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Eric A. Hudson  
Louis J. Terminello  
Brian E. Viani  
Tobias Reich  
Jerome J. Bucher  
David K. Shuh  
Norman M. Edelstein

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# X-RAY ABSORPTION STUDIES OF URANIUM SORPTION ON MINERAL SUBSTRATES

ERIC A. HUDSON\*, LOUIS J. TERMINELLO\*, BRIAN E. VIANI\*, TOBIAS REICH\*\*, JEROME J. BUCHER\*\*\*, DAVID K. SHUH\*\*\*, AND NORMAN M. EDELSTEIN\*\*\*

\* Lawrence Livermore National Laboratory, Livermore, CA 94551

\*\* Forschungszentrum Rossendorf e. V., Institut für Radiochemie, Postfach 51 05 19, D-01314 Dresden, Germany

\*\*\* Lawrence Berkeley Laboratory, Berkeley, CA 94720

## ABSTRACT

Uranium  $L_3$ -edge x-ray absorption spectra have been measured for uranium-mineral sorption systems. An expandible layer silicate, vermiculite, was treated to obtain a collapsed and non-expanding phase, thereby limiting access to the interior cation exchange sites. Samples were prepared by exposing the finely powdered mineral, in the natural and modified form, to aqueous solutions of uranyl chloride. EXAFS spectra of the encapsulated samples were measured at the Stanford Synchrotron Radiation Laboratory. Results indicate that the uranyl ion possesses a more symmetric local structure within the interlayer regions of vermiculite than on the external surfaces.

## INTRODUCTION

Aqueous transport of actinides in the geosphere can be significantly retarded by sorption and/or precipitation upon mineral surfaces. Despite the importance of this effect to environmental remediation efforts and nuclear waste repository design, there is only limited direct knowledge about the microscopic nature of the actinide-mineral interactions. X-ray Absorption Spectroscopy (XAS) is one of the few techniques which can study the local environment of elements present in low concentrations in a complex solid matrix, because it is element-specific and probes only the short-range electronic and geometric structure. The penetrating abilities of hard x-rays allow the *in-situ* study of encapsulated samples, which is particularly desirable in the study of radioactive materials. In the experiments described here, XAS was used to characterize uranium in contact with vermiculite, an expandible layer silicate mineral. Vermiculite particles are characterized by  $\approx 10$  Å Mg-Al-silicate layers which are negatively charged due to isomorphous substitution. The negative charge is countered by cations residing between the layers. These interlayer regions are normally hydrated and thus accessible to aqueous-phase cations, permitting cation exchange. Results of our Extended X-ray Absorption Fine Structure (EXAFS) measurements indicate that the uranyl ion possesses a more symmetric local structure within the interlayer regions of vermiculite particles than on the external surfaces.

## EXPERIMENT AND ANALYSIS

### Minerals

Vermiculite from Sanford, North Carolina was supplied by Ward Natural Science Establishment, Inc. The mineral was ground in a shatter box and the  $<45\text{ }\mu\text{m}$  fraction was separated by sieving. A Scintag PAD-V diffractometer with a Cu radiation source was used to obtain X-Ray Diffraction (XRD) patterns, which verified the mineral structure and demonstrated that grinding had not significantly damaged the crystallinity. A modified form of vermiculite was also used in which the interlayer spacing was reduced by exchange of the interlayer cation, which is predominantly  $\text{Mg}^{2+}$  in the original mineral, for the  $\text{K}^+$  cation. The process used here first replaces the  $\text{Mg}^{2+}$  with  $\text{Li}^+$ , and then replaces  $\text{Li}^+$  with  $\text{K}^+$ , thereby insuring a more complete exchange. One gram of dried, ground natural vermiculite was stirred in 100 ml of 2.0 M LiCl solution for 5 hours at  $60^\circ\text{ C}$ . The solid phase was separated by centrifugation and the procedure was repeated with fresh solution. The resulting wet solid was then similarly treated with 50 ml of 2.0 M KCl, to give the potassium-exchanged solid, referred to here as K-vermiculite. XRD analysis revealed differences in the basal-plane layer (001) spacings for the two forms of saturated vermiculite as follows: (1) Mg-vermiculite (i.e. the natural form) showed a sharp peak at  $14.44\text{ \AA}$ , indicating the presence of two layers of water in the interlayer region, (2) K-vermiculite showed a broad peak centered  $\approx 10.3\text{ \AA}$ , indicating collapse of the layers to a non-hydrated mica-like structure, and a very small  $\approx 14.4\text{ \AA}$  peak, indicating that only a trace amount of Mg-vermiculite and/or Li-vermiculite remained. These spacings compare well to tabulated values for relatively high-charge vermiculite.<sup>1</sup>

### Exposure of minerals to uranium

To obtain samples containing uranium bound to the mineral substrates, the solids were exposed to aqueous uranyl solutions. Conditions were selected to provide a simple uranium speciation in solution, with uranium concentration high enough to give final samples suitable for the limited sensitivity of XAS. All solutions were prepared in air using deionized, filtered water with resistivity  $> 15\text{ M}\Omega\text{-cm}$ . The uranium solutions contained  $1.0\text{--}10^{-3}\text{ M }$   $\text{UO}_2\text{Cl}_2$  in  $1.2\text{--}10^{-2}\text{ M }$  HCl. After addition to the vermiculite, the pH of each exposure solution was adjusted to pH = 3.5, using 0.1 M or 0.01 M NaOH or HCl as necessary. Thermodynamic calculations based upon established constants<sup>2</sup> predict that, under these conditions, the uranyl ( $\text{UO}_2^{2+}$ ) ion exists predominantly in solution as the fully hydrated species  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ . One hundred milligram portions of each mineral sample were exposed to 40 ml of uranium solution for 24 hours, with vigorous rotary shaking to keep the solid in suspension. Twice during each exposure the pH was measured, and adjusted as necessary to pH = 3.5. Afterwards, the solids were separated by centrifugation and the resulting wet pastes were double-sealed in 2-mil polyethylene bags for XAS analysis. A solution of 0.2 M uranyl chloride in 0.5 M HCl, referred to here as  $\text{UO}_2^{2+}$  (aq.), was also prepared for XAS analysis.

### XAS measurements

$L_3$ -edge XAS spectra were measured simultaneously in transmission and fluorescence mode at the undulator beamline IV-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) using a Si(111) double-crystal monochromator. To reject higher-order harmonics, crystal alignment

was detuned to give 10% or 30% of the total flux. The energy scale for each spectrum was calibrated by simultaneously measuring the fluorescence spectrum of a concentrated  $\text{UO}_2^{2+}$  reference solution placed downstream from the sample. Transmission spectra of the sample were measured using two ionization chambers containing argon. X-ray fluorescence from the sample was measured using a single-element, four-pixel germanium detector, gated to the  $L_\alpha$  fluorescence lines of U. Typical total count rates were <300 kHz, which is within the range of linear response for the detector system. Fluorescence from the reference solutions was detected using an ionization chamber equipped with Soller slits. Multiple scans were collected for all sample spectra.

### EXAFS analysis

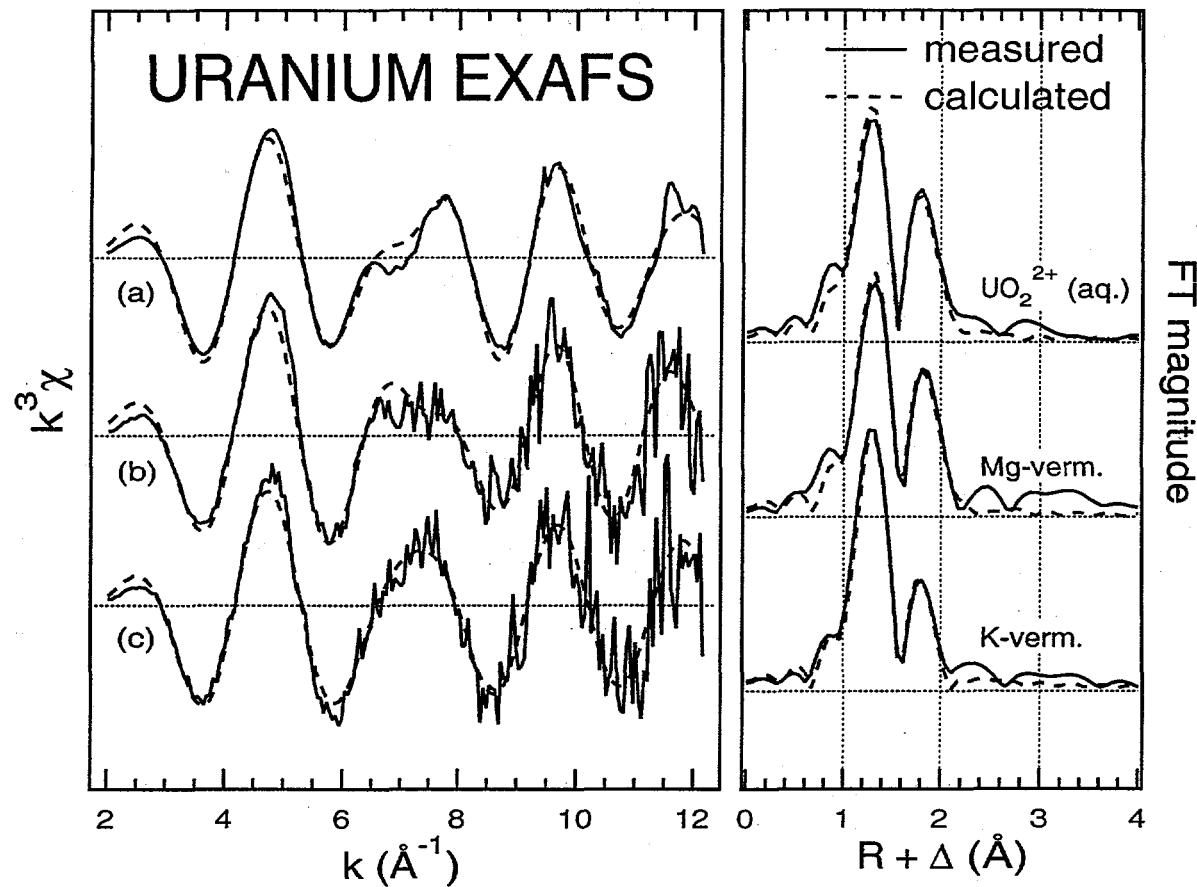
EXAFS results were analyzed using the EXAFSPAK software developed by G. George and I. Pickering at SSRL. Transmission or fluorescence spectra were normalized, background-subtracted, and renormalized to a smooth spline function with Victoreen corrections. The resulting chi curves, weighted by a factor of  $k^3$ , were modeled by least-squares fitting using scattering amplitudes and phase shifts calculated for each pair of atoms by the FEFF V code.<sup>3</sup> The FEFF calculations assumed the published structures for  $\alpha\text{-UO}_2(\text{OH})_2$ .<sup>4</sup> As a test, derived phase shifts and amplitudes for  $\text{ThO}_2$  were used to fit experimental  $\text{ThO}_2$  results, with good agreement (not shown here), indicating that the FEFF calculations are reliable even for heavy elements. Distinct amplitudes and phase shifts were obtained for the axial oxygens of the uranyl species and the surrounding equatorial oxygens, and were used separately for these two shells in the fits. The ionization threshold ( $E_0$ ) for the experimental data was assumed to be 17185 eV, and the relative  $E_0$  used in the fits was fixed at -9 eV for all shells. The relative values were selected based on fits to several data sets where  $E_0$  allowed to vary. The EXAFS range was limited by a monochromator crystal imperfection, which produced a glitch at  $\approx 12.5 \text{ \AA}^{-1}$ .

