

# U L<sub>3</sub>-Edge XAS Measurements of Sediment Samples from U-Contaminated Mine Ponds

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## Introduction

Contamination of sediments and water by actinides including U is a serious international problem. The discovery that bacteria can convert mobile uranyl carbonate ions to uraninite (UO<sub>2</sub>) spurred the development of strategies for *in situ* bioremediation of U-contaminated lands. These approaches are based on the extremely low solubility of uraninite ( $K_{sp} \sim 10^{-61}$ ). Though the products of biological actinide reduction are known to be amorphous or poorly crystalline, their detailed structure, form, and reactivity and the implications of these characteristics for U mobility have not been completely determined. We have made a number of XAS measurements that led to several forward strides in understanding the microbial reduction of U and the resulting by-products.

## Methods and Materials

We examined uraninite formed when complex natural U-contaminated sediments were incubated with an organic substrate designed to stimulate growth of native anaerobic bacteria. XAFS measurements were made on samples held in a Teflon sample holder and sealed between two pieces of Kapton film to maintain anoxic conditions. We also measured a uraninite standard diluted 1:100 with SiO<sub>2</sub> in fluorescence mode. All XAFS measurements were made at MRCAT [1]. The energy of the incident x-rays was selected by using a Si(111) monochromator. Higher harmonics were rejected by using reflection from a Rh mirror. The incident x-ray intensity was monitored with a nitrogen-filled ion chamber, and the fluorescent x-ray intensity was monitored with an Ar-filled fluorescence detector in the Stern-Heald geometry [2]. A Sr filter of three absorption lengths was used to reduce the background signal. Linearity tests [3] indicated less than 0.30% 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.

The sample was exposed to the x-ray beam for approximately 1 min for each measurement. Measuring several successive spectra at a sample location in this way 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 (Fig. 1). XANES data were normalized by using standard procedures. The transmission XAFS signal of a Y foil was used as a reference to accurately align the edge energy positions of U(IV) (UO<sub>2</sub>) and U(VI) (UO<sub>3</sub>) standards and sediment samples. In all, 30-50 scans from six different locations on each sample were averaged.

## Results

The XANES results confirmed that most of the U in the sediment was reduced to U(IV) in the biotic samples supplied with an electron donor, whereas the biotic samples not supplied with an electron donor show mostly U(VI). The EXAFS results indicate that uraninite nanoparticles are formed because of the

low coordination number for the number of U-U neighbors ( $5.6 \pm 4.0$ ).

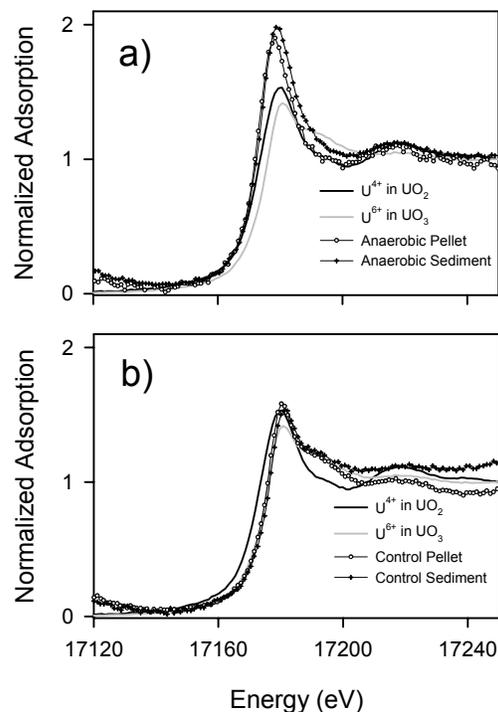


Fig. 1. Average normalized absorption data for UO<sub>2</sub>, UO<sub>3</sub>, and sediment samples (a) supplied or (b) not supplied with an electron donor.

## Discussion

Our results demonstrate the following:

1. Biogenic uraninite particles are almost as small as crystals can be [4]. This small particle size might make uraninite much more mobile than was previously thought, because of particulate transport. Therefore, bioremediation strategies based on the formation of uraninite might not diminish the transport of uranium in the subsurface.
2. Incubation of sediments with organic substrates removed U almost entirely from solution within one month [5].
3. Enzymatic U(VI) reduction by *Desulfosporosinus* was verified [6].

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