

*Subsurface Conditions Controlling Uranium Incorporation in Iron Oxides:
A Redox Stable Sink
(Proposal Number DE-SC0006772)*

Final Report

Principal Investigator: Scott Fendorf (Stanford University)

Co-principal Investigators: Peter S. Nico (Lawrence Berkeley National Laboratory), and Gordon E. Brown, Jr. (Stanford University)

No-Cost Collaborators: John Bargar (Stanford Synchrotron Radiation Lightsource), and Eugene Ilton and Ravi Kukkadapu (Pacific Northwest National Laboratory)

RESEARCH MOTIVATION AND OBJECTIVES

Toxic metals and radionuclides throughout the U.S. Department of Energy Complex pose a serious threat to ecosystems and to human health. Disposal of toxic metals and radioactive wastes generated at DOE facilities has historically involved shallow land burial *via* pits, trenches, and cribs. Since much of this waste was not encapsulated or surrounded by physical or chemical barriers, unimpeded migration of contaminants into the surrounding soils and groundwaters has occurred. The magnitude of this problem is massive, with many of the larger DOE sites had a complex history of waste disposal practices. Of particular concern is the redox-sensitive radionuclide uranium, which is classified as a priority pollutant in soils and groundwaters at most DOE sites owing to its large inventory, its health risks, and its mobility with respect to primary waste sources.

The **goal** of this research was to contribute to the long-term mission of the Subsurface Biogeochemistry Program by determining reactions of uranium with iron (hydr)oxides that lead to long-term stabilization of this pervasive contaminant. We proposed (and have accomplished) developing a detailed mechanistic and predictive understanding of the processes by which soluble, oxidized uranium (U(VI/V)) becomes sequestered in iron (hydr)oxides. The outcome of our work aids in decision making for long-term management of uranium in the subsurface of contaminated DOE sites, such as those found at the Oak Ridge Y-12 complex, the Hanford 300 area, and the Old Rifle UMTRA site. By exploring U incorporation into Fe (hydr)oxides under fluctuating redox conditions, the proposed work fills an important knowledge gap between efforts that have explored the adsorption/desorption behavior of U(VI) complexes under oxidizing conditions and those that have characterized the biotic and abiotic reductive precipitation of U(IV) under reducing conditions. The distinction is significant since large areas of U-contaminated DOE sites are neither strictly anaerobic nor fully aerobic, and U incorporation/association in/with Fe (hydr)oxides may be a mechanism governing long-term

stabilization. While the potential for U sequestration within Fe (hydr)oxides is great, it had received little attention as a process for mitigating U migration. Our research supplement previous OBER-supported efforts by providing an improved fundamental and predictive understanding of the formation and long-term stability of mixed phase U-Fe minerals that are resistant to reoxidation; the latter being a common problem for simple anaerobic reductive conditions.

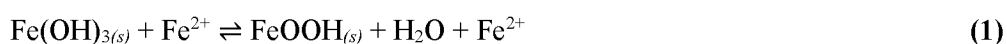
The research **objectives** of this project were thus to (1) identify the (bio)geochemical conditions, including those of the solid-phase, promoting uranium incorporation in Fe (hydr)oxides, (2) determine the magnitude of uranium incorporation under a variety of relevant subsurface conditions in order to quantify the importance of this pathway when in competition with reduction or adsorption; (3) identify the mechanism(s) of U(VI/V) incorporation in Fe (hydr)oxides; and (4) determine the stability of these phases under different biogeochemical (inclusive of redox) conditions.

To accomplish these objectives, we conducted detailed laboratory studies involving hydrostatic and flow-through column experiments in which iron (hydr)oxides of varying composition were formed or transformed under oxidative or reductive conditions, and we examined both abiotic and biotic driven processes. Furthermore, used both synthetic and naturally occurring iron phases (the latter from the Rifle, CO site). Using a range of geochemical conditions that simulate groundwater and the various iron solids, we determined the importance of aqueous and solid phase chemistry on U fate. Using a host of spectroscopic, x-ray scattering, and microscopic analyses coupled with the macroscopic experimental observations (laboratory and field), we unraveled the mechanisms of U incorporation in Fe (hydr)oxides, the controlling (bio)geochemical conditions, and the resistance of the reaction products to oxidative (or reductive) dissolution. Our research findings herein thus provide critical details concerning uranium sequestration pathways relevant to DOE sites.