## RESULTS AND DISCUSSION

Figure 1 compares measured and calculated EXAFS for several uranium samples. In the calculation, the uranyl local structure was modeled by two shells of oxygen atoms, representing the axial and equatorial ligands. Coordination numbers were fixed at 2 and 5, respectively, based upon previously reported values for the hydrated uranyl species.<sup>5,6</sup> Bond distances and Debye-Waller factors were allowed to vary for each shell, yielding the numerical results listed in Table I.

The  $\text{UO}_2^{2+}$  (aq.) sample used here is expected to be an approximately equal mixture of the fully hydrated and monochloride species, based upon thermodynamic calculations using established constants.<sup>2</sup> An alternative three-shell model, using the fixed coordination numbers 4.5 for oxygen in the equatorial shell and 0.5 for chlorine, gave a better fit to the shoulder at  $\approx 2.4 \text{ \AA}$  in the Fourier transform (FT) (not shown). However, the numerical results for the axial and equatorial oxygen were not significantly altered by the three-shell fit. They therefore provide a reliable model of hydrated uranyl for the purposes of comparison.

The most striking feature of the experimental FT's in Fig. 1 is the variation in the equatorial peak at  $\approx 1.8 \text{ \AA}$ , which is much less intense for U/K-vermiculite. This difference is seen in the numerical fit results as a smaller Debye-Waller (DW) factor for U/Mg-vermiculite than obtained for U/K-vermiculite. In principle, a decreased FT peak intensity could also arise from a reduction in coordination number, with little change in the DW factor. However the variation observed here would require an unreasonably large change of  $>1.5$  in the coordination number.



**Figure 1:** Uranium  $L_3$  EXAFS results. Measured (solid lines) and calculated (dashed lines) chi curves (left) and the corresponding Fourier transforms (right) are compared for: (a) hydrated uranyl ion in aqueous solution; (b) uranium bound to Mg-vermiculite; and (c) uranium bound to K-vermiculite. Note that the abscissa scale,  $R+\Delta$ , in the FT plots represents bond distances which are not corrected for scattering phase shift effects. Thus the actual bond distances, as derived from the least-squares analysis (see Table I), differ from the peak positions plotted here.

The assumption of a constant coordination number for the equatorial shell is also supported by the fairly small variations in the derived equatorial bond distances. Therefore the trend in DW factors is judged to be significant.

