

Structure of uranium sorption complexes at montmorillonite edge sites

By C. Hennig^{1,*}, T. Reich¹, R. Dähn² and A. M. Scheidegger²

¹ Forschungszentrum Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510 119, D-01314 Dresden, Germany

² Paul Scherrer Institute, Waste Management Laboratory, CH-5232 Villigen, Switzerland

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Summary. Extended X-ray absorption fine structure (EXAFS) spectroscopy at the uranium L_{III} -edge was used for determining the structural environment of aqueous uranyl sorbed onto montmorillonite. The study reveals that uranyl uptake at pH ~ 5 – ~ 7 and at an initial uranyl concentration of 5×10^{-5} M takes place at amphoteric surface hydroxyl sites as inner-sphere complex. The measured bond distances between uranium and the equatorial oxygen atoms are in the range of 2.34 Å and 2.37 Å indicating an inner-sphere coordination. At ~ 3.4 Å the presence of a U–Al backscattering pair was determined. This backscattering pair indicates that the binding of the uranyl unit to amphoteric surface hydroxyl sites occurs preferred as a bidentate inner-sphere complex on aluminol groups.

Introduction

Sorption on clay minerals strongly affects the fate and mobility of radioactive contaminants in the geosphere. Therefore, an atomic level understanding of sorption mechanisms of contaminants on mineral surfaces is of fundamental importance for maintaining environmental quality and assessing the long-term stability of waste repositories. It is planned that bentonite, a mixture of phyllosilicates consisting predominantly of montmorillonite, is used as a back-fill material in the near field for high level nuclear waste [1]. Montmorillonite is a dioctahedral 2:1 clay mineral. The montmorillonite layers consist of two infinite sheets of $[\text{SiO}_4]$ tetrahedra, linked together in pseudo-hexagonal rings, with the apical oxygen atoms of one sheet facing the apical oxygen atom of the next sheet, creating close-packed octahedral sites between the sheets. Due to the misfit between the apical oxygen atoms in the tetrahedral sheet and the vertices of the octahedra, pairs of adjacent tetrahedra are rotated alternately clockwise and counterclockwise perpendicular to the basal plane what lowers the sheet symmetry from hexagonal to trigonal and creates ditrigonal cavities in the tetrahedral layer. Oxygen atoms on the siloxane surface (*i.e.* the basal tetrahedrally coordinated $[\text{SiO}_4]_{\infty}$ layers) are fully saturated and therefore less reactive. 2/3 of the octahedral sites are

occupied by Al^{3+} ions. Isomorphic ion substitutions of Mg^{2+} and Fe^{2+} for Al^{3+} occur in the octahedral sheet, resulting in a permanent negative charge, which is compensated by the adsorption of cations on the basal planes. This permanent negative charge dominates the mineral's cation exchange capacity (CEC). Montmorillonite has its layer charge resulting exclusively from octahedral substitutions. Sorption to the siloxane surfaces and exchange processes with interlayer cations are evoked by the permanent negative layer charge. Aqueous metal cations can coordinate to these sites *via* pH-independent ion-exchange processes. The isomorphic substitution in the octahedral sheet of montmorillonite distributes the resulting excess negative charge over a more enhanced range than in the case of isomorphic substitutions in the tetrahedral sheet [2]. In the montmorillonite structure, an interlayer swelling occurs when it is exposed to water. The swelling procedure depends on valencies and atomic radii of the exchangeable cations. Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites. Based on crystallographic considerations, the ratio of aluminol to silanol groups on the edges of smectite crystallites is determined to 0.83 [3]. The complexation process of aqueous metal species exhibits a strong pH dependency. Surface precipitates can also be created.

