. Since the inner potential corrections (ΔE₀) in the Th sorption samples varied between 5.5-6.5 eV, the parameter was fixed to 6 eV in order to reduce the number of free fit parameters. Furthermore, the amplitude reduction factor (S₀²) was set to 1.0.

The theoretical Th-O, Th-Si and Th-Th phase and amplitude functions calculated with FEFF 8.0 were tested by fitting the EXAFS spectrum of a synthetic thorite compound provided by Farges (1991). The results gave an average coordination number and bond distance of 8.5 ± 1.7 O atoms at 2.39 Å (σ² = 0.005 Å²), of 5.3 ± 1.1 Th atoms at 3.9 Å (σ² = 0.005 Å²) and of 3.9 ± 0.8 Si atoms at 3.92 Å (σ² = 0.005 Å²). The structural parameters for thorite as determined by X-ray diffraction (XRD) are four equatorial O at 2.36 Å, four axial O at 2.47 Å, four Si at 3.9 Å and four Th at 3.9 Å (Taylor *et al.* 1978). The differences between EXAFS and XRD structural data are within the uncertainty of EXAFS parameters, that is ~ 20% for coordination numbers and ~ 0.02 Å for interatomic distances.

3. Results

Fig. 2 shows the background subtracted, normalized, and k^3 -weighted EXAFS spectra of montmorillonite treated with Th (sorbed Th concentrations of 14, 40 and 166 $\mu\text{mol/g}$). The corresponding RSFs are shown in Fig. 3. For the lowest Th concentration the first peak is split into two and the amplitude is reduced, and the second peak is shifted to higher distance with higher Th concentration.

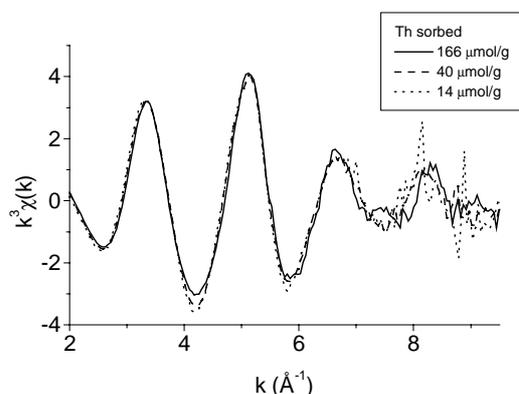


Fig. 2: k^3 -weighted Th L_{III} -edge EXAFS spectra for Th sorbed on montmorillonite (pH=5).

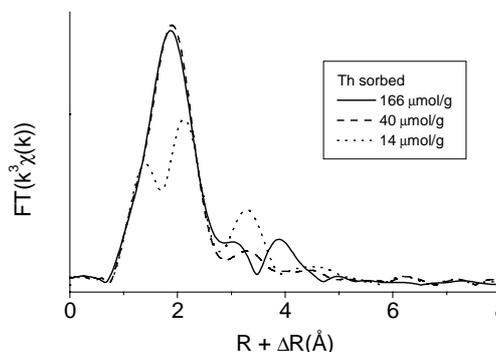


Fig. 3: RSFs of k^3 -weighted Th L_{III} -edge EXAFS spectra for Th sorbed on montmorillonite (pH=5).

The simulation of the Fourier filtered χ_o functions obtained by back transforming first RSF peaks ($\Delta R = 1\text{-}2.5 \text{ \AA}$) indicated that two nearest O distances are present in all Th sorption samples. To constrain fit parameters, the Debye-Waller (DW) factor of the second oxygen shell was fixed to $\sigma^2 = 0.005 \text{ \AA}^2$, as in the thorite reference. Furthermore, the DW of the first oxygen shell was set to $\sigma^2 = 0.002 \text{ \AA}^2$ in order to obtain a total coordination number of 10 for the two O shells. For crystallographic and steric reasons the total number of oxygen atoms in the first and second shell should not exceed 10. EXAFS structural parameters for the two nearest O shells are listed in

Table 1. The shorter shell consists of 2.6-3.0 O atoms at 2.27 – 2.28 \AA and the longer of 6.6-7.1 O atoms at 2.45 – 2.46 \AA .