RESEARCH FINDINGS

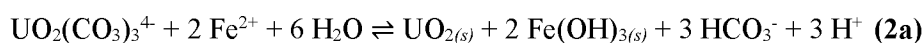
There are three primary (broadly grouped) retention processes that limit the migration of uranium: adsorption on solid surfaces, reduction of U(VI) to U(IV) and subsequent precipitation of uraninite, and uranium incorporation within iron (hydr)oxide solids. The reactions governing U fate are (all reactants/products are aqueous species unless otherwise specified):

- *Ferrihydrite transformation to goethite:*

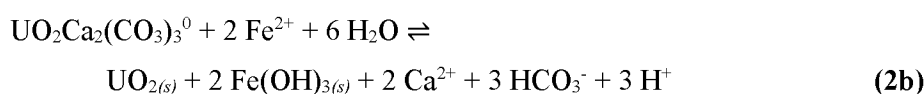


- *U(VI) reduction to UO₂:*

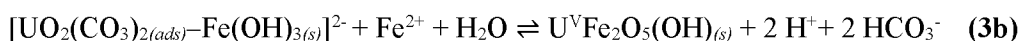
For the uranyl-carbonato aqueous species,



For the uranyl-calcium-carbonato species,

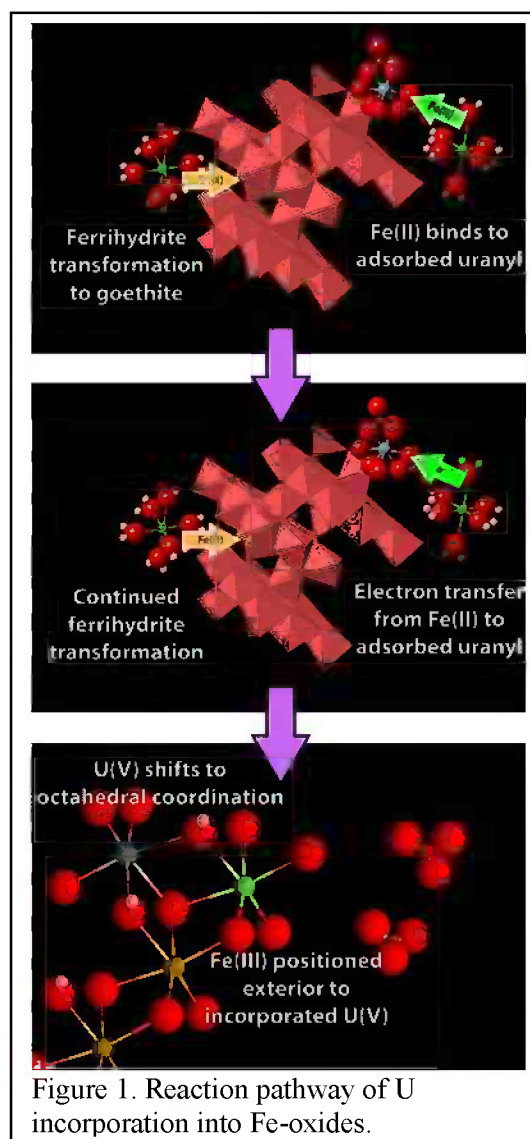


- *U(V) incorporation, considering uranyl and uranyl-carbonato adsorption complexes:*



Uranium incorporation into goethite is likely initiated with an adsorbed uranyl species reacting with Fe(II), as indicated in reaction 3 above and detailed in Figure 1. The rate of U adsorption is presumed to be rapid in comparison to reduction and incorporation, with nearly complete adsorption occurring in minutes, and equilibrium reached in hours (Giammar and Hering, 2001). The aqueous chemical factors that affect the kinetics of, and subsequent competition between, reaction pathways include: (1) Fe(II) concentration; (2) U concentration; (3) pH; and (4) Ca concentration (in the presence of carbonate). The first three factors, Fe(II) and U concentrations, and pH, exert strong controls due to their effects on iron oxide transformation and the thermodynamic favorability of U reduction. The most important parameter in determining iron oxide products and U fate is Fe(II) concentration, due to its central role in the three competing reactions of ferrihydrite transformation, U(VI) reduction, and U(V) incorporation. Calcium modifies these overall pathways due to its effects on uranyl aqueous speciation, with higher U concentrations favoring reduction and the presence of Ca retarding reduction.