Extended X-ray absorption fine structure (EXAFS) spectroscopy has proven as an useful tool for determining local bond lengths and coordination numbers of neighboring atoms in order to distinguish between inner- and outer-sphere complexes and to analyze the complex structures. Several EXAFS studies have been carried out to identify and differentiate the sorption sites of uranyl species on phyllosilicate minerals under different chemical conditions. Dent *et al.* [4] proposed the formation of an outer-sphere uranyl sorption complex onto montmorillonite by an ion-exchange mechanism and discussed the possibility of exchange reactions of uranyl carbonate complexes in the interlayer of montmorillonite at pH 5. Using EXAFS Chrisholm-Brause *et al.* [5] observed the relation between inner-sphere and outer-sphere uranyl complexes as a function of surface coverage. At a high surface coverage, the EXAFS of the sorbed uranyl species resembles the EXAFS of fully hydrated uranyl species. At low coverage, the

* Author for correspondence (E-mail: hennig@esrf.fr).

authors proposed the presence of sorption complexes at edge sites of montmorillonite. Sylwester *et al.* [6] observed that at pH 3.2–4 the uranyl ion preserves its structure moiety and undergoes an ion exchange process whereas at near-neutral pH and high ion concentration (0.1 M NaCl) two separate equatorial shells could be observed in the Fourier transform indicating the presence of an inner-sphere uranyl complex. Thompson *et al.* [7] investigated the nature of U(VI) sorption by kaolinite. They observed scattering contributions from Al or Si and proposed the presence of mononuclear inner-sphere uranyl species at the kaolinite surface. At pH values ≥ 7.0 , the authors observed the formation of multinuclear U species in the presence of air. The uranium uptake on the basal planes of muscovite, where the internal surfaces are occupied by fixed K^+ ions and the external surfaces are the source of permanent charge, was suggested by Moyes *et al.* [8] through equatorial coordination of the uranyl unit with two adjacent surface oxygen atoms from a siloxane $[SiO_4]$ tetrahedron. Giaquinta *et al.* [9] proposed that under hydrothermal conditions and in the presence of organic coatings of methoxy silanes the reduction of U(VI) to U(IV) at a bentonite clay surface can occur. Finally, Hudson *et al.* [10] investigated the uptake of uranyl on the vermiculite and the hydrobiotite surface on either permanent charged ion exchange sites or amphoteric edge sites. The authors obtained the formation of surface precipitates and/or oligomeric complexes for conditions which favour sorption at surface edge sites. Using samples with uranyl localized in permanent charged sites, polarization dependent EXAFS measurements indicated a preferred orientation of the uranyl ion with its $U=O$ axis parallel to the basal plane.

In spite of the above cited EXAFS studies, the question, whether uranyl species coordinate at montmorillonite preferred at the silanol or aluminol edge sites under conditions designed to promote surface sorption at amphoteric edge sites, remained open. The aim of this investigation is to determine the uranyl complex structure and the sorption position on amphoteric edge sites of montmorillonite in more detail.

Sample preparation

The montmorillonite used in this study (STx–1) was purchased from the Source Clay Minerals Repository of the Clay Minerals Society. The idealized structural formula of montmorillonite is $Ca_{0.33}Al_{1.67}(Mg, Fe)_{0.33}Si_4O_{10}(OH)_2 \cdot nH_2O$ with a layer charge resulting only from octahedral substitutions. The reported cation exchange capacity (CEC) for STx–1 is 0.84 meq/g and its external surface area, calculated from a N_2 -BET isotherm is $84 \text{ m}^2/\text{g}$ [11]. The fraction $< 0.5 \mu\text{m}$ was selectively obtained by centrifugation and converted to the sodium form by repetitive contacting with 1 M $NaClO_4$ solution in dialyse bags. The final cation exchange capacity was determined to be 1.01 meq/g and the external surface area is $89 \text{ m}^2/\text{g}$ [12]. The uranyl uptake experiments were carried out in a glove-box under N_2 atmosphere and using solutions which were prepared from previously degassed deionized water. The sorption samples were prepared by adding uranyl solution from a $2 \times 10^{-3} \text{ M}$

Table 1. Summary of U sorption samples.