The DW factor determined for the hydrated uranyl species is very close to that of U/Mg-vermiculite, indicating that the latter sample has a similarly ordered local environment. The larger DW factor for U/K-vermiculite reflects greater disorder, most likely static disorder resulting from a mixture of different equatorial bonding distances. Note that an increase in *thermal* disorder, i.e. larger vibrational motions, could also cause an increased DW factor, but would be accompanied by a detectable increase in the corresponding bond distance, which was not observed here. The equatorial bond length still has the same *average* value, as measured by the derived bond distance, but has larger variations. These variations could arise from a range of bond distances within the equatorial shell of a single species, or from a mixture of species with different bond distances in the equatorial shell. The former explanation seems more likely in this case, upon examination of the DW factors derived for the axial oxygens. If the

**Table I:** Results of the EXAFS analysis. Derived bond distances, R, and Debye-Waller factors,  $\sigma^2$ , are tabulated. Uncertainties, as determined by the least-squares minimization, are given in parentheses.

Sample	Shell	R (Å)	$\sigma^2$ (Å <sup>2</sup> )
$\text{UO}_2^{2+}$ (aq.)	axial oxygen	1.776 (0.001)	0.00250 (0.00011)
	equatorial oxygen	2.411 (0.002)	0.00826 (0.00028)
$\text{UO}_2^{2+}$ / Mg-vermiculite	axial oxygen	1.798 (0.002)	0.00236 (0.00025)
	equatorial oxygen	2.391 (0.004)	0.00787 (0.00054)
$\text{UO}_2^{2+}$ / K-vermiculite	axial oxygen	1.784 (0.002)	0.00181 (0.00024)
	equatorial oxygen	2.389 (0.008)	0.01267 (0.00118)

U/K-vermiculite disorder were caused by a mixture of species with differing equatorial bond distances, the axial bond distance would also assume a range of values, due to the roughly inverse relationship between axial and equatorial bond lengths.<sup>7</sup> Such a variation in axial bond length would lead to an increased DW factor for the axial oxygens, as compared to U/Mg-vermiculite or  $\text{UO}_2^{2+}$  (aq.). In fact, the opposite effect is observed—the derived axial DW factor is *less* for U/K-vermiculite. This result is more consistent, therefore, with a larger range of equatorial bond distances within a single species which possesses, at the most, two discrete axial bond distances. The uranyl ion is known to exhibit such distortions of the equatorial shell for a number of different complexes in the solid state.<sup>6,8</sup>

The  $\approx 25\%$  decrease in axial DW factor, which occurs in the change from U/Mg-vermiculite to U/K-vermiculite, can be explained in part by a strengthening of the uranyl axial bonding in the latter sample. This would decrease the thermal broadening of the axial bond distance by reducing the vibrational motion of the bond. The measured 0.014 Å decrease in axial bond distance provides evidence of this axial bond strengthening. In summary, the following modifications of the local uranyl structure are proposed upon changing from U/Mg-vermiculite to U/K-vermiculite: (1) The average equatorial bond distance remains constant, but the individual bonds assume a wider range of values, thereby increasing the equatorial DW factor; (2) The axial bond strengthens, leading to a shorter bond distance and smaller DW factor.

The EXAFS results can be interpreted by considering known structural differences between the two forms of vermiculite. Mg-vermiculite is known to have two layers of partially ordered water in the interlayer region. The interlayer  $\text{Mg}^{2+}$  cation occupies a highly symmetric interlayer site, with six equidistant waters of hydration.<sup>9</sup> EXAFS results indicate that the uranyl ion has a relatively uniform set of equatorial bond distances, suggesting that it also occupies a fairly symmetric site in the interlayer region. For the collapsed K-vermiculite, the interlayer region is no longer hydrated and  $\text{K}^+$  irreversibly occupies the interlayer cation-exchange sites.<sup>10</sup> This leaves only the external surfaces of the vermiculite particles to the aqueous phase. (For the Mg-vermiculite, some uranyl ions should also be bound to external surfaces, but this represents only a small fraction of the total basal surface.) At the relatively low pH used here, specific adsorption at amphoteric sites on the edge surfaces is not expected, so the uranium most likely

populates cation exchange sites on the *external* basal plane surfaces. For these sites, the ordering influence of an opposing basal plane surface is absent, and the structural order which characterizes the interlayer region is therefore reduced. EXAFS results indicate that the uranyl ion adopts a more distorted equatorial shell in this case. This suggests the interpretation that uranyl ions in the interlayer region are influenced by both basal plane layers to produce a fairly symmetric species, while uranyl ions on external basal plane surfaces experience less balanced forces, leading to a reduced symmetry. It is noteworthy that there are features at  $R > 2.5 \text{ \AA}$  in the FT for U/Mg-vermiculite which are about half as intense for U/K-vermiculite. These peaks have not been analyzed, but the observed intensity trend supports the interpretation that uranyl ion interacts with both basal plane surfaces in the interlayer regions of Mg-vermiculite.

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