Ferrihydrite transformation is affected by pH and Fe(II) concentration, with higher pH or Fe(II) favoring magnetite and lower pH or Fe(II) favoring goethite (Hansel et al., 2005). The pH of the system, as well as Fe(II) concentrations, can also affect iron oxide transformation kinetics. For example, Yang et al. (2010) found that Fe(II)-induced transformation of 6-line ferrihydrite to goethite and/or magnetite occurred at pH 6.8 on a timescale of days to several weeks. Boland et al. (2011) observed that 2-line ferrihydrite transformed to goethite within 4 days at pH 6.5 in the presence of 1 mM Fe(II). Hansel et al. (2005) observed the transformation of 2-line ferrihydrite ~70% goethite and ~30% ferrihydrite within 12 h at pH 7.2 upon reaction with 2 mM FeSO₄, but with 0.2 mM FeSO₄, the



transformation to a mixture of goethite and lepidocrocite took ~40 h. Ferrihydrite transformation products and reaction kinetics are the result of an intimate interplay between Fe(II) concentrations and pH. In our system, a slight difference in initial pH led to strikingly different ferrihydrite transformation products in otherwise similar systems with 300 μM Fe(II) and 100+ μM U (Massey et al., 2014a). The inhibition of goethite formation at higher pH is consistent with previous studies (Hansel et al., 2005). The slight pH increase also produced strikingly different results with respect to U incorporation, since the decrease in goethite formation corresponded with a decrease in U incorporation (Massey et al., 2014a).

In addition to ferrihydrite transformation kinetics, U redox reaction kinetics also play a key role in the evolution of the system. The abiotic reduction of U(VI) to UO_2 may occur more rapidly than iron oxide transformation. Liger et al. (1999) observed the reduction of 0.5 μM U by 160 μM Fe(II) in the presence of a hematite suspension in less than 30 h. Du et al. (2011) found that 0.21 mM U(VI) was completely reduced by 1 mM Fe(II) at pH ~8.9 in ~20 minutes, and that a pH ~6.2 substantially slowed but did not completely inhibit U reduction. We observed that faster UO_2 precipitation relative to goethite formation led to substantially more UO_2 in the 1 mM Fe(II) system versus a comparable system at a slightly lower initial pH with 300 μM Fe(II) (Massey et al., 2014a). The interplay between variations in reaction conditions and vastly differing reaction kinetics and products illustrates the complexity of the U/ferrihydrite/Fe(II) system.

We observe that for U concentrations ranging from 1 to 10 μM , U incorporation into goethite is the dominant retention pathway, ranging from 64 to 89% depending on the reaction conditions. Under conditions leading to Fe(II) production, therefore, U incorporation into goethite is likely an important and overlooked retention pathway at U concentrations < 10 μM (in cases where Fe(II) concentrations are on the order of hundreds of μM). Given the substantial impact of carbonate and calcium on U biogeochemistry, and the ubiquity of both ions in the environment, the present findings substantiate the competitiveness of the U incorporation process in low-U systems containing carbonate and Ca.

We conclude that uranium incorporation into goethite is a dominant U retention pathway in low-U systems, and is also a competitive U retention pathway across the wide-range of aqueous reaction conditions explored in this study. Incorporated U is a substantial component of the total U budget in all systems studied. The relative contributions of the UO_2 pathway, however, increased with increasing initial aqueous U concentration, until consumption of Fe(II) limited further U reduction to U(IV). Generally, when Fe(II) concentration was not limiting, higher U concentrations accelerated U(VI) reduction to U(IV), resulting in subsequent precipitation of UO_2 becoming an increasingly prominent retention pathway. Even with initial concentrations of Fe(II) as high as 3 mM, however, U incorporation into goethite remained a contributing retention pathway.

Effect of uranyl aqueous speciation and retention processes

While the presence of calcium decreased U retention (Figures 1 and 9) and the amount of U incorporated into iron oxide, EXAFS analysis demonstrated that U incorporation remained an operative retention process (Figures 5 and 10). Boland et al. (2011) achieved similar EXAFS results in systems absent of carbonate, suggesting that U incorporation into ferrihydrite during Fe(II)-induced transformation does not require a particular U aqueous species. In the present study, U incorporation occurred, and was an important sequestration process, regardless of the dominant uranyl aqueous species. Incorporation occurred even though uranyl-carbonato and uranyl-calcium-carbonato complexes decreased the extent of U adsorption (Waite et al., 1994; Stewart et al., 2010). The fraction of adsorbed uranyl, even when decreased by the uranyl-calcium-carbonato complexes, appears to provide ample precursor concentration for U incorporation.

