XAFS Investigations of the Interaction of U(VI)
with Bio-oxidizing *Dechlorosoma suillum*

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Introduction

Here we demonstrate the potential of a novel microbial remediation strategy for U(VI) stabilization in reducing environments. This strategy is based on the recently described anaerobic metabolism in nitrate-dependent Fe(II) oxidation. Our studies focused on *Dechlorosoma* species, which we previously showed to be ubiquitous environmental Fe(II) oxidizers that can couple anaerobic oxidation of Fe(II) to the reduction of either nitrate or (per)chlorate. Bio-oxidation of Fe(II) and precipitation of Fe(III) oxides by these organisms resulted in the rapid adsorption and removal of soluble uranium from solution. X-ray absorption spectroscopy analysis indicated that the uranium was bound to the biogenically produced Fe(III) oxides, was present as U(VI), and formed bidentate and tridentate inner-sphere complexes with the Fe(III) oxide surfaces.

Methods and Materials

The U-bio-oxidized sample was centrifuged, and fluorescence x-ray absorption fine structure (XAFS) measurements were made on the wet homogeneous paste. A hydrated uranyl standard ([U] = 500 ppm in doubly distilled deionized water, pH 0.96) was also measured in fluorescence mode. All XAFS measurements were made at the Materials Research Collaborative Access Team (MR-CAT) sector at the APS [1]. The energy of the incident x-rays was selected by using a Si(111) monochromator. The incident x-ray intensity was sampled with a nitrogen-filled ion chamber. The fluorescent x-ray intensity was filtered by using a Sr foil of six absorption lengths and sampled by using an Ar-filled fluorescence detector in the Stern-Heald geometry [2]. Linearity tests [3] indicated less than 0.38% nonlinearity for a 50% decrease in incident x-ray intensity. The incident x-ray intensity varied by less than 15% throughout the energy range of the XAFS measurements. Three scans were collected at six different locations on the sample to reduce radiation exposure. The sample was exposed for approximately 1 min for each measurement at each location. Measuring several spectra at each of the six sample locations enabled determination of radiation-induced chemical effects at the 1-min time scale. No time-dependent change in the XAFS data was observed for any of the samples.

The codes contained in the University of Washington UWXAFS package [4] were used to analyze the data. The program FEFF7 [5] was used to construct the theoretical models on the basis of model structures. The error analysis and the goodness-of-fit parameters were calculated by the fitting routine FEFFIT.

X-ray absorption near-edge structure (XANES) is useful in determining the average valence state of U in bio-oxidized samples. The energy position of the edge step is directly related to the U valence state. Therefore, careful monitoring of the monochromator energy is paramount when making these comparisons. The edge positions for the U(IV) and U(VI) standards differed by approximately 4.3 eV, as determined by the energy value at half the step height of the normalized data. For the 0.7-mm vertical beam size used in these experiments, the line width of the monochromator at 17 keV is ~4.0 eV, and the step accuracy of the monochromator at 17 keV is ±0.13 eV. As described elsewhere [6], the transmission XAFS signal of a Y foil was used as a reference for accurately aligning the edge-energy positions of the U(IV) (uraninite) and U(VI) (γ-UO_3) standards and the U-bio-oxidized data.

Results

An example of the aligned, normalized adsorption data for the standards and the U-bio-oxidized samples is shown in Fig. 1. The data clearly indicate that the U(VI) added to the solution was not reduced to U(IV) by either bacteria or x-ray radiation. The U XANES data from the U-bio-oxidized samples measured in these experiments indicate a single U(VI) valence state.

Theoretical models based on the crystal structure of hydrogen uranyl phosphate tetrahydrate [7] and sodium uranyl(VI) triacetate [8] were generated by FEFF7. First a model for a hydrated uranyl standard was developed. The fit of this model to the data showed the importance of the multiple scattering paths from the two closely bound axial oxygen atoms of the uranyl; therefore, they were included in the model for the bio-oxidized sample. Including two equatorial oxygen paths in the model for the bio-oxidized data improved the quality of the fit, decreasing the reduced-chi-squared value by a factor of 2.6. This result indicates two different equatorial oxygen groups, approximately 5.7 oxygen atoms at 2.2 Å and 1.7 oxygen atoms at 2.4 Å. The data at 2-3.5 Å in the Fourier
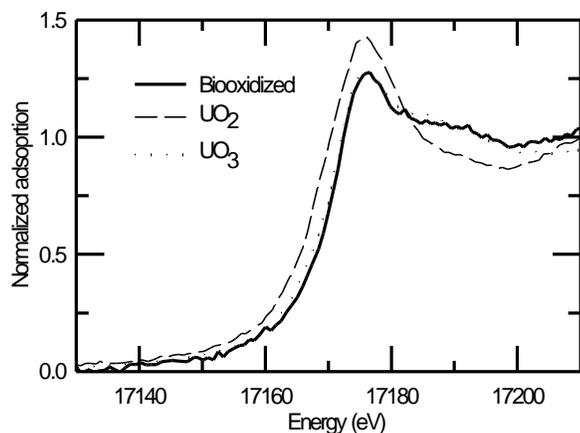
FIG. 1. Average normalized absorption data from UO₂, UO₃, and U-bio-oxidized sample.

transform were modeled with C, P, U, and Fe shells at 2.9 and 3.5 Å. The model, including two Fe shells, was statistically better than any others, reducing the reduced-chi-squared value by a factor of 3 to 7. A U-Fe distance of approximately 3.5 Å had been observed previously [9]. An illustration of the quality of the fit to the data is shown in Fig. 2. The best-fit values to these data are in Table 1. The sum of the average number of Fe atoms in both shells is consistent with one, indicating that the uranyl is surface absorbed to the iron oxide.

