Reduction of Uranium(VI) by Mixed Fe(II)/Fe(III) Hydroxide (Green Rust)

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Introduction

Green rusts (GRs), mixed ferrous/ferric hydroxide minerals found in many suboxic environments, are believed to play a central role in the biogeochemistry of Fe. Recently, GRs have been shown to be capable of reducing a number of organic and inorganic contaminants, suggesting that GRs may play a role in the redox chemistry of several trace elements in suboxic environments. This paper reports on the use of x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopy to study the reduction of uranium(VI) by GR.

Materials and Methods

Suspensions containing 2 g of $GR_{SO_4^{2-}}$ in 45 ml of water were spiked with 200 µmol U(VI) (as uranyl acetate), yielding a molar U/Fe ratio of 0.01. After 48 h, the suspensions were centrifuged. The pellets were resuspended in distilled deionized water and centrifuged again. The GR was washed twice more in this manner. After the final washing, the GR pastes were mounted in holes machined in Plexiglas sample holders. All XAFS measurements were made at the MRCAT sector 10-ID[1] beamline at the Advanced Photon Source.

Data for XANES and EXAFS spectra were collected at the U L_{III} edge. The incident x-ray intensity was measured with an ion chamber filled with N_2 gas, while the x-ray fluorescence intensity was measured with a Lytle detector in the Stern-Heald configuration[2] filled with free-flowing Ar at atmospheric pressure. Linearity tests[3] indicated less than 0.35% 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. To reduce radiation-induced chemical effects, energy scans were collected at six different locations, with two to five one-minute measurements made at each location. No time-dependent change in the XANES data was observed for any of the samples. The codes contained in the UWXAFS package[4] were used to analyze the XAFS data. Standard procedures were used to align the data and subtract the background. The XANES data were aligned by simultaneously monitoring the absorption edge of a Y foil in transmission mode.[5]

Results and Discussion

The XANES spectra of UO_3, UO_2, and U in a GR suspension (Fig. 1) clearly show that U(VI) is reduced to U(IV) by GR. A qualitative comparison of the EXAFS spectra of UO_2 and U in the GR suspension indicates an average local chemical environment about U in the GR similar to that of U in UO_2 (Fig. 2). However, the decrease in Fourier transform amplitude of the GR sample relative to the UO_2 standard indicates a decrease in the average number of atoms surrounding the U and/or an increase in the disorder of the average local environment of U in the GR sample. This qualitative observation is consistent with the presence of multiple U environments, which can be explained by (1) U sorption to the iron oxide surface followed by the formation of a UO_2 precipitate/coating on the iron oxide surface, or (2) the formation of UO_2 nanoparticles.

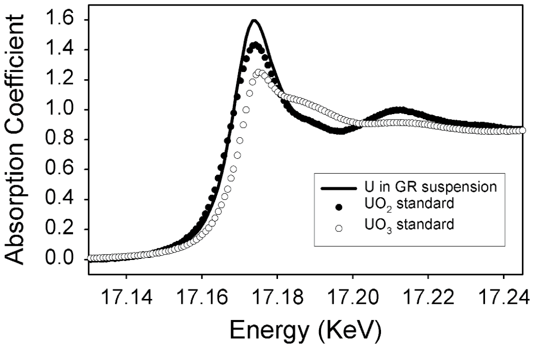

FIG. 1. Comparison of step-height normalized U L_{III}-XANES spectra for UO_3, UO_2, and U in a green rust suspension.

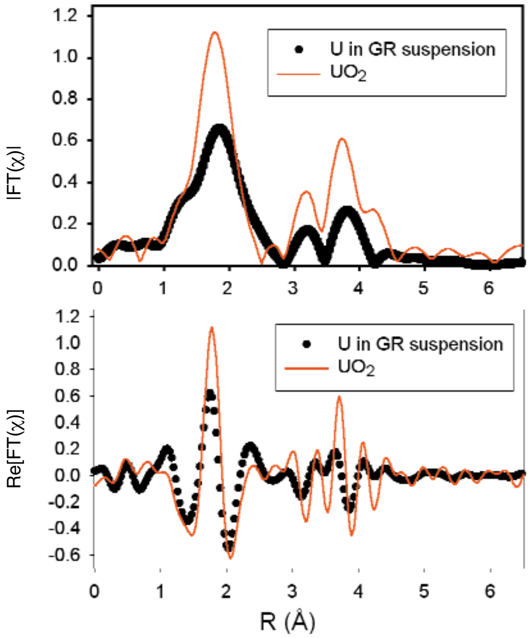

FIG. 2. The magnitude $|FT(\chi)|$ and real part $Re[FT(\chi)]$ of the Fourier transform of $\chi(k)*k$ data for U in a green rust suspension and in UO_2.

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