Despite the relative lack of impact of calcium on the U incorporation process, as shown by the EXAFS LCF analysis (Figures 5 and 10), the presence of uranyl-calcium-carbonato ternary complexes can substantially impact the fate of uranium by altering the mass balance (Figures 1 and 9) and exerting a secondary influence on solid phase products. Uranyl-calcium-carbonato ternary complexation decreases the rate and extent of U(VI) reduction to U(IV) compared to Ca-free systems (Brooks et al., 2003; Hua et al., 2006; Neiss et al., 2007), and thus increased the proportion of incorporated U relative to UO_2 (at $[\text{Fe(II)}]_{\text{initial}} \geq 1 \text{ mM}$). Consequently, when Fe(II) is not limiting, proportionally more incorporated U occurs under conditions conducive to the formation of uranyl-calcium-carbonato ternary complexes (Figure 10). At lower Fe(II) concentrations, $[\text{Fe(II)}]_{\text{initial}} = 0.3 \text{ mM}$, the presence of uranyl-calcium-carbonato ternary complexes decrease both the rates of U incorporation and U reduction to U(IV), and increase the relative rate of ferrihydrite transformation to goethite. This leads to proportionally more UO_2 on the solid, since U incorporation tapers off as more goethite is formed (Figure 5). Computations by Wander et al. (2006) suggested that reduction of uranyl-carbonato complexes occurs after Fe(II) binding to the triscarbonato complex; uranyl-calcium-carbonato ternary complexation likely slows the rate of U reduction by aqueous Fe(II) by partially blocking the binding site of Fe(II) on the uranyl ternary complex and subsequent electron transfer. A decrease in the rate of U reduction due to U ternary complexes would explain the observed differences between U reduction and U incorporation in the presence of Ca.

Uranium valence state and incorporated uranium in Fe oxides

We used X-ray absorption spectroscopy to examine the oxidation state and coordination environment of U within the solids. Unfortunately, XAS is insufficient for distinguishing between pentavalent and hexavalent oxidation states, as the U L_3 -edge x-ray absorption edge cannot be sufficiently resolved to distinguish between U(V) and U(VI). Further, post-edge features are chiefly due to uranate coordination geometry rather than U valence state, and distinguishing between U(VI) and U(V) depends on qualitative comparison of these features or *a priori* structural models (e.g., Soldatov et al., 2007). X-ray photoelectron spectroscopy, by

contrast, can distinguish directly and quantitatively between U valence states using the relative energies of the U4f primary and satellite peaks (Ilton and Bagus, 2011).

X-ray photoelectron spectroscopic analysis of 10 μM U and 100 μM U goethite samples in the present study indicated that the dominant oxidation state is U(V). There is good agreement between EXAFS-derived and XPS-derived estimates of U(VI) and U(V), with the caveat that the surface-sensitivity of the XPS technique may underestimate U(V) if it is incorporated in the goethite structure. Furthermore, trends in the data with increasing initial aqueous U concentration, such as an increase in surface-associated UO_2 particles (i.e., U(IV) in the XPS measurements), are consistent with the conclusion that U(IV) and U(VI) are predominantly surface-associated, while U(V) is incorporated in the goethite structure itself. We conclude that incorporated U is U(V) based on XAS and XPS data.

Therefore, since incorporated U is in the pentavalent state, electron transfer must occur from Fe(II) to U(VI), resulting in a U(V) state that is preserved within the structure of the goethite. The reduction of U to U(V) underscores the importance of redox cycling in ambient-temperature U incorporation into goethite. Indeed, without reduction of U to U(V), the transformation from uranyl coordination geometry to uranate coordination geometry may not be possible at ambient temperature on this timescale.

Detection of surface-bound U(IV) in the 10 μM U samples suggests that some U in the system may exist as surface-adsorbed, poorly-crystalline or monomeric U(IV). The XPS-determined U(IV) parallels the EXAFS- and TEM-detectable UO_2 with increasing aqueous U concentration. Consequently, under reducing conditions, pentavalent uranium tends to be stabilized within the structures of both hematite and goethite, while U(VI) and U(IV) species may be found associated with the iron oxide surface.

Mechanism of pentavalent uranium incorporation in Fe oxides

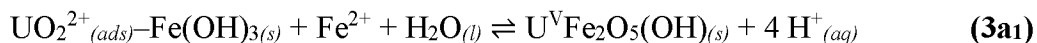
Uranium incorporates into goethite during the Fe(II)-induced transformation of ferrihydrite under a wide variety of solution conditions. Uranium addition after ferrihydrite transformation yielded only 18% incorporated U, likely from ferrihydrite formed after reduction of the added U(VI); this indicates the necessity of a ferrihydrite precursor for U incorporation. We observe that co-precipitation of U and Fe during ferrihydrite synthesis by hydrolysis does not yield incorporated U. Rather, U is co-precipitated as distinct uranyl hydroxide phases or as an adsorbed phase. Adsorption of U onto ferrihydrite also does not produce incorporated U in the absence of an Fe(II)- or heat-induced transformation (at least on the timescale of the present study)—although some adsorbed U can be “strongly retained/sorbed” and resistant to chemical extraction. Taken together, this evidence suggests that a redox-induced transformation of U(VI) to U(V) is necessary to induce U incorporation into goethite at ambient temperature on timescales of hours to days.

