Scaling of Molecular Processes to Quantify Biogeochemical Reaction and Transport of Uranium in Subsurface Systems

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The transport of contaminants, nutrients, and dissolved constituents in water links unseen biogeochemical processes in the subsurface with natural and human-impacted surface ecosystems. Accurate prediction of the transformation, transport, and flux of dissolved contaminants such as uranium in the subsurface requires (i) identifying the kinetic or thermodynamic mechanisms that control dissolved concentrations in dynamic systems, and (ii) quantification of competing or coupled processes that may depend on aqueous speciation, solid dissolution and precipitation, surface adsorption, labile organic matter, and/or microbial catalysis. Results from batch and flow-through column experiments in sediment and model-analog systems demonstrate how laboratory investigations employing spectroscopic and genomic tools can be integrated and scaled using reactive transport modeling to quantify biotic and abiotic reaction networks.

In abiotic uranyl systems, batch and flow-through column experiments of Hanford sediment reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations showed that the solubility of uranyl-phosphate phases exerts a strong thermodynamic control over U partitioning into solids. Without phosphate, U speciation was controlled by the pH-dependent rate of silicate weathering and the rate of formation of Si-bearing uranyl solids. In desorption experiments, U release in phosphate-free systems is apparently controlled by the dissolution rates of uranyl oxide hydrate phases (compreignacite, becquerelite and schoepite) and possibly U-neoformed phases. Measurement of dissolution rates of synthetic comprignacite and Na-compreignacite in flow-through columns and spectroscopic characterization of reaction products suggests that the rate-determining step is the desorption of uranyl from within an altered surface layer.

In studies of the anaerobic, oxidative dissolution of biogenically produced U(IV)-oxide, either chemical oxidants (nitrate or nitrite) or enzymatic catalysis by Thiobacillus denitrificans, a chemolithoautotrophic bacterium capable of nitrate-dependent U(IV) oxidation, were compared in column experiments. Uranium release was quantified using reactive transport modeling that included thermodynamic solubility, irreversible overall abiotic and biotic kinetic reactions, and uranyl sorption. Abiotic oxidation of U(IV)-oxide in the presence of nitrate under anaerobic conditions is slow but faster than control experiments of non-oxidative dissolution. Abiotic U(IV)-oxide oxidation by nitrite is significantly faster by about 1-2 orders of magnitude. In the presence of T. dentrificans and dissolved nitrate, higher rates of dissolved U release were observed compared with abiotic controls, suggesting that T. dentrificans catalyzed the oxidative dissolution of U(IV)-oxide in addition to abiotic oxidation pathways. Bacterial catalysis was supported by experiments with a mutant strain of T. dentrificans that was ~50% defective in enzymatic U(IV) oxidation.