Spectroscopic Verification of Biotic and Abiotic Reduction of Uranium at Mineral Surfaces

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Introduction

As part of our studies of metal bioremediation by sulfate-reducing bacteria (SRB) we examined the nature of adsorbed and precipitated U phases that formed on mineral surfaces after treatment with abiotic sulfide or SRB.

Methods and Materials

Samples consisting of natural quartz grains (α-SiO_2, 212-300 µm) and fine-grained synthetic goethite (α-FeOOH, 56 m^2 g^{-1}) were incubated under anoxic conditions at room temperature in a modified lactate-C medium containing aqueous U(VI). One set of samples was inoculated with *Desulfovibrio desulfuricans,* while a second set of samples served as a control. A separate abiotic experiment with U(VI) was also conducted in which aqueous Na_2S was added as a reductant, and then quartz sand was added after completion of the reaction. In all experiments, the mineral grains were removed from solution after three weeks, dried, and stored under an N_2 atmosphere. Specimens were mounted between Kapton windows in a multispecimen Al sample holder modified to fit into a Lytle detector chamber. XANES spectra at the U L_3-edge were collected in fluorescence mode at the PNC-CAT bending-magnet beamline (20-BM) using a scintillation detector with a single-channel analyzer to define the energy window. A natural uraninite (nominally UO_2) sample from Maine was also analyzed in transmission mode. During XANES analysis, the Lytle detector chamber was fitted with an Sr filter and was continuously flushed with He(g) to prevent oxidation of the samples by air. Resulting spectra were normalized for comparative purposes.

Results

The U L_3-edge XANES spectra (Fig. 1) for the Na_2S-treated (abiotic) sample and the natural uraninite were essentially identical and indicated that little if any U(VI) was present. The goethite/quartz sample that was incubated in the absence of SRB adsorbed some of the U to yield a typical U(VI) XANES spectrum distinguishable from the uraninite by a slightly higher edge energy, a slightly less intense white line just above the edge, and a greater intensity in the region 15-35 eV above the edge. Exposure of the Na_2S-treated (abiotic) sample to air resulted in the reoxidation of the U(IV) to yield a spectrum (data not shown) identical to that for the uninoculated goethite/quartz sample. The goethite/quartz sample incubated with SRB yielded a spectrum similar to that of uraninite but having distinct features, notably a much more intense and slightly broader white line.

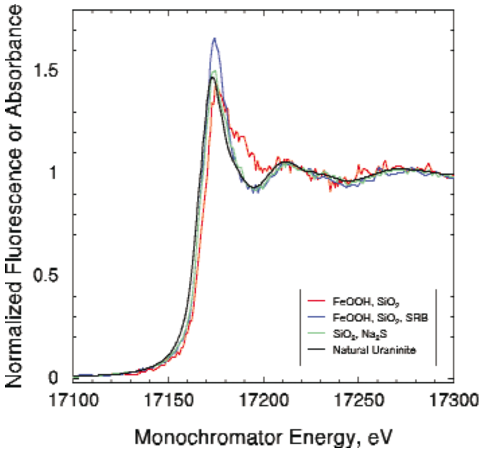

FIG. 1. Uranium L-edge XANES spectra for natural uraninite and for other minerals treated with U(VI) solutions under nonreducing and abiotic or biotic reducing conditions.

Discussion

The U XANES data demonstrate both biotic and abiotic chemistry may be involved in the removal of U from solution by SRB treatments. The unique features of the biotically reduced spectrum suggest either a different bonding environment for U(IV) that results in a lower degree of screening of the core hole and a stronger white line[1] or the presence of some of the U in a lower oxidation state, such as U(III). Based on U M_5-edge XANES spectra, Francis et al. (1994) concluded that some U(III) was produced along with U(IV) when U(VI) was reduced biotically by *Clostridium sp.* [2]A similar result could be expected in our experiments with SRB.

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