

## Reoxidation of biologically reduced uranium with Fe(III)-(hydr)oxides under sulfate-reducing conditions

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In batch experiments, using *Desulfovibrio desulfuricans* G20, the effects of hematite, goethite, and ferrihydrite on the microbial reduction of U(VI) were evaluated under lactate-limited sulfate-reducing conditions. With lactate present, G20 reduced U(VI) in both 1, 4-piperazinediethane sulfonate and bicarbonate buffer. Once lactate was depleted, however, microbially reduced U served as an electron donor to reduce Fe(III) present in Fe(III)-(hydr)oxides. With the same initial amount of Fe(III) (10 mmol/L) for each Fe(III)-(hydr)oxide, reoxidation of U(IV) was greater with hematite than with goethite or ferrihydrite. As the initial mass loading of hematite increased from 0 – 20 mmol Fe(III)/L, the rate and extent of U(IV) reoxidation increased. Subsequent addition of hematite (15 mmol Fe(III)/L) to stationary phase cultures containing microbially reduced U(IV) also resulted in rapid reoxidation to U(VI). Analysis by U L<sub>3</sub>-edge XANES spectroscopy of microbially reduced U particles yielded spectra similar to that of natural uraninite. Observations by HR-TEM, SAED, and EDS analysis confirmed that precipitated U associated with cells was uraninite with particle diameters of 3–5 nm. Using the same techniques, iron sulfide precipitates were found to have a variable Fe and S stoichiometry. The *d*-spacings of randomly selected Fe-rich precipitates were most closely related to greigite. The results have strong implications for field application of *in situ* biological reduction of U(VI). Implications are that with biological immobilization of U, care should be taken to maintain the organic substrate in excess throughout the system, such that the aquifer is electron-acceptor limited, rather than electron-donor limited, at least until available Fe(III) is depleted from the system. Failing to maintain sufficient substrate concentrations until available Fe(III) is reduced could lead to unfavorable consequences for the long-term stability of immobilized uranium.

## Reduction of uranyl by trace to minor structural Fe(II) in phyllosilicates

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Bacterially mediated and abiotic heterogeneous reduction of uranyl is of great interest due to the threat posed by uranium in the environment and the strong influence that oxidation state has on uranium solubility. Ilton et al. (2004) showed that ferrous micas can reduce sorbed U<sup>6+</sup> to U<sup>4+</sup>. However, the evidence for reduction was restricted to Fe(II) rich specimens. In this work, we reacted single-crystal Fe(II) poor micas for 1 to 3 days with solutions containing 0.1 mM U<sup>6+</sup> at pH 4-4.5, either under N<sub>2</sub> or air. Two samples were used that had particularly low Fe: a muscovite and phlogopite with about 0.3 and <0.04 atomic percent Fe(II), respectively. The diffusion front into the interlayer region was mapped with X-ray absorption spectroscopy at 2 micron lateral resolution and the redox state of U was characterized at selected intervals from the crystal edge with XANES.

Sorption fronts traveled about 50-200 microns into the interlayer region, with U concentrations peaking at about 10<sup>-3</sup> to 10<sup>-4</sup> atomic percent. Under anoxic conditions, strong reduction of U was recorded for both the muscovite and phlogopite samples, with little change in either concentration or redox state after 1 day of reaction. Under aerated conditions, U was also reduced in the interlayer region, but to a lesser degree. In contrast to anoxic conditions, sorbed U decreased from 1 to 3 days, although the redox state of U did not change appreciably.

We suggest that U reduction was noticeable because concentrations of structural Fe(II), although low, were higher than concentrations of sorbed U<sup>6+</sup>. Sorption of U<sup>6+</sup> was limited by the strong affinity of K for the interlayer region and by batch reactor conditions. Reduction of U<sup>6+</sup> under aerated conditions implies that the interlayer region provided some shielding against reoxidation. Eventually, oxidation dominates, converting reduced U back to U<sup>6+</sup>. Preferential desorption of U<sup>6+</sup>, perhaps due to resorption of K, might explain the conservation of U valence state in the interlayer as sorbed U decreased.

### References

Ilton E.S., Haiduc A., Moses C.O., Heald S.M., Elbert D.C. and Veblen D.R., (2004) *Geochim. et Cosmochim. Acta* **68**, 2417-2435.