The mechanism of U incorporation into goethite occurs in four steps: (1) adsorption of the uranyl cation on the ferrihydrite surface; (2) binding and electron transfer from Fe(II) to the

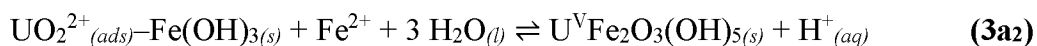
adsorbed uranyl cation, producing U(V) (Figure 1); (3) a shift in U(V) to octahedral coordination; and, (4) continued growth of goethite around the U(V). In the first step, uranyl adsorption occurs as a mononuclear, bidentate inner-sphere surface complex at pH 7. In the presence of carbonate, the uranyl cation may act as a bridge between the mineral surface and the carbonate ion at circumneutral pH (Bargar et al., 1999). In either case, the mononuclear, bidentate inner-sphere uranyl surface complex is the likely precursor of incorporated U, and is the common link between the carbonate-free, carbonate, and calcium-carbonate systems. In the second step, Fe(II) complexes with the adsorbed uranyl complex, leading to electron transfer and creation of U(V) and Fe(III) (Figure 1). It is also possible, but seems less likely to us, that Fe(II) sorbed on ferrihydrite induces electron transfer through the solid (via electron hopping) and ultimately electron donation to adsorbed U(VI). In either case, U(VI) is reduced by Fe(II) to U(V) on the ferrihydrite surface. The formation of a U(V) species appears to provide a pathway to overcome a major limitation of uranyl incorporation—a mismatch in coordination of U with that of the cation sites in the goethite (or other iron oxide) lattice. The strong trans-dioxo bonds to axial oxygen atoms within the hexavalent uranyl cation would otherwise inhibit U incorporation within the iron oxide. The axial oxygen atoms reside at a distance of ~1.8 Å in uranyl, while measurements of incorporated U indicate a bond distance of 2.10-2.18 Å. We therefore propose that electron transfer from Fe(II) induces a relaxation of the trans-dioxo bonds and an extension of the bond length between the U atom and axial O atoms from 1.80 Å to 2.10-2.18 Å (Massey et al., 2014a). The electron transfer also triggers a coordination change from two axial and 5-6 equatorial O in adsorbed uranyl to octahedral coordination in the incorporated U(V)—the third step in the U incorporation mechanism (Figure 1).

The fourth and final step in the incorporation mechanism is the formation of an Fe(III), produced by the electron transfer, that is positioned toward the exterior of the mineral relative to the newly-incorporated U(V) (Figure 1), enabling continued crystal growth of the goethite lattice (Figure 15). On the basis of our experimentally-determined U-O and U-Fe distances and coordination numbers in comparison with the modeling predictions, de-protonation of hydroxyls is the most likely charge-balancing mechanism given substitution of U for Fe(III). Further, the calculated U(V)-O distances are a better match to the EXAFS data than the calculated U(VI)-O distances.

A representative chemical reaction for Fe(II)-induced U incorporation into goethite during ferrihydrite reductive transformation is given by Equation 3a:



Equation 3a₁ shows charge balance achieved by de-protonation only. The reaction with a Fe(III) vacancy and protonation of a hydroxyl is shown by Equation 3a₂:



As discussed above, our measurements of U oxidation state and U coordination geometry suggest that Equation 3a₁ is the likely interpretation of the U(V) incorporation mechanism (Figure 1).

Impacts of Aluminum Incorporation

Uranium retention processes (adsorption, precipitation, incorporation into host minerals) control its dissolved concentrations and impact its mobility in the environment. Ferrihydrite, a ubiquitous iron hydroxide in soils and sediments, can both adsorb uranium and, upon Fe(II)-induced transformation to goethite, incorporate it within the crystal lattice. However, ferrihydrite seldom exists as a pure phase within soils or sediments, and structural impurities such as Al alter its reactivity. The presence of Al in ferrihydrite, for example, decreases the rate of transformation to goethite, and thus may impact the retention (pathway or extent) of elements such as U. We investigated the extent and pathways of U(VI) retention on Al-ferrihydrite during Fe(II)-induced transformation. Ferrihydrite containing 0%, 1%, 5%, 10%, and 20% Al was reacted with 10 μM U and 300 μM Fe(II) in the presence of 0 mM and 4 mM Ca^{2+} and 3.8 mM carbonate at pH 7.0. Solid reaction products were characterized using U L_{3} -edge EXAFS spectroscopy to differentiate between U adsorbed or incorporated into the goethite lattice. Uranium incorporation into Al-ferrihydrite declined from $\sim 70\%$ of solid-phase U at 0% and 1% Al to $\sim 30\%$ of solid phase U at 20% Al content (Massey et al., 2014b). The decrease in U incorporation with increasing Al concentration was due to two main factors: 1) decreased transformation of ferrihydrite to goethite; and, 2) shrinking of the goethite lattice with increasing Al, making the lattice less compatible with large U atoms. Uranium incorporation can occur even with an Al-substituted ferrihydrite precursor, in the presence and absence of Ca^{2+} , suggesting that the process of U incorporation into Al-goethite may be a long-term sink of U in subsurface environments where Al-substituted iron oxides are common, albeit at lower levels within increasing Al content. Our results support the overriding impact of uranyl speciation on the reaction pathway of U retention, and indicate that natural ferrihydrites retain their capacity to incorporate uranium (Stewart et al., 2015).

