

U L₃-Edge EXAFS Measurements of Sediment Samples from Oak Ridge National Laboratory, Tennessee, U.S.A.

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Introduction

Successful remediation strategies at the Natural and Accelerated Bioremediation (NABIR) Field Research Center (FRC) at Oak Ridge National Laboratory, Tennessee, USA, and elsewhere depend on knowledge of the initial speciation of U within sediments throughout a contaminated volume containing a heterogeneous mixture of sediment phases. Because of the complexity of the FRC sediments, the initial speciation of U in the sediments may depend on depth. XAFS spectroscopy is ideally suited for these types of investigations, as measurements can be made before bioremediation on sediments under anoxic conditions and at a variety of spatial scales. We used XAFS spectroscopy to determine the valence state and chemical speciation of U at a variety of depths in the contaminant plume.

Methods and Results

Uranium L₃-edge XAFS spectra were collected at the MRCAT sector 10-ID beamline [1] on four samples representing two cores collected at the NABIR FRC site and three different depths. The sample from the middle of the treatment zone at 40 ft (FWB101-08-12) had a brownish color, while the sample from the bottom of the treatment zone at 45 ft (FWB101-0603) had a greenish gray color. The sample and replicate at 46 ft (FWB100-06-12A and FWB100-06-12G, respectively) had a black color. These samples were mounted in Plexiglas sample holders and sealed with Kapton film windows. The samples were kept anoxic during the EXAFS measurements.

For the U L₃-edge XAFS measurements, the second harmonic of the undulator was tapered by 3.5 keV to reduce the variation in the x-ray intensity to less than 15% in the scanned energy region at 17–18 keV. Energy selection was accomplished with a double-crystal Si(111) monochromator. X-rays of higher harmonic energies were removed by a Pt-coated mirror. The incident x-ray intensity was monitored with an ion chamber filled with a 1:1 mixture of He and N₂ gases. The fluorescent x-rays were monitored by a 13-element solid-state (Canberra with XIA electronics) detector. An energy reference spectrum from a dilute hydrogen uranyl phosphate standard was measured by using scattered x-rays as described previously [2]. The incident x-ray beam contains $\sim 5 \times 10^7$ x-rays per second in a 1-mm-square area. EXAFS spectra were collected from different regions of the sample. Each EXAFS spectrum required about 1 h of collection time. No time-dependent changes were detected in the EXAFS spectra.

The EXAFS spectra from the 40-ft, 46-ft (A), and 46-ft (G) sediments are nearly identical. They were co-refined on the basis of a uranyl bound to carbon- and phosphorous-containing ligands (Fig. 1). The EXAFS spectrum from 45 ft shows a larger signal at wave numbers greater than 8.0 \AA^{-1} . The cause was determined to be a U–U signal(s).

Discussion

The results of the EXAFS spectral analysis from the 40-ft and 46-ft sediments indicate that the uranyl is bound predominantly

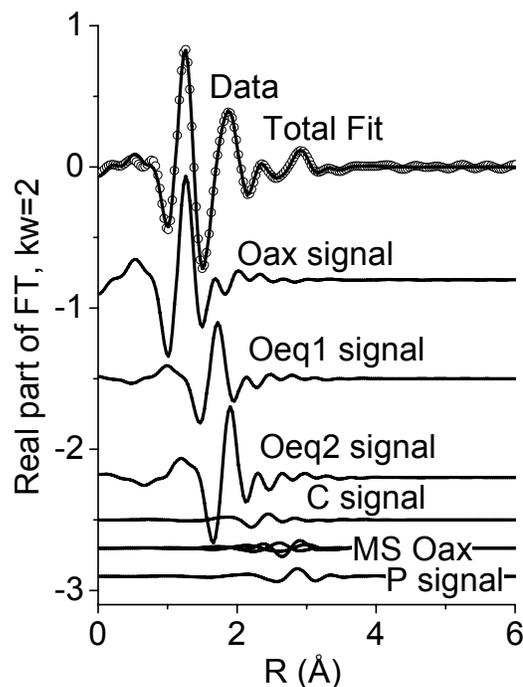


Fig. 1. EXAFS data and model from the 46-ft (FWB100-06-12A) sediment sample. Real part of Fourier transform of the data (open symbols) and fit (solid line), followed by the contribution from each scattering path included in the fit.

to monodentate phosphate and bidentate carbonate groups. The EXAFS results are consistent with uranyl bound to the surface of mineral or organic matter, rather than the formation of uranyl precipitates. In contrast, the EXAFS spectral analysis of the 45-ft sediment sample shows a small amount of a crystal structure resembling uranyl hydroxide ($16\% \pm 11\%$), in addition to some C-containing ligands. No P-containing ligands bound to the uranyl were needed to model the EXAFS spectrum for the 45-ft sediment. These results demonstrate the importance of investigating heterogeneity with depth at the FRC site.

Acknowledgments

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