Sample	Final pH	$[NaClO_4]$ (molal)	Initial $[UO_2^{2+}]$ (molal)	Uranium loading (ppm)	Uranium uptake (%)
A	5.02	0.1	5.04×10^{-5}	1751	58.4
B	5.14	0.1	8.40×10^{-5}	2473	49.4
C	5.17	0.01	5.04×10^{-5}	2613	87.1
D	5.98	0.1	5.04×10^{-5}	2241	74.7
E	7.08	0.1	5.04×10^{-5}	2961	98.7

uranyl stock solution, with a background electrolyte concentration given in Table 1, to the montmorillonite suspension with a solid to liquid ratio of 4 g/L. To evaluate the influence of pH on the uptake mechanism, the reaction pH (Table 1) was varied by the addition of small amounts of $HClO_4$ and $NaOH$. The uranyl/montmorillonite suspensions were shaken for 24 h. Thereafter, the reaction mixture was centrifuged at $6000 \times g$ and the supernatant solution was analyzed by ICP-MS. The data obtained by ICP-MS analysis were used for determining the uranyl content sorbed onto montmorillonite (Table 1). In addition, the uranium amount was determined directly from a total digestion of the uranyl sorbed montmorillonite. Due to the similarity of both values, losses of uranium to the container walls can be neglected. Quantitative details of the clay samples are provided in Table 1.

For EXAFS measurements the montmorillonite slurry was removed from the tube and the wet pastes were filled in Teflon sample holders.

EXAFS measurements

EXAFS measurements were carried out on the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) [13]. The monochromator, equipped with a water cooled Si(111) double-crystal system, was used in channel-cut measuring mode. Higher harmonics were rejected by two Pt coated mirrors. The samples were sealed with polyethylene foil and all measurements were performed at room temperature. The samples were measured in fluorescence mode using a four-pixel Ge detector with a sample orientation of 45° to the incident beam. The energy was calibrated by assigning the first inflection point at the K-edge absorption spectrum of a Y metal foil to 17 038 eV.

The *ab initio* curved-wave multiple-scattering program FEFF8.0 [14] was used to calculate the backscattering phase and amplitude functions of the neighboring atoms in order to perform a fitting of the raw data. The crystal structure of soddyite, $(UO_2)_2(SiO_4) \cdot 2H_2O$ [15], was used as reference because previous investigations have shown precise backscattering distances and coordination numbers for uranium-silica interactions [16]. Additional backscattering phase and amplitude functions were obtained from a hypothetical $[AlO_6]$ cluster with a bidentate coordinated $[UO_2]$ unit. The EXAFS spectra were analyzed according to standard procedures using the computer program EXAFSPAK [17]. Fits were performed in k -space in the range of $3.1\text{--}11.4 \text{ \AA}^{-1}$. The scaling factor, S_0^2 , was set to 1.

Results and discussion

Variations in pH affect both the solution speciation and the preferred type of the sorption sites on the montmorillonite surface. The presence of uranyl solution species as a function of pH can be predicted by a modeling code using thermodynamic data. The speciation was calculated using the EQ3NR program [18] and the thermodynamic data given in [19]. Additional parameters for the calculation were $T = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ M NaClO}_4$, $5 \times 10^{-5}\text{ M U}$, and absence of CO_2 . The main species present in the solution at pH 5 are 47% UO_2^{2+} , 13% $\text{UO}_2(\text{OH})^+$, 9% $(\text{UO}_2)_2(\text{OH})_2^{2+}$, 8% $\text{UO}_2(\text{OH})_2(\text{aq})$ and 4% $(\text{UO}_2)_3(\text{OH})_5^+$. With increasing pH the uranyl unit becomes more hydrolyzed and forms oligomeric solution species. The thermodynamic calculations predict the formation of solid hydrated uranyl oxides at $\text{pH} > 5.4$. However, the formation of surface sorption complexes can be kinetically favored in comparison to hydrated uranyl precipitates. Due to their characteristic spectral features in EXAFS spectra, it is possible to analyze the precipitates if they were present in significant amounts.

