Biogeochemical Processes Controlling Microbial Reductive Precipitation of Radionuclides

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This project will identify and quantify coupled biogeochemical reactions that control reductive precipitation of U(VI) and Tc(VII). Both batch and continuous flow experimental methods in combination with aqueous geochemical and spectroscopic analyses are being used. Most equilibrium speciation models predict the dominant U(VI) aqueous species in groundwater will be uranyl-carbonate complexes. A recent description of a calcium-uranyl-carbonate (Ca-U(VI)-CO_3) complex indicates this species may dominate the aqueous speciation of U(VI) in many environments, including FRC and UMTRA sites. Bacterial reduction of U(VI) in bicarbonate-buffered solution in presence and absence of Ca was monitored. XAFS measurements confirmed the presence of a Ca-U(VI)-CO_3 complex in the initial solutions containing Ca. Ca, at concentrations of 0.45–5 mM, caused a significant decrease in rate and extent of bacterial U(VI) reduction. Reduction of U(VI) by facultative (*Shewanella putrefaciens* strain CN32) as well as obligate (*Desulfovibrio desulfuricans*, *Geobacter sulfurreducens*) anaerobes was affected by the presence of Ca. U(VI) reduction ceased when system Eh reached –0.034 ± 0.001 V, based on the $Ca_2UO_2(CO_3)_3 \rightarrow UO_{2,cr}$ couple. Results are consistent with the hypothesis that U is a less effective electron acceptor when present as the $Ca_2UO_2(CO_3)_3$ complex. Microbial $Tc(VII)O_4^-$ reduction under identical conditions was unaffected by the presence of Ca, suggesting inhibition of U reduction was not a result of generalized inhibition of microbial activity. Preliminary investigations probing influence of periplasmic precipitation of UO_2 on viability of *S. putrefaciens* CN32 suggest the viable CN32 population decreases during U reduction by 100- to 1000-fold, as measured by cultivation on TSB+fumarate agar, but that viability appears not to be directly linked to UO_2 precipitation. Higher populations of viable cells were maintained with lactate as an electron donor compared to H_2. U precipitates were observed in association with cell periplasm and outer membrane as reduction proceeded, suggesting it proceeded concurