# SLAC SFA Project Overview: Biogeochemical processes governing the speciation, dynamics, and stability of uranium in reduced aquifers

J.R. Bargar (SLAC National Accelerator Laboratory); R. Bernier-Latmani (Ecole Polytechnique Federale de Lausanne); G.E. Brown, Jr. (Stanford University), S.E. Fendorf (Stanford University), and D.E. Giammar (Washington University, St. Louis).

The molecular- and nano-scale biogeochemistry of uranium has a profound impact on its fate and transport in complex subsurface systems. While a large body of work has focused on U(VI) behavior in sediments, relatively little is known about the pathways of transformation to U(IV) under reducing conditions *in aquifers*, the identities of the obtained species, their stability, and their dynamics in groundwater. Natural reducing conditions are common at uranium-contaminated aquifers under DOE-EM and DOE-LM management across the Western U.S. Uranium sediment concentrations are significantly elevated in these zones, and uranium solute exchange between these zones and surrounding aquifers is suspected to contribute to the persistence of these large and intractable uranium plumes. The chemical and physical forms of organic carbon, S, and Fe, as well as diffusive solute dynamics, are posited to control U(IV) speciation and release rates from naturally reduced zones (NRZs). U(IV) is also fundamentally important to the performance of redox-based in-situ aquifer remediation techniques such as stimulated bioremediation.

The SLAC SFA program is using a suite of innovative laboratory and field-based approaches to develop a fundamental understanding of U(IV) speciation in reduced sediments at molecular and nanometer scales, its impact on uranium dynamics in aquifers, and its relationship to biogeochemical C, S, and Fe cycling. In the past year, we have focused on the following research questions: (1) What is the occurrence, nature, and stability of U(IV) species in time and space in naturally and artificially reduced *aquifers*?; (2) What geochemical and microbiological factors control the production of biomass-bound noncrystalline forms of U(IV)?; (3) What is the stability of different forms of U(IV) under aquifer conditions? And, (4) What controls the structure and reactivity of poorly crystalline iron oxides, and how do they impact uranium attenuation?

Work in the past year has shown that both uraninite and biomass-bound U(IV) are important in field-reduced sediments. In-aquifer experiments show the latter to be the least stable form under aquifer conditions. Laboratory-based work has shown that both phosphate and calcium solute concentrations help to govern the production of noncrystalline U(IV), and that solutes such as Ca retard uraninite oxidative dissolution. Going forward, we will examine the impact of organic carbon, S and Fe mineralogy, and sediment heterogeneity on the formation of NRZs and naturally reduced U(IV), the chemical and physical form of the obtained U(IV), its distribution over nano- to millimeter scales, and its stability under seasonally variable aquifer conditions. Research performed by the SLAC SFA is providing new concepts for uranium dynamics in aquifers and quantitative parameters that provide the basis for improved biogeochemical models.