Uranium L_{III} -edge EXAFS spectra of the uranyl treated montmorillonite are shown in Fig. 1 together with the corresponding Fourier transforms (FT's) representing radial distribution functions of the atoms surrounding the uranium atom. The FT's are not corrected for EXAFS phase-shifts, Δ , causing peaks to appear at shorter distances ($R + \Delta$) relative to the real near-neighbor distances (R). The results of the data analysis are listed in Table 2.

The uranium atoms in all samples are coordinated by axial oxygen atoms (O_{ax}) at a distance of 1.77–1.78 Å. The $\text{U}-\text{O}_{\text{ax}}$ coordination number varied between 1.9 to 2.0 and was obtained without constraining any fit parameters. The multiple-scattering (MS) path of the uranyl moiety was linked to the $\text{U}-\text{O}_{\text{ax}}$ scattering parameters as described in [20] without introducing additional variable fit parameters (not explicitly listed in Table 2).

Depending on the reaction conditions, the distances between the $\text{U}-\text{O}_{\text{eq}}$ pair vary slightly between 2.34 Å and 2.37 Å and the coordination numbers $N(\text{U}-\text{O}_{\text{eq}})$ are in the

Table 2. EXAFS structural parameters (sample description see Table 1).

Sample	Shell	R [Å] ^a	N ^b	σ^2 [Å ²]	ΔE_0	Error
A	U–O _{ax}	1.78	2.0 (2)	0.0026	0.4	0.50
	U–O _{eq}	2.36	6.2 (15)	0.017		
	U–Al	3.43	0.6 (2)	0.003 ^c		
B	U–O _{ax}	1.78	2.0 (2)	0.0022	0.2	0.26
	U–O _{eq}	2.36	6.1 (8)	0.015		
	U–Al	3.43	0.5 (2)	0.003 ^c		
C	U–O _{ax}	1.77	1.9 (2)	0.0016	0.5	0.34
	U–O _{eq}	2.37	5.7 (8)	0.014		
	U–Al	3.44	0.5 (2)	0.003 ^c		
D	U–O _{ax}	1.77	2.0 (2)	0.0033	0.4	0.41
	U–O _{eq}	2.35	5.9 (7)	0.015		
	U–Al	3.41	0.8 (2)	0.003 ^c		
E	U–O _{ax}	1.78	1.9 (2)	0.0021	–0.1	0.33
	U–O _{eq}	2.34	5.8 (9)	0.013		
	U–Al	3.40	0.6 (2)	0.003 ^c		

a: Errors in distances R are ± 0.02 Å;

b: Errors in coordination numbers N are $\pm 25\%$ with standard deviations in parentheses, σ^2 is the Debye–Waller factor which accounts for the effects of thermal and statistic disorder;

c: Value fixed during the fit. The multiple-scattering path of the uranyl moiety was linked to the $\text{U}-\text{O}_{\text{ax}}$ scattering parameters as described in [20], without introducing any additional variable fit parameters.

range of 5.7 to 6.2. These distances are far from values for mononuclear outer-sphere uranyl aquo-complexes with $\text{U}-\text{O}_{\text{eq}}$ distances between 2.41 Å–2.43 Å obtained at lower pH values by Dent *et al.* [4], Chrisholm-Brause *et al.* [5], and Sylwester *et al.* [6]. The short $\text{U}-\text{O}_{\text{eq}}$ distances indicate that an inner-sphere complexation process dominates the sorption under the used experimental conditions. The Debye–Waller factor for the $\text{U}-\text{O}_{\text{eq}}$ shell is very large. This indicates a strongly distorted arrangement of the oxygen atoms. The large Debye–Waller factor indicates a splitting of the O_{eq} shell as observed by Sylwester *et al.* [6] for uranyl sorption on montmorillonite in a comparable pH

