Uranium Biogeochemistry in Organic-Rich Sediments: Laboratory Analog Studies

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Zones of organic-rich reduced sediments at the Old Rifle, CO uranium ore processing site have been identified. These naturally reduced zones (NRZs) contain more than 100-fold higher U than ambient sediments and are perceived dominant contributors to uranium persistence in groundwater. Further, NRZs are likely 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.

The SLAC SFA program seeks to elucidate the biogeochemical processes governing the formation, accumulation/reduction of uranium, and speciation of the biogeochemically active elements C, S, and Fe within NRZs. We have observed the formation of diffusion-limited reduced zones within artificial NRZ sediments, where the extent of reduction is governed by the NOM concentration and the spatial distribution of reduced zones by the sediment porosity. Further, we note that U(VI) is not strongly associated with particulate organic carbon and does not accumulate in sediments prior to the onset of reducing conditions. Subsequent to the onset of reduced conditions, U(IV) associates with particulate organic carbon, leading to the depletion of aqueous U. Additionally, U is not accumulated preferentially with any particular component of the biomass (inclusive of detrital plant residue). We are now exploring uranium distribution, speciation, and partitioning at varying U:OC ratios.

At low biomass levels, uraninite is a dominant product of U(VI) reduction. In order to assess the stability of authogenic uraninite, we have conducted long-term (21 month) oxidation studies of biogenic uraninite in Rifle wells. Our results indicate that uraninite can persist in suboxic aquifers for long periods of time (decades) in the absence of reducing conditions. Moreover, we show that Ca2+ bonds to uraninite surfaces with extremely high affinity, likely passivating it with respect to oxidation.

We are using a combination of approaches to characterize the distribution and speciation of C, S, Fe, and U in natural and simulated NRZs. In particular, we utilize x-ray absorption spectroscopy, micron-scale x-ray microprobe imaging, and scanning transmission x-ray microscopy (STXM) and nano-SIMS to determine the distribution and products of uranium reduction. 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.