

## **SLAC SFA: Biogeochemistry of U(IV) and carbon in organic-rich sediments in the upper Colorado River Basin**

**Program Affiliation:** Subsurface Biogeochemical Research

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Fine-grained, organic-rich sediments are common in the uranium-contaminated floodplain at the Rifle, Colorado DOE research site. Many of these sediment zones are reduced and exhibit U(IV) concentrations up to 100-fold higher than uranium in surrounding sediments, along with abundant iron sulfides and other redox-active metals. Exposure of naturally reduced zones (NRZs) to oxidizing conditions has the potential to re-release stored U(IV), which has prompted us to better understand their physical and biogeochemical characteristics. NRZs are believed to be general features of floodplains, leading to the hypothesis that they are regionally important in contaminated alluvial aquifers within the upper Colorado River Basin (CRB). The SLAC SFA is studying: (i) U(IV) biogeochemistry in contaminated upper CRB floodplains and (ii) the reactivity and composition of organic carbon (OC) within NRZs. By collecting and integrating information at the regional scale, we are improving our understanding of the reactivity of NRZs and their potential to impact uranium mobility and biogeochemical critical element (BCE, including C, N, S, and Fe) cycling.

In the past year, we have investigated NRZs at Grand Junction, Gunnison, Naturita, and Rifle, CO; Riverton, WY; and Shiprock, NM. As part of this effort, we performed induced polarization (IP) geophysical measurements to delineate subsurface regions enriched in (semi)conductive mineral phases, such as metal sulfides, often present within NRZs. IP data collected across the Rifle floodplain were used to define drilling locations where NRZs subsequently were recovered. IP surveys conducted at the Shiprock and Gunnison sites have identified potential subsurface distributions of NRZs, which will be sampled in spring and fall 2015.

New sediment cores from the Grand Junction, Naturita, Rifle, and Riverton sites show that NRZs are indeed present at these locations. Both U and sulfide were found to be concentrated in NRZs, supporting our initial hypothesis. C K-edge X-ray absorption spectroscopy (XAS) shows that bulk organic carbon (OC) in NRZs exhibits the same functional group types and relative abundances as the OC in surrounding organic-poor sediments, possibly indicating that OC in both locations has the same source. XAS and Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) are being used to discern differences in OC speciation in NRZs and neighboring organic-poor sediments through examination of the following fractions: water extractable C, particulate C, micro-aggregate associated C (metal-complexing, freshly precipitated mineral fraction), and mineral-associated C. Overall these results are helping to shape new models for biogeochemical cycling of uranium and BCEs in organic-rich aquifer sediments.