

## SLAC SFA: Molecular pathways of U(VI) reduction in organic-rich sediments

**Program Affiliation:** Subsurface Biogeochemical Research

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The fate of redox-active radionuclides such as uranium, and biogeochemical critical elements (including C, N, S, and Fe), are profoundly affected by microbial processes in organic-rich sediments within floodplain aquifers. Accordingly, we are examining the processes that produce natural reduced zones (NRZs), which are usually manifested as thin, discontinuous tabular bodies. In particular, we are focusing on (i) syntrophic communities linking organic carbon degradation to metal reduction and (ii) the impacts of ligands that bind U(VI) and alter the reduction mechanism and U(IV) products within diffusive controls zones. This effort is also helping to elucidate the speciation of organic-associated U(IV) in uranium-contaminated floodplains.

The dominant source of reducing equivalents used in microbial respiration arises from particulate organic carbon (POC) inputs. Under the anaerobic conditions present in NRZs, a consortium of organisms is required to degrade POC, with hydrolytic enzymes providing soluble polymers that are decomposed by fermenters into products that fuel respiring organisms. We are examining the syntrophic relation in organic matter degradation linked to uranium (and iron) reduction using both natural consortia and isolates of the fermenter *Clostridium acidisoli* and the metal reducing bacterium *Geobacter metallireducens*. Utilizing advanced microspectroscopic methods coupled with microbial imaging (primarily fluorescence in situ hybridization), reaction products and the spatial organization of the consortia are being resolved within the complex subsurface matrices. For natural consortia, over a 9-week incubation, addition of POC as ground root tissue results in complete reduction of U(VI). Uranium(IV) resulting from microbially-mediated reduction are a combination of (primarily) complexed U(IV), with smaller amounts of uraninite (UO<sub>2</sub>). Uraninite formation is controlled by incubation time and initial U(VI) concentration, with longer incubation times and higher U(VI) concentrations favoring uraninite.

To establish the influence of U(VI) speciation, and U(IV) products, on the redox fate of uranium, we are using adsorptive stripping voltammetry (AdSV). By determining AdSV reduction potentials for compounds having known stability constants, values for unknown U(VI)-ligand complexes can be determined within simulated and natural subsurface systems. A range of U(VI) inorganic and organic ligands are being tested as well as natural organic matter plant extracts from the Upper Colorado River Basin. The combined assessment of U-ligand complexes and the syntrophic relation of microbial communities linking organic carbon degradation to metal reduction within complex physical environments of the subsurface will provide much needed information on the fundamental mechanisms controlling uranium, as well as carbon and nitrogen, fate in the subsurface.