Discussion

Results from U L-III edge XANES analysis determined the average valence state of the U in the bio-oxidized sample to be U(VI). Results from the U L-III extended XAFS (EXAFS) analysis indicate uranyl surface adsorption to the iron oxide in two different binding geometries and a splitting of the U-equatorial oxygen shell distances.

The results of this study demonstrate the potential for this novel approach to the stabilization and immobilization of environmental radionuclides and heavy metals. This strategy can be applied in two ways. The first way is by precipitating Fe(III) oxides over previously immobilized heavy metal/radionuclide contaminants *in situ.* This forms an insoluble barrier that will crystallize with time, thus inhibiting future bioreduction and adsorbing any leached metal contaminants. The second way is by engineering a semipermeable Fe(III) oxide wall *in situ,* downstream of the immobilized heavy metal-radionuclide contamination, to "catch" and adsorb any heavy metals and radionuclides that might be solubilized and remobilized as a result of environmental fluxes such as reoxidation (biotic or abiotic) or ligation.
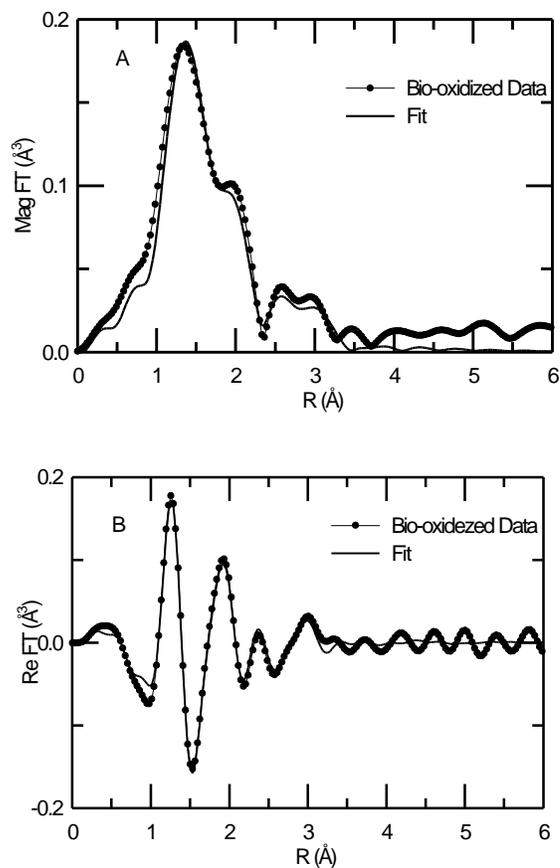

FIG. 2. (a) The magnitude and (b) the real part of the Fourier transform of the best-fit model and data from the U-bio-oxidized sample.

Table 1. Best-fit values for the U-bio-oxidized sample. S_0^2 was held at 1.0 ±0.2, as determined from the hydrated uranyl standard. $\mathbf{D}Eo$ was determined to be -1.5 ±2.0 for all paths. The fit had nine independent points in the data and seven variables.

Path	N_{degen}	R (Å)	σ^2 $(10^{-3}$ Å$^2)$
U-Oax	2.0	1.80±0.02	0.0±0.2
U-Oeq	4.7±4.5	2.38±0.05	5.1±15.3
U-Oeq	1.7±0.7	2.16±0.14	5.1±15.3
U-Oax1-U-Oax1	2.0	3.59±0.03	0.0±0.7
U-Oax1-Oax2	2.0	3.59±0.03	0.0±0.7
U-Oax1-U-Oax2	2.0	3.59±0.03	0.0±0.7
U-Fe1	0.7±0.2	2.92±0.03	0.0±15.4
U-Fe2	0.5±0.4	3.52±0.06	0.0±15.4

References

[1] C. U. Segre, N. E. Leyarovska, and L. D. Chapman et al., in *Proceedings of the Synchrotron Radiation Instrumentation: Eleventh U.S. Conference,* CP521, 419-422 (2000).

[2] E. A. Stern and S. M. Heald, Rev. Sci. Instrum. **50**, 1579-1583 (1979).

[3] K. M. Kemner, A. J. Kropf, and B. A. Bunker, Rev. Sci. Instrum. **65**, 3667-3669 (1994).

[4] E. A. Stern, M. Newville, and B. Ravel et al., Physica B **208** and **209**, 2995-3009 (1995).

[5] S. I. Zabinsky, J. J. Rehr, and A. Ankudinov et al., Phys. Rev. B **52** (4), 2995-3009 (1995).

[6] J. L. Cross and A. I. Frenkel, Rev. Sci. Instrum. **70**, 38-40 (1998).

[7] B. Morosin, Acta Crystallogr. Sec. B **34**, 3732-3734 (1978).

[8] D. Templeton, A. Zalkin, and H. Ruben et al., Acta Crystallogr. Sec. C **41**, 1439-1441 (1985).

[9] J. R. Barger, R. Reitmeyer, and J. J. Lenhart et al., Geochim. Cosmochim. Acta **64** (17), 2737-2749 (2000).