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ABSTRACT TITLE: SLAC SFA: Biogeochemical controls over C, S, Fe, and U redox cycling in NOM-rich naturally reduced aquifer sediments

ABSTRACT: Work by the DOE-BER Rifle IFRC has identified zones of organic-rich reduced sediments at the Old Rifle, CO uranium ore processing site. These naturally reduced zones (NRZs) contain more than 100-fold higher U than ambient sediments and are suspected to play significant roles in maintaining the persistent uranium groundwater plume at this site. The similarity of Old Rifle to other uranium-contaminated alluvial aquifers, coupled with observations of naturally reduced uranium at other sites, suggests that NRZs may be regionally important to uranium plume persistence in the Colorado River Basin. The presence of natural organic matter (NOM) and low sediment permeability were concluded to be of central importance to the development of NRZs and their acquisition of uranium. These deeply buried NOM-rich zones also provide information on carbon cycling and sequestration processes associated with export of litter-derived organic carbon to the subsurface.

The SLAC SFA program is performing work to elucidate the biogeochemical processes governing the formation, reactivity, and oxidation of the biogeochemically active elements C, S, and Fe within NRZs. Process-based mechanistic models will be developed to understand the fate of uranium and carbon within NRZs. Key questions that we seek to investigate are: what is the spatial extent of the NRZs in the aquifer? How does the speciation of C, S, Fe, and U vary spatially within the NRZs? How do C, S, and Fe within NRZs undergo transform upon oxygenation during annual and long-term de-saturation, and how do these transformations impact U oxidation? What is the role of NOM as a complexing and reducing agent for U(VI)? We are presently characterizing NRZ sediments from the Old Rifle site and conducting a series of diffusion-limited NOM-amended experiments to simulate the formation of NRZs. We have observed a spatial distribution of uranium retention processes across redox gradients created by simulated NRZs, with U(VI) adsorption transpiring in the external regions, progressing through U(V) incorporation into goethite, and developing uraninite within the interiors of the NRZs. Further, we note that Fe(II) concentrations have the primary role in dictating the specific retention process of uranium within these systems. Subsequent to our investigation of NRZ formation within simulated environments, we will explore their oxidation. We are using a combination of approaches to characterize the distribution and speciation of C, S, Fe, and U in these materials and experiments, including x-ray absorption spectroscopy, micron-scale x-ray microprobe elemental and mineral-specific imaging, and scanning transmission x-ray microscopy (STXM) and nano-SIMS. This work will provide molecular-scale insights into the redox cycling of C, S, and Fe, and their implications for uranium behavior. Ultimately, this work will inform accurate descriptions of subsurface carbon, trace nutrient, and contaminant behavior in earth systems models.