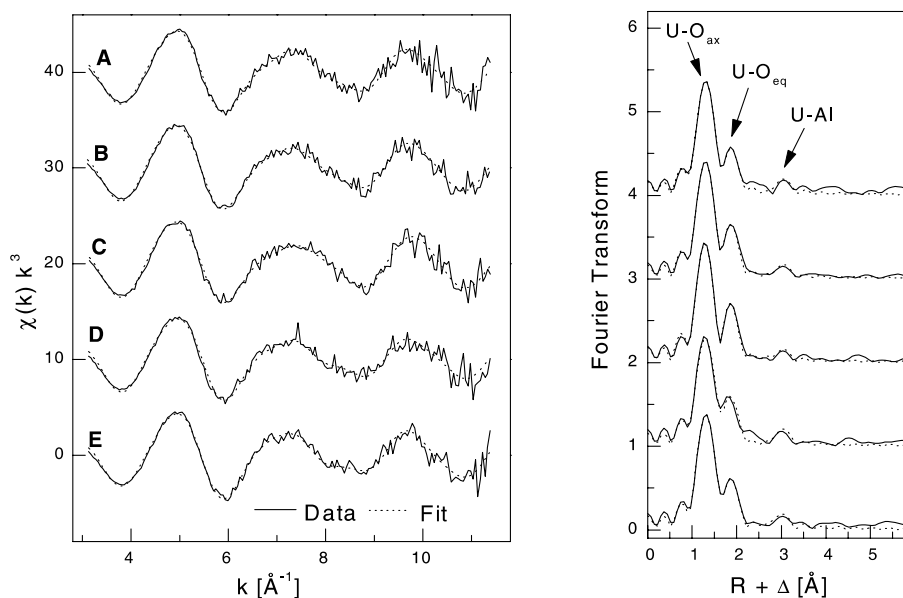


Fig. 1. Uranium L_{III} -edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transforms (right) of the uranyl-montmorillonite samples.

range ($U-O_{eq} = 2.30 \text{ \AA}$ and 2.48 \AA). The authors attributed the splitting in the equatorial oxygen shell to the binding of the uranyl unit onto amphoteric surface hydroxyl sites. Due to the shorter k -range used in the presented measurements, it is difficult to resolve this splitting.

Complexation at the aluminol and silanol sites becomes more likely at higher pH values due to the increasing deprotonation of these sites. A comparison of the samples **A**, **D**, and **E** with identical background electrolyte concentration shows that with increasing pH the $U-O_{eq}$ distance decreases only slightly from 2.36 \AA to 2.34 \AA within the error limit of the distance determination. At the high concentration of the background electrolyte, cation exchange processes are suppressed and sorption onto edge sites is favored [21]. For comparison, the electrolyte concentration in sample **C** was reduced to 0.01 M NaClO_4 . For this sample, the best fit for the distance $U-O_{eq}$ is 2.37 \AA , indicating no significant increase of the uranyl fraction bound by outer-sphere complexation in the interlayers. The obtained structural parameters indicate that also for the lower ionic strength the inner-sphere coordination is predominant at pH 5. In comparison Sylwester *et al.* [6] observed at low ionic strength (0.01 M NaCl) and pH 4 that outer-sphere complexation is the predominant uranyl uptake mechanism on montmorillonite. However, it seems that at pH 5 the inner-sphere complexation mechanisms are favored. Uranium loading was varied for samples **A** (1751 ppm U) and **B** (2473 ppm U). A change in the relation between inner-sphere and outer-sphere uranyl species as a function of surface coverage was not observed as described by Chrisholm-Brause *et al.* [5] for much higher differences in uranium loading.

In case of precipitation of uranyl hydroxides such as schoepite, $UO_2(OH)_2 \cdot 2H_2O$, the observation of a $U-U$ interaction would be expected for the EXAFS data from crystal structure parameters [22]. $U L_{III}$ edge EXAFS measurements on solid schoepite performed by Allen *et al.* [23] have shown $U-U$ distances of 3.84 \AA and 4.53 \AA . Inner-sphere multinuclear sorption complexes or surface precipitates such as observed by Thompson *et al.* at uranyl sorbed onto kaolinite [7] have shown $U-U$ distances of 3.87 \AA . The EXAFS data of uranyl sorbed onto montmorillonite (Fig. 1) enclose no significant peak which could indicate a $U-U$ interaction.

