ABSTRACT: Stimulation of microbial uranium reduction in the subsurface can lead to substantial quantities of this toxic element being immobilized, but 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 uranium 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 and conditions optimal for its retention.

In order to examine the mechanism of uranium incorporation within iron oxides, and conditions conducive to its incorporation, we conducted a series of batch experiments coupled with spectroscopic and microscopic analysis of the reaction products. Through our experiments, we determine: (i) the oxidation state of incorporated U, (ii) the effects of calcium and carbonate (influencing U aqueous speciation) concentration, (iii) the pathway-dependence on Fe(II) and U(VI) concentrations, and, (iv) the competitiveness of U incorporation versus U reductive precipitation (to UO₂). A series of batch reactions with ferrihydrite were conducted at pH ~7, [U(VI)] from 1 to 170 μM, [Fe(II)] from 0 to 3 mM, [Ca] at 0 or 4 mM. Uranium valence state was measured using x-ray photoelectron spectroscopy, and U sequestration mechanisms were identified and quantified using extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray powder diffraction, and transmission electron microscopy (TEM). Depending on the reaction conditions, 12 to 80% of total U was incorporated into goethite. Uranium incorporation was a particularly dominant retention pathway at U concentrations ≤50 μM independent of U(VI) speciation, accounting for 70-80% of total U. With increasing U(VI) and Fe(II) concentrations, U(VI) reduction to UO₂ became more prevalent, but U incorporation remained an operative retention pathway. However, at high Fe(II) concentrations (3 mM), reduction to U(IV) and precipitation of UO₂ dominated. 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-UO₂-CO₃ 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 retention pathway across a variety of aqueous phase and mineralogical conditions. Ultimately, it is critical to recognize that multiple retention processes of uranium will occur in the subsurface, which must be considered in the long-term fate of this hazardous element.