

# Reduction of Uranium(VI) to Uranium(IV) by Biogenic Mixed Fe(II)/Fe(III) Hydroxide (Green Rust)

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## Introduction

Dissimilatory iron-reducing bacteria (DIRB) are a diverse group of microorganisms that couple the oxidation of organic compounds or hydrogen to Fe<sup>III</sup> reduction. The reduction of Fe<sup>III</sup> by DIRB typically results in the formation of a suite of Fe<sup>II</sup> species, including soluble Fe<sup>II</sup> complexes; Fe<sup>II</sup> surface complexes with organic and inorganic solid phases; and a host of Fe<sup>II</sup>-bearing minerals including magnetite, siderite, vivianite, ferruginous smectite, and green rust. Green rusts, mixed ferrous/ferric hydroxide minerals found in many suboxic environments, are believed to play a central role in the biogeochemistry of Fe. Recent research has shown that green rusts are capable of reducing a number of organic and inorganic contaminants, suggesting that green rusts may be highly reactive reductants in suboxic environments. We previously reported the reduction of U<sup>VI</sup> to U<sup>IV</sup> by synthetic green rust, resulting in the formation of nanoparticulate UO<sub>2</sub> [1].

The recent identification of green rusts as products of the reduction of Fe<sup>III</sup> oxyhydroxides by DIRB, coupled with the ability of synthetic green rust to reduce U<sup>VI</sup> species to insoluble UO<sub>2</sub>, suggests that biogenic green rusts may play an important role in the speciation (and thus mobility) of U in Fe<sup>III</sup>-reducing environments. This paper reports on the use of XANES to study the reduction of U<sup>VI</sup> by biogenic green rust.

## Methods and Materials

A sample of biogenic green rust, prepared by the reduction of ferrihydrite by *Shewanella. putrefaciens* strain CN32 as described by Fredrickson et al. [2], was generously provided by Jim Fredrickson of Pacific Northwest National Laboratory. A suspension of biogenic green rust (0.5 g of lyophilized biogenic green rust in 25 mL of 18 Mohm-cm water), prepared in a 50-mL conical polypropylene centrifuge tube with a screw cap, was spiked with 5 mL of 10 mM U<sup>VI</sup> (as uranyl acetate). The resulting suspension had an initial U<sup>VI</sup> concentration of 1.7 mM and an initial pH of 7.3. Experimental setup and sample handling were conducted in an anoxic atmosphere (4-6% H<sub>2</sub> in N<sub>2</sub>). After 48 h, the pH of the suspension was measured, the suspension was centrifuged, and the supernatant was saved for U analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The solids were resuspended in deoxygenated, 18 Mohm-cm water and centrifuged again; the solids were washed two more times in this manner. After the final washing, subsamples of the hydrated solids (hereafter designated as U-bioGR) were mounted in holes machined in Plexiglas sample holders, sealed with Kapton film, and maintained in an anoxic atmosphere until they were analyzed by XAFS.

Fluorescence XAFS measurements at the U L<sub>3</sub> absorption edge (17166 eV) were performed at the MRCAT beamline 10-ID [3]. The incident and transmitted x-ray ion chambers were both filled with N<sub>2</sub>, and the fluorescent x-ray intensity was monitored with a 13-element solid-state detector (Canberra with

X1A electronics). The incident x-ray beam profile was 0.7 mm square.

Several precautions were taken in collecting XANES data. First, to ensure accurate response of the detectors, linearity tests as first described by Kemner et al. [4] were performed on the biogenic green rust samples. The results of these tests indicated less than 0.1% nonlinearity for a 50% decrease in incident X-ray intensity. Second, energy scans were collected at three different locations on the sample to reduce radiation exposure. The sample was exposed for approximately 1 min for each of the scans at each location. Measuring two spectra at each location enabled determination of radiation-induced chemical effects at the 1-min time scale. No time-dependent change in the data was observed for any of the samples. Finally, the energy position of the absorption edge of the XANES data is directly related to the valence state of the U. Careful monitoring of the monochromator energy is paramount for making these comparisons. We used the transmission XAFS signal of a U<sup>VI</sup> standard, as described by Cross and Frenkel [5], as a reference for accurately aligning the edge energy positions of U<sup>IV</sup> (UO<sub>2</sub>) and U<sup>VI</sup> (UO<sub>2</sub>HPO<sub>4</sub>) powder standards, along with the U-bioGR data.

## Results and Discussion

Uranium was readily removed from solution in the presence of biogenic green rust. Within 48 h, solution-phase U concentrations decreased from 1.7 mM to 0.9 μM, as determined by ICP-OES. The final pH of the suspension was 7.2. A comparison of the U-XANES spectra of the U<sup>IV</sup> and U<sup>VI</sup> standards and U-bioGR (Fig. 1) clearly shows that the U<sup>VI</sup> added to the biogenic green rust suspension is partially reduced to U<sup>IV</sup>.

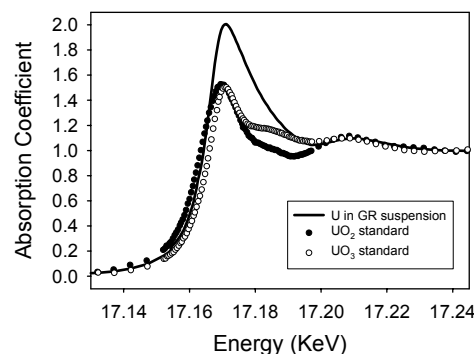


Fig. 1. Comparison of step-height-normalized U L<sub>3</sub>-XANES spectra for UO<sub>3</sub>, UO<sub>2</sub>, and U in a green rust suspension.

The edge positions for the U<sup>IV</sup> and U<sup>VI</sup> standards differed by approximately 2.9 eV, as determined by the energy value at half the step height of the normalized data (Fig. 1). The difference between these two edge energy values (2.9 eV) is significant, as

the step accuracy of the monochromator at 17 keV is  $\pm 0.13$  eV. A generous estimation of the uncertainty in the U valence state determination is  $\pm 10$  %. The U-bioGR data have an energy value at half the step height that is approximately midway between the value for the  $U^{IV}$  and  $U^{VI}$  standards, corresponding to 52% reduction of the initial  $U^{VI}$  added to the green rust suspension. The incomplete reduction of  $U^{VI}$  can be attributed to the excess of  $U^{VI}$  added to this system relative to the mass of biogenic green rust; complete reduction to  $U^{IV}$  can be anticipated with lower  $U^{VI}$  loadings. based on a report format of two columns, each 3.25 in. wide.

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