Table 1: Structural Information derived from EXAFS Analysis.

Sample	Th-O			Th-O			ΔE_0^f [eV]	%Res
	N	R [\AA]	σ^{2f} [\AA^2]	N	R [\AA]	σ^{2f} [\AA^2]		
166 $\mu\text{mol/g}$	2.6	2.27	0.002	6.6	2.45	0.005	6	15.7
40 $\mu\text{mol/g}$	2.6	2.27	0.002	6.9	2.45	0.005	6	16.5
14 $\mu\text{mol/g}$	3.0	2.28	0.002	7.1	2.46	0.005	6	6.6

N, R, σ^2 , ΔE_0 are the coordination numbers, interatomic distances, Debye-Waller factors and inner potential corrections; f: Fixed during the fit procedure

The deviation between the fitted and the experimental spectra is given by the relative residual in percent, %Res.

The k^3 -weighted Fourier back-transformed spectra of second RSF peaks ($\Delta R = 2.9\text{-}4.2 \text{ \AA}$ for the highest concentrated sample and $\Delta R = 2.9\text{-}3.7 \text{ \AA}$ for the two other) are shown in Figure 4. The structural results obtained by data analysis using Th and Si as backscatter atoms are shown in Table 2.

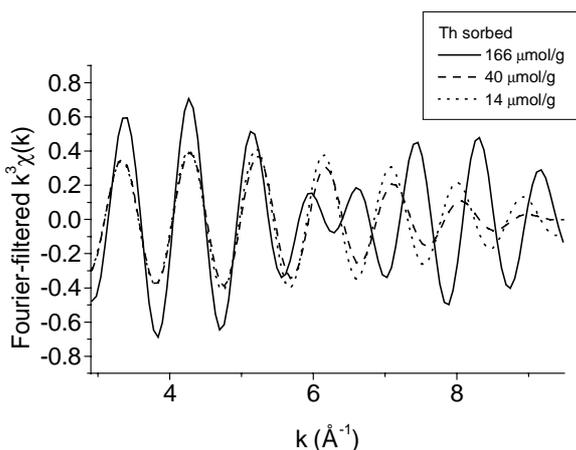


Fig. 4: k^3 -weighted EXAFS functions obtained by Fourier back-transforming second RSF peaks in Fig. 3 ($\Delta R = 2.9\text{-}4.2 \text{ \AA}$ for 166 $\mu\text{mol/g}$ and $\Delta R = 2.9\text{-}3.7 \text{ \AA}$ for 14, 40 $\mu\text{mol/g}$).

Table 2: Structural Information derived from EXAFS Analysis.

Sample	Th-Si			Th-Th			ΔE_0^f [eV]	%Res
	N	R [Å]	σ^2 [Å ²]	N	R [Å]	σ^2 [Å ²]		
166 $\mu\text{mol/g}$	A reasonable fit could not be achieved							
40 $\mu\text{mol/g}$	1.5	3.84	0.005	0.7	3.76	0.005	6	29.7
14 $\mu\text{mol/g}$	1.7	3.85	0.005	0.7	3.77	0.005	6	25.0

f: Fixed during the fit procedure

Accordingly, the second peak consists of 1.5-1.7 Si at $\sim 3.85 \text{ \AA}$ and ~ 0.7 Th at 3.77 \AA (14 and 40 $\mu\text{mol/g}$). The σ^2 terms were set to 0.005 \AA^2 as in the thorite reference. The spectrum of the most concentrated Th sample (166 $\mu\text{mol/g}$) clearly differs from the spectra of the two less concentrated samples (14 and 40 $\mu\text{mol/g}$), indicating differences in the Th coordination environment. For example, there is a beat pattern near 6.5 \AA^{-1} in the most concentrated Th sample which indicates the presence of at least two cationic subshells containing heavy atoms such as Th.