Uranium Incorporation within Silicates

Finally, we examined uranium incorporation into opaline silicates, both through experimentation and analysis of natural materials. Uranium retention mechanisms in these silicates have implications for mineral formation conditions, as well as U retention and release characteristics in the environment. In particular, competition between U host phases such as silicates or iron oxides impacts U retention in the resulting solid material. In order to elucidate U retention mechanisms in opals and amorphous silicates, natural opals were compared with synthetic U-bearing silicate precipitates. The synthetic precipitates (with and without ferrihydrite inclusions) were synthesized from solutions of 37 μM uranyl acetate and 20 mM sodium metasilicate, buffered at pH ~ 5.6 and incubated for 28 days at 25°C; ferrihydrite slurry was used to form solids with ferrihydrite inclusions. Solids were analyzed with U L_{3} -edge extended x-ray

absorption fine structure (EXAFS) spectroscopy and a suite of other solid phase analysis techniques such as powder x-ray diffraction (XRD) and secondary ion mass spectrometry. In the U-bearing amorphous silicate precipitate, U was coordinated by 6 oxygen atoms, including 2 from silicate in a monodentate coordination geometry (second-neighbor Si at $\sim 3.8\text{-}3.9$ Å) and a small amount of silicate in a bidentate coordination geometry (second-neighbor Si at $\sim 3.10\text{-}3.15$ Å); the U EXAFS spectrum resembled the U EXAFS spectrum of a natural opal-CT sample (Massey et al., 2014c). Uranium was adsorbed to iron in the iron-bearing synthetic solid, and the adsorption complex also contained silicate in both monodentate and bidentate coordination geometries. Further, the U EXAFS spectrum matched very closely with that of a natural iron- and U-bearing opal from Virgin Valley, Nevada, United States. Therefore, U can partition onto iron inclusions in geochemical environments rich in silicate, with subsequent inclusion of the U-iron phase into opaline silica. Additionally, U-bearing silicate solids can be synthesized in weeks to months that have molecular-level U coordination environments similar to natural opals that retain U for millions of years—an important finding for remediation of uranium containing sites.

Conclusions

Our research demonstrates that redox transformations are capable of achieving U incorporation into goethite at ambient temperatures, and that this transformation occurs within days at U and Fe(II) concentrations that are common in subsurface geochemical environments with natural ferrihydrites—inclusive of those with natural impurities.

In the presence of ferrihydrite, with $[\text{U}_{\text{initial}}]$ in the range of 1-170 μM , and $[\text{Fe(II)}_{\text{initial}}]$ of 300 μM , U(V) incorporation was a dominant U retention pathway at pH 7.0. Redox processes including Fe(II)-induced transformation of ferrihydrite to goethite and electron transfer from Fe(II) to U(VI) are crucial to the U incorporation process. Increasing Fe(II) or U concentration, or initial pH, made U(VI) reduction to U(IV) a more competitive sequestration pathway in this system, presumably by increasing the relative rate of U reduction. Uranium concentrations commonly found in contaminated subsurface environments are often on the order of 1-10 μM , and groundwater Fe(II) concentrations can reach exceed 1 mM in reduced zones of the subsurface. The redox-driven U(V) incorporation mechanism may help to explain U retention in some geologic materials, improving our understanding of U-based geochronology and the redox status of ancient geochemical environments. Additionally, U(VI) may be incorporated within silicate minerals through encapsulation of U-bearing iron oxides, leading to a redox stable solid. Our research detailing previously unrecognized mechanism of U incorporation within sediment minerals may even lead to new approaches for *in situ* contamination remediation techniques, and will help refine models of U fate and transport in reduced subsurface zones.

