Subsurface Conditions Controlling Uranium Incorporation in Iron Oxides: A Redox Stable Sink

University-led Research

M. Massey, M. Jones, G.E. Brown, Jr., and S. Fendorf (PI)—*Stanford University*; J. Lezama, and J. Bargar—*SSRL*; P. Nico—*LBNL* ; Ravi Kukkadapu—*PNNL*

Although large quantities of uranium can be potentially immobilized through microbially mediated U(VI) reduction, the potential for re-oxidative mobilization causes long-term stabilization to be technically challenging. Within natural environments, however, uranium often correlates with iron rather than existing as a discrete uranium oxide phase; uranium incorporation into iron oxides is a mechanism that can explain the co-occurrence of these two elements and may represent a natural attenuation pathway for uranium. Further, incorporated U(VI/V) within Fe (hydr)oxides appears stable with respect to oxidative dissolution, representing a potential means for long-term sequestration of uranium in the subsurface. Within this project we are examining the molecular mechanisms by which uranium is retrained by iron oxides, conditions optimal for retention, and the long-term stability of sequestered uranium.

Uranium incorporation into an iron (hydr)oxide lattice is dependent on Fe(II) propagated transformation of ferrihydrite. However, Fe(II) can also induce reduction of U(VI) to U(VI), with subsequent precipitation of UO_2, and thus represents a competing retention process for uranium. Deciphering (bio)geochemical factors influencing the predominance of each pathway is therefore critical to determine uranium fate within the subsurface. To elucidate the factors controlling uranium retention, we first conducted batch incubations where ferrihydrite slurries (100 mL of ~180 mg L^{-1}) were reacted with U(VI) and Fe(II) under varying water compositions (varying U(VI), Fe(II), and Ca concentrations, with total carbonate at 3.8 mM and pH buffered at 7.0). Using high-resolution synchrotron X-ray powder diffraction and extended X-ray absorption fine structure (EXAFS) spectroscopy, we identified the reaction products and thus the retention pathway. Incorporation of U into goethite is the dominant sequestration pathway at < 10 μM aqueous U concentration, with lesser amounts of UO_2 and U(VI) adsorption contributing to uranium retention. Similarly, low Fe(II) concentrations (<0.3 mM) promote incorporation over reductive precipitation of UO_2. Importantly, conditions conducive to the formation of uranyl-calcium-carbonato complexes were critical for incorporation, retarding reduction of U(IV). However, at high Fe(II) concentrations (3 mM), reduction was the dominant sequestration pathway independent of uranyl speciation or concentration. We further investigated the impact of mineralogical impurities common to the subsurface and found that although Al can inhibit ferrihydrite transformation, U(VI/V) incorporation occurred even at Al contents as high as 20% in Al-ferrihydrite. The combination of Ca-UO_2-CO_3 aqueous complexes and structural Al in ferrihydrite, however, resulted in limited incorporation or reduction. Our results demonstrate that U incorporation can be a major U sequestration pathway across a variety of aqueous phase and mineralogical conditions. However, multiple retention processes of uranium will occur in the subsurface and it is critical to appreciate the dominant pathway when considering the long-term fate of this hazardous element.