ABSTRACT TITLE: Update on the factors controlling U(IV) speciation during (bio)reduction of aqueous and solid-phase U(VI): effects of phosphate and Ti(IV)

ABSTRACT: Uranium is a radionuclide contaminant of significant concern at DOE nuclear material production facilities such as Oak Ridge, TN, Rifle, CO, and Hanford, WA. Reductive remediation approaches, whereby soluble U(VI) is reduced to U(IV), have been studied extensively because of their potential to decrease U concentrations below the drinking water standard (<30 µg/L) through the precipitation of uraninite (UO₂). However, experiments at the Rifle, CO, site show that reduced U(IV) is not present as uraninite in the solid phase (Bargar et al., PNAS 2013, p.4506), and the analysis of reduced sediments from the Oak Ridge field site during the 2009 Emulsified Vegetable Oil (EVO) biostimulation campaign shows that U(VI) is reduced to a non-uraninite U(IV) form (Boyanov et al., in prep.). Despite these observations, the factors controlling the molecular speciation of U(IV) following U(VI) reduction and the stability of non-uraninite U(IV) remain poorly understood. Improved knowledge is essential for advancement of the current predictive models and in the design of nuclear fuel repositories.

As part of understanding uranium transformations and speciation in field-site sediments, we are continuing to study the biological and abiotic reduction of U(VI) in laboratory systems of increasing complexity. Here we show that Ti(IV) impurities inhibit uraninite formation during the abiotic reduction of aqueous U(VI) by magnetite and by other FeII-containing phases. Ti(IV) is commonly incorporated in natural magnetite and is also found in the magnetic sediment fraction at the Hanford nuclear site. Titanium-doped magnetite of varying Ti content (Fe₃₋ₓTixO₄, 0<x<0.5) was reacted with aqueous U(VI). Analysis of the solids by U LIII edge XANES and EXAFS spectroscopy indicates that Ti incorporation in magnetite does not affect its ability to reduce U(VI) to U(IV). Reactions with Ti-doped magnetite resulted in a non-uraninite U(IV) phase, whereas reactions with pure magnetite resulted in nanoparticulate uraninite. Analysis of the EXAFS data indicates that the non-uraninite U(IV) is stabilized abiotically by the formation of a previously unobserved corner-sharing complex between Ti and U(IV), with a U(IV)-Ti distance of 3.43 Å.

We are also continuing to study the biomolecular mechanisms of U(VI) reduction by metal-reducing bacteria. Here we show that Shewanella, Anaeromyxobacter, and Geobacter spp. are able to slowly reduce U(VI) added in the form of hydrogen uranyl phosphate solids (HUP). Comparisons between bioreduction experiments that either favored or inhibited HUP dissolution suggest that these bacteria reduce predominantly the dissolved U(VI) fraction, despite their known capabilities to inject electrons into solid-phase Fe(III) oxidants. Analysis of the reduced U(IV) species in the solid-phase indicate the formation of a non-uraninite, edge-sharing U(IV)-phosphate complex, with a U(IV)-P distance of 3.40 Å. A similar form of U(IV) was observed in U(VI) reduction by the field-site isolate Anaeromyxobacter strain FRC-R5.

The stabilization of diverse non-uraninite U(IV) species by trace phosphate or Ti(IV) suggests that the U(IV) geochemistry relevant to subsurface systems may be more complex than just the formation of the least soluble form of U(IV), uraninite. Further studies are needed to elucidate the formation/stability of U(IV) species and to obtain the necessary information for their incorporation in computational field-scale models.