Literature Cited

- Bargar J., Reitmeyer R. and Davis J. (1999) Spectroscopic Confirmation of Uranium(VI)-Carbonato Adsorption Complexes on Hematite. *Environ Sci Technol* 33, 2481–2484
- Boland D. D., Collins R. N., Payne T. E. and Waite T. D. (2011) Effect of Amorphous Fe(III) Oxide Transformation on the Fe(II)-Mediated Reduction of U(VI). *Environ Sci Technol* 45, 1327–1333
- Du X., Boonchayaanant B., Wu W.-M., Fendorf S., Bargar J. and Criddle C. S. (2011) Reduction of Uranium(VI) by Soluble Iron(II) Conforms with Thermodynamic Predictions. *Environ Sci Technol*, 45, 4718–4725
- Giammar D. and Hering J. (2001) Time Scales for Sorption-Desorption and Surface Precipitation of Uranyl on Goethite. *Environ Sci Technol* 35, 3332–3337.
- Hansel C. M., Benner S. G. and Fendorf S. (2005) Competing Fe(II)-Induced Mineralization Pathways of Ferrihydrite. *Environ Sci Technol* 39, 7147–7153.
- Ilton E. S. and Bagus P. S. (2011) XPS determination of uranium oxidation states. *Surf. Interface Anal.* 43, 1549–1560.
- Liger E., Charlet L. and Van Cappellen P. (1999) Surface catalysis of uranium(VI) reduction by iron(II). *Geochimica et Cosmochimica Acta* 63, 2939–2955
- Massey, M. M., J. Lezama Pacheco, J. Nelson, S. Fendorf, and K. Maher. (2014a) Uranium incorporation into amorphous silica. *Environ. Sci. Technol.* 48: 8636–8644.
- Massey, M. M., J. Lezama Pacheco, and S. Fendorf. (2014b) Uranium incorporation into aluminum-substituted ferrihydrite during iron(II)-induced transformation. *Environmental Science: Processes & Impacts.* 16: 2137-2134.
- Massey, M. S. J. S. Lezama-Pacheco, M. E. Jones, E. S. Ilton, J. Cerrato, J. R. Bargar, and S. Fendorf. (2014c) Competing retention pathways of uranium upon reaction with Fe(II). *Geochim. Cosmochim. Acta* 142: 166-185.
- Soldatov A. V., Lamoen D., Konstantinović M. J., Van den Berghe S., Scheinost A. C. and Verwerft M. (2007) Local structure and oxidation state of uranium in some ternary oxides: X-ray absorption analysis. *Journal of Solid State Chemistry* 180, 54–61.
- Stewart, B.D., A. C. Cismasu, K. H. Williams, B. M. Peyton, and P. S. Nico. (2015) Reactivity of uranium and ferrous iron with natural iron oxyhydroxides. *Environ. Sci. Technol.* 49: 10357-10365.
- Yang L., Steefel C. I., Marcus M. A. and Bargar J. R. (2010) Kinetics of Fe(II)-Catalyzed Transformation of 6-line Ferrihydrite under Anaerobic Flow Conditions. *Environ Sci Technol* 44, 5469–5475.

PRODUCTS RESULTING FROM THIS RESEARCH PROJECT

Publications (peer-reviewed)

Massey, M. M., J. Lezama Pacheco, J. Nelson, S. Fendorf, and K. Maher. 2014. Uranium incorporation into amorphous silica. *Environ. Sci. Technol.* 48: 8636–8644. DOI /10.1021/es501064m

Massey, M. M., J. Lezama Pacheco, and S. Fendorf. 2014. Uranium incorporation into aluminum-substituted ferrihydrite during iron(II)-induced transformation. *Environmental Science: Processes & Impacts.* 16: 2137-2134. DOI: 10.1039/C4EM00148F

Massey, M. S. J. S. Lezama-Pacheco, M. E. Jones, E. S. Ilton, J. Cerrato, J. R. Bargar, and S. Fendorf. 2014. Competing retention pathways of uranium upon reaction with Fe(II). *Geochim. Cosmochim. Acta* 142: 166-185. DOI:10.1016/j.gca.2014.07.016

Stewart, B.D., A. C. Cismasu, K. H. Williams, B. M. Peyton, and P. S. Nico. 2015. Reactivity of uranium and ferrous iron with natural iron oxyhydroxides. *Environ. Sci. Technol.* 49: 10357-10365. DOI: 10.1021/acs.est.5b02645

Dissertations

Mike Massey, Ph.D. in Earth System Science, Stanford University. Dissertation title: *Long-term stable sinks of uranium in soils and sediments.* 2013.