The FT of all samples shows a peak at $R + \Delta \approx 3.0 \text{ \AA}$. A similar feature is indicated by Thompson *et al.* [7] for uranyl sorption on kaolinite and Hudson *et al.* [10] for uranyl sorption on vermiculite and hydrobiotite as a result of the interaction between the uranyl moiety and the substrate. The commonly observed problem is that this peak is a superposition of multiple-scattering (MS) effects of the $U-O_{ax}$ shell and single scattering contribution from the substrate. The best approach seems to be a fit of this shell with Si or Al including fixed Debye-Waller factors together with the constrained parameters of the $U-O_{ax}$ MS contribution. This procedure gives distances of approximately $3.40\text{--}3.44 \text{ \AA}$ and a coordination number between 0.5 and 0.8 (Table 2). Thompson *et al.* [7] observed that the amplitude function of the filtered EXAFS spectrum of the peak at $R + \Delta \approx 3.0 \text{ \AA}$ shows the characteristic shape of the Al and Si amplitude function. The authors emphasized that it is impossible to distinguish between Al and Si because of their similar scattering amplitude and phase functions.

Due to the clear geometrical differences of $[SiO_4]$ tetrahedra and $[(Al, Mg)O_6]$ octahedra in the montmorillonite structure, it seems to be possible to identify the coordination of the uranyl ion based on a comparison of characteristic bond lengths using crystalline or hypothetical model structures. Sodydite, $(UO_2)_2(SiO_4) \cdot 2H_2O$ [15], can serve as a reference for different binding types between $[UO_2O_{x-eq}]$ and $[SiO_4]$ polyhedra. In this structure, the uranyl unit is connected in a bidentate fashion (edge-sharing) to $[SiO_4]$ with a $U-Si$ distance of 3.16 \AA and is bound *via* a monodentate coordination (corner-sharing) with a $U-Si$ distance of 3.81 \AA . A monodentate connection between $[UO_2O_{x-eq}]$ and $[SiO_4]$ polyhedra with an $U-Si$ distance of 3.61 \AA exists in the crystal structure of $Ba(UO_2)(SiO_2O_6)$ [24]. Both, the bidentate and the monodentate connection within these reference structures are not in agreement with the experimental observed distance of $3.40\text{--}3.44 \text{ \AA}$ in uranyl sorbed onto montmorillonite. It should be mentioned that the $U-Si$ distance of uranyl sorbed onto silica, characterized as bidentate bonding at a distance of around 3.08 \AA [6], is also significantly shorter than the value in uranyl sorbed onto montmorillonite. Therefore, a bidentate complex formation between the $[SiO_4]$ tetrahedra and the uranyl unit can be excluded.

However, the aluminol sites are considered much more reactive than the silanol sites [25], and therefore, we have focused our attention on corresponding references. A $U-Al$ interaction was not observed for uranyl sorbed onto γ -alumina, that could serve as a reference sample [6]. No crystallographic data of compounds with direct links of the uranyl unit to $[AlO_6]$ octahedra exist in the literature so far. Therefore, a model was created by using an $[AlO_6]$ octahedra with typical $Al-O$ distances between $1.85\text{--}1.97 \text{ \AA}$ [26] in edge-sharing connection with the $U(VI)$ polyhedron with $U-O_{eq}$ distances of 2.35 \AA . This approximation gives $U-Al$ distances of $3.3\text{--}3.5 \text{ \AA}$. The hypothetical $U-Al$ bond distance assuming a monodentate bonding between the uranyl unit and the $[AlO_6]$ octahedra exceeds the experimental data. Only the model structure with a bidentate connection between uranyl unit and the $[AlO_6]$ octahedron is in agreement with the experimental value. Therefore, we conclude that the substrate peak at $R + \Delta \approx 3.0 \text{ \AA}$ originates from a preferred sorption to the hydroxylated aluminol edge sites by an inner-sphere, mononuclear complexation mechanism in bidentate fashion.

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