At high Th concentration (166 $\mu\text{mol/g}$) neither a Th-Th and Th-Si, nor a Th-Th₁ and Th-Th₂ two-shell model provided a good fit to the experimental spectrum. Nevertheless, it is possible to propose an uptake mechanism for Th in this sample. In Fig 5 the EXAFS spectra of thorite (Farges 1991) and amorphous Th(OH)₄ are compared to the 166 $\mu\text{mol/g}$ Th sample. The likeness of the sorption sample and the Th amorphous precipitate is striking, and suggests the formation of a similar precipitate at high Th concentration. Again it was not possible to fit Th(OH)₄ data with just one or two Th-Th backscattering pairs. The reason lies probably in the fact, that the second peak of the Th(OH)₄ compound is too disordered to be fitted with a two-Th shell harmonic model (Östhols *et al.* 1997).

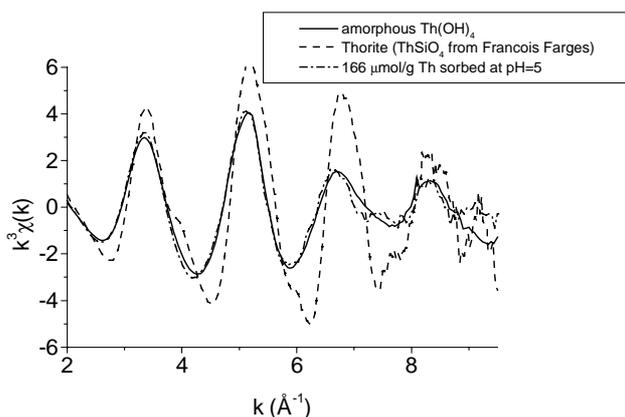


Fig 5: Comparison of k^3 -weighted XAFS functions of reference compounds and the highest concentrated Th sample.

4. Discussion

The results obtained in this study for the two most diluted samples compare well with those reported by Östhols et al (1997) for the sorption of Th on amorphous silica: 1.7-2.7 O at 2.27-2.34 Å vs. 2.6-3.0 O at 2.27-2.28 Å (this study), 4.4-5.4 O at 2.53-2.56 Å vs. 6.9-7.1 O at 2.45-2.46 Å (this study), and 1.3-2.7 Si at 3.79-3.89 Å vs. 1.5-1.7 Si at 3.84-3.85 Å (this study). While the coordination numbers and interatomic distances for the first O and the Si shell match well, the second Th-O distance in the Th/montmorillonite system is significantly shorter. The distance of the second shell is characteristic for Th-H₂O bonds (2.44-2.45 Å) (Moll *et al.* 1999) and therefore does not modify the structural interpretation. EXAFS structural parameters for Th-sorbed silica were interpreted by Östhols et al. (1997) as the formation of a double corner-sharing Th surface complex. Based on the similarity of structural parameters in the two systems, Th can be hypothesized to be bound to Si tetrahedra in a similar manner.

In conclusion, this study reveals the presence of two Th-O coordination spheres for the uptake of Th on montmorillonite at pH = 5. At low Th concentration (14 and 40 µmol/g), Th is bound to about two Si tetrahedra by a double-corner sharing mechanism as in Th sorbed silica. At high Th concentrations (166 µmol/g), Th precipitated as a Th(OH)₄-like amorphous thorium hydroxide.

Based on the data obtained in this study two structural mechanisms can be inferred for the samples with low Th concentration: The formation of a Th surface complex at the montmorillonite surface or the precipitation/neof ormation of a Th-silicate. The neof ormation of mixed (i.e. sorbate + sorbent metals) precipitates has been recently demonstrated in the case of Ni uptake on clay minerals (Scheidegger *et al.* 1997; Dähn *et al.* 2000; Scheinost *et al.* 2000) and Co on quartz (Manceau *et al.* 1999).

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