SLAC-SFA: Speciation of Uranium in Biologically Reduced Sediments during Iron and Sulfate Reduction in the Old Rifle Aquifer

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The speciation and dynamics of uranium(IV) in naturally and artificially bioreduced sediments, as well as its local nanometer to millimeter scale physical and chemical environment, controls its stability, susceptibility to oxidation, and subsequent transport behavior in aquifers. Uraninite is widely believed to be the most stable and therefore desirable form of uranium in bioreduced sediments. However, non-polymerized forms of U(IV), generally referred to as monomeric U(IV), also have been observed in laboratory axenic culture, column, and microcosm studies. Similar types of studies generally have not been performed in reduced aquifers but are required to develop a better understanding of U(IV) reaction products produced in these complex subsurface systems. For those studies where U(IV) products were observed in sediment systems, it has not been certain if U(VI) reduction was accomplished by organisms (*i.e.*, direct enzymatic reduction) or via reaction with inorganic reductants such as magnetite or FeS. Knowledge of mechanisms, species, chemical/physical environment, stability, and dynamics, is required to construct biogeochemical models that can predict uranium behavior under varying aquifer conditions.

We have studied the speciation of U, Fe, and S following electron donor amendment to aquifers at the Rifle IFRC. This technique uses *in-situ* columns to obtain direct access to sediment U(IV) species, aquifer microbial populations, reaction rates, groundwater compositions, temperature, and pH, among other natural controls. A major advantage of the Old Rifle site for this study is the ability to temporally distinguish between iron- and sulfate-reducing conditions and therefore to study U(IV) transformation products across these regimes. We have studied U(IV) bioreduction over periods of 4 to 55 days and subsequent aging in the aquifer up to 1 year. Whole sediments were examined using x-ray and electron microscopy, x-ray absorption spectroscopy, and chemical extractions in order to determine the speciation and spatial distributions of U, Fe, and S. Under sulfate-reducing conditions, U(IV) was found to be associated with Fe- and S-rich coatings on the grain scale, but to be coordinated to oxygen atoms. The dominant mineral in the coatings was mackinawite with some FeS_2 also present. At the scale of and within individual coatings (tens of µm down to hundreds of nm), U and Fe concentrations were not correlated, and EXAFS spectra were consistent with U(IV) bound to biomass, suggesting a primarily biological U(VI) reduction pathway. The presence of sulfide minerals intimately associated with U(IV) implies substantially retarded reoxidation. Under Fe reducing conditions, U(IV) again appeared to be bound to biomass, although grain coatings were not observed. Uraninite was present as a minority species during and after bioreduction, but in some cases became enriched in relative concentrations during subsequent aging in the aquifer. This work establishes the importance of both monomeric U(IV) complexes and uraninite as bioreduction products in the Old Rifle aquifer and provides conceptual models of U(VI) bioreduction and U(IV) fate in complex subsurface systems.