SLAC SFA: Molecular mechanisms controlling oxidative release of uranium from organic-rich sediments: role of nitrification and denitrification

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Elevated U(IV) concentrations exist in fine-grained, organic-rich naturally reduced sediments in contaminated floodplains at ore processing sites across the upper Colorado River Basin. Recent evidence from Rifle, CO suggests that microbial nitrogen cycling is stimulated in organic-rich sediments by seasonal groundwater table fluctuations. Nitrate and nitrite produced by this activity are strong oxidants for U(IV). Consequently, there is concern that biogeochemical nitrogen cycling drives re-release of uranium from naturally reduced sediment zones (NRZs) to groundwater. The SLAC-SFA is investigating this subject using an integrated program of (i) laboratory incubation and column studies of Rifle sediments, (ii) studies of functional gene markers for nitrifying and denitrifying organisms, and (iii) biogeochemical reactive transport modeling.

Rifle NRZs were exposed to nitrate in diffusion-limited reactors. The greatest amount of aqueous U(VI) was released during the first two weeks of the experiment; however, solid-phase associated U(VI) continued to accumulate within 1 cm of the sediment-solution interface until the end of the experiment (70 days). Our work suggests that U(IV) oxidation by nitrate occurs on a time scale relevant to the field (ca. 2 – 3 months), but that release of aqueous U(VI) is diffusion-limited once the U(IV) at the sediment-solution interface is depleted. Experiments underway are investigating whether water-level fluctuations can promote nitrification of ammonium present in the sediments, causing seasonally elevated nitrate concentrations.

We are also investigating the diversity and abundances of nitrifying and denitrifying populations throughout NRZs recovered from Rifle, Grand Junction, and Naturita, CO using functional gene markers for ammonia oxidation (*amoA*) and denitrification (*nirK*, *nirS*). Functional gene abundances are specifically targeted through qPCR, elucidating how relative numbers of nitrifiers and denitrifiers vary with depth and location and relate to uranium release in sediment cores. Sequence data obtained from Rifle indicate that subsurface archaeal *amoA* diversity spans the Group 1.1b *Thaumarchaeota*, and includes soil, freshwater, and estuarine relatives. Populations of *nirK*- and *nirS*-type denitrifiers have also been detected. These results indicate that robust communities of ammonia-oxidizing archaea (AOA) and denitrifiers coexist, both of which can produce nitrite.

We are using biogeochemical reactive transport modeling approaches to quantify the relationships among groundwater table variations and the production of nitrate, nitrite and U(VI) in diffusion-limited reduced zones, and the importance of the spatial distribution of NRZs in determining aquifer-scale U(VI) concentrations. These results will integrate biogeochemical activity and uranium behavior observed in the field and laboratory, and provide critical guidance for future reactive transport experiments.