

SLAC SFA: Molecular controls over uranium mobility in organic-rich sediments

Program Affiliation: Subsurface Biogeochemical Research

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The fate and transport of uranium is largely dictated by oxidation state. Within floodplains, physical heterogeneity produces organic-rich, sulfidic, fine-grained zones within otherwise organic-poor siliciclastic aquifers. Reduction of U(VI) in these naturally reduced zone (NRZ) sediments leads to the accumulation of non-crystalline U(IV), which can subsequently resupply U to contaminated floodplain aquifers. Numerous questions remain unaddressed regarding U reduction under these dilute, organic-rich natural conditions. The relative importance of bacterial versus abiotic reduction is unresolved. So-called “non-crystalline” U(IV) species are poorly characterized, and the mechanistic “switch” leading to crystalline and non-crystalline products is unknown. We examined U(VI) reduction pathways and products in a model system designed to emulate key NRZ conditions (nutrient limitation, natural consortia, organic sorbents, and dilute U(VI)). Uranium(VI) was reduced by dissimilatory microbial communities, whereas reduction of U(VI) by aqueous S(-II) was not appreciable. Uranium(IV) adsorption complexes were the dominant products at U(VI) concentrations $\leq 10 \mu\text{M}$, indicating that U(IV) complexes likely prevail at many contaminated sites that exhibit similar or lower U concentrations. Precipitation of uraninite at higher U(VI) concentrations is consistent with thermodynamics.

We used cyclic voltammetry to examine the effects of pH, and concentrations of uranium, carbonate, and calcium on the redox transitions of the uranyl ion. Redox potentials of U(VI) to U(V), U(V) to U(IV), and U(IV) to U(III) transitions between pH 3-8 were determined. Similar to bacterial and Fe(II) reduction, Ca within the dicalcium complex blocks the electron transfer pathway, illustrating the utility of electrochemistry for resolving redox reaction mechanisms.

Oxidant incursions driven by seasonal water table fluctuations drive uranium transformation and release from NRZs. We posit that nitrate, as well as oxygen, are important oxidants. To test this hypothesis, we examined how diffusion-limited mass exchange between NRZ sediments (Riverton, WY site) and groundwater impacted the magnitude and rate of U(VI) release. We employed diffusion-limited flow reactors under anoxic (control), oxygenated (250 μM O₂) and elevated nitrate (1 mM) conditions. Although DO led to sustained U release from the sediments, nitrate-induced oxidative release was suppressed by sulfate reduction. Sedimentary organic matter in the NRZ sediments supports microbial respiration with SO₄²⁻ at attenuated U(VI) oxidation, although denitrification co-occurred. Our work demonstrates that the magnitude and duration of oxidative U release from NRZ sediments depends on the interplay between terminal electron acceptor (TEA) supply (O₂, NO₃⁻, or SO₄²⁻) and the availability of organic matter for microbial respiration with different TEAs.