Understanding Uranium Transformations in Reduced Sediments: an Integrated Bottom-Up and Top-Down X-ray Spectroscopy Approach

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Uranium dynamics in reducing environments are intimately tied to the biogeochemical cycling of the major elements, particularly the redox cycling of C, Fe, and S. The resulting multitude of coupled biotic-abiotic reactions occur in the presence of biological surfaces, minerals, and dissolved ligands, potentially resulting in a distribution of reduced U^{IV} species. However, due to lack of sufficient understanding of U^{IV} speciation, current transport models use only amorphous uraninite($U^{IV}O_2$) as a reference U^{IV} phase. Our group and others have recently demonstrated the formation of reduced non-uraninite species (i.e., U^{IV} atoms complexed to surfaces or coordinated by ligands) both in laboratory systems and in sediments (e.g., Boyanov et al. GCA 2007; Kelly et al. ES&T 2008; Fletcher et al. ES&T 2010; Boyanov et al. ES&T 2011). The importance of these findings is that non-uraninite U^{IV} species have uncharacterized thermodynamic and kinetic properties that may be significantly different from those of uraninite, resulting in inaccurate descriptions of U transport and subsurface redox dynamics. One of the goals of the Argonne Subsurface Science Focus Area project is to identify the factors and mechanisms that lead to distinct U transformations under reducing conditions, to characterize the structure of reduced U phases and their stability to remobilization, and to use this knowledge to understand the redox transformations of U, Fe, C, and S observed in soils and in sediments from contaminanted field sites.

As part of the "bottom-up" component of these efforts we investigated the reduction of U^{VI} by several gram-positive and gram-negative bacteria (*Shewanella*, *Anaeromyxobacter*, *Desulfitobacterium* spp.) and by several Fe^{II}-containing phases (stoichiometric and partially oxidized magnetite, vivianite, Fe^{II} sorbed to carboxyl functionalized microbeads). Experiments were performed under defined conditions in laboratory batch reactors, and U speciation in the solid phase was determined using synchrotron x-ray absorption spectroscopy (XANES and EXAFS). Results suggest that small amounts of phosphate in the solution phase (as low as P:U = 1:1) inhibit uraninite formation regardless of the method used to reduce U^{VI}. In the absence of phosphate, we observed significant variability in the U^{IV} species formed by the different reductants. *Shewanella* and *Anaeromyxobacter* produced nanoparticulate uraninite, as expected, whereas U^{VI} incubation with five strains of *Desulfitobacterium* spp. and with AH_2DS resulted in a carbonate-complexed, non-uraninite U^{IV} species. Factors such as the chemical conditions at the location of electron transfer can be offered to explain this variability; conversely, the formation of distinct U^{IV} products during U^{VI} reduction may be used to infer the location and mechanisms of electron transfer. In a separate set of abiotic experiments we found that inner-sphere coordination between two or more Fe^{II} atoms significantly enhanced U^{VI}-Fe^{II} reactivity, suggesting that Fe^{II} incorporated in solid phases will be, in general, highly reactive. However, the reactivity of magnetite towards U^{VI} reduction depended on the magnetite's Fe^{II} content in a step-wise fashion, and vivianite (ferrous phosphate) did not reduce U^{VI} over extended periods. Observed U^{IV} products resulting from reduction by Fe^{II} ranged from nanoparticulate uraninite to complexed non-uraninite U^{IV} species, presumably sorbed to surfaces.

The results from the well-defined laboratory systems above are used to understand the speciation of U^{IV} observed in natural sediments. Using XANES and EXAFS spectroscopy at the U L_{III} edge we examined the speciation of U in unmodified sediments from the Oak Ridge IFRC. In one set of experiments, contaminated sediments extracted from surge wells were incubated for 4 years in diffusion-limited columns with or without an initial ammendment of ethanol. Intensive geochemical monitoring revealed the gradual establishment of sulfate- and iron-reducing conditions over a period of 2 years. U speciation was determined *in situ* with EXAFS and shown to evolve from oxidized U^{VI} to reduced U^{IV} as the reducing conditions propagated through the sediment phase. U^{IV} was present as non-uraninite species in all cases. Similar non-uraninite U^{IV} speciation was observed in unmodified sediments extracted from the injection wells of the field-scale biostimulation experiment in Area 2 using emulsified vegetable oil (EVO) as the electron donor. In a separate set of experiments, U^{VI} was reacted with a naturally reduced soil from Hedrick, Iowa. EXAFS analysis revealed that reduced U^{IV} was present as a non-uraninite U^{IV} species (Latta et al., Appl. Geochem. 2012). All of the results above indicate that non-uraninite U^{IV} species are ubiquitous and persistent in natural and biostimulated sediments, suggesting the need for further studies to understand their structure, stability, and the factors controlling their formation.