Presentations

1. Lezama-Pacheco, J. S., J.R. Bargar, J.E. Stubbs, R. Bernier-Latmani, E. Suvorova, K.H. Williams, J.A. Davis, P.M. Fox, D.E. Giammar, J.M. Cerrato, and P.E. Long. “Spectroscopic insights on U(VI) species in biologically reduced sediments at the Old Rifle aquifer”. Presented at the 2011 GSA Annual Meeting, Session on 88. Symposium on Uranium in Groundwater: Biogeochemical Controls on Mobility and Persistence, Minneapolis, MN, Oct. 10, 2011 [Invited]
2. Massey, M.S., J.S. Lezama-Pacheco, M.E. Jones, J.R. Bargar, and S. Fendorf. “Iron(II)-induced competitive uranium retention pathways” Presented at the SSRL/LCLS 2012 User’s Meeting and Workshops, Menlo Park, California, October 3-6, 2012 [Poster]
3. Massey, M.S., J.S. Lezama-Pacheco, K.H. Williams, J.R. Bargar, and S. Fendorf, “Uranium Sequestration Pathways within a Diffusion-Limited Groundwater Transport Model System” Presented at the SSRL/LCLS 2011 User’s Meeting and Workshops, Menlo Park, California, October 22-26, 2011 [Poster]
4. Massey, M.S., J.S. Lezama-Pacheco, P.S. Nico, J.R. Bargar, and S. Fendorf, “Structural Incorporation of Uranium into Iron Oxides: A Competitive Secondary Sequestration Pathway Mediated by Fe(II)”. Presented at the American Geophysical Union, Fall Meeting 2011, symposium H24A, San Francisco, December 5-9, 2012 [Oral]
5. Lezama-Pacheco, J.S., M.S. Massey, J.R. Bargar, S.E. Fendorf, and F.M. Michel, “Structural

- Incorporation of Uranium During the Fe(II)-Induced Transformation of Ferrihydrite”. Presented at the 2011 Goldschmidt Geochemistry Conference, Symposium on Understanding the Fate and Transformations of Metal and Radionuclide Contaminants in Unsaturated and Saturated Subsurface Environments, Prague, Czech Republic, Aug. 14-19, 2011. [Oral]
6. Lezama-Pacheco, J.S., M.S. Massey, J.R. Bargar, S.E. Fendorf, and F.M. Michel, “Structural Mechanisms of Uranium Incorporation in Iron Oxides”. Presented at the 241st ACS National Meeting, Symposium on Geochemical Implications in Toxic Trace Metal Remobilization from Sediments to the Surrounding Aqueous Environment, Anaheim, CA, Mar. 30, 2011. [Oral]
 7. Massey, M.S., J.S. Lezama-Pacheco, P.S. Nico, J.R. Bargar, and S. Fendorf, “Uranium Reduction and Structural Incorporation into Iron Oxides: Competing Sequestration Pathways Under Reducing Conditions”. Presented at the SSRL/LCLS 2010 User’s Meeting and Workshops, Menlo Park, California, October 17-21, 2010 [Poster]
 8. Massey, M.S., J.S. Lezama-Pacheco, P.S. Nico, J.R. Bargar, and S. Fendorf, “Uranium Reduction and Structural Incorporation into Iron Oxides: Competing Sequestration Pathways Under Reducing Conditions”. Presented at the ASA, CSA, and SSSA 2010 International Annual Meeting, Long Beach, California, October 31-November 4, 2010 [Poster]
 9. Fendorf, S. 2012. The impact of on mineral surfaces on metal-contaminant redox cycles. Geochemical Society’s Goldschmidt Conference. Montreal, Canada. **[Invited]**
 10. Fendorf, S. 2012. The Dynamic Nature of Iron Oxides on Modes of Ion Retention. Geochemical Society’s Goldschmidt Conference. Montreal, Canada. **[Invited]**
 11. Fendorf, S. 2013. Deciphering Molecular-Scale Processes to Describe Field-Scale Phenomena in Carbon and Metal Cycling. 2013 TES/SBR Investigators Meeting, Potomac, MD **[Invited]**
 12. Fendorf, S. 2013. Global Water Contamination. Stanford's Woods Institute for the Environment Annual Meeting. Aptos, CA. **[Invited]**
 13. Fendorf, S. 2014. Threats to Groundwater Quality Imposed by Contaminants of Natural Origin. Willie Woltz Seminar, North Carolina State University, Raleigh, NC. **[Invited]**
 14. Fendorf, S., M. Keiluweit, M. Kleber, P.S. Nico. 2014. Complexity in Soil Biogeochemical Processes Arising from Aggregate-Scale Heterogeneity. Complex Soil Systems Conference, Berkeley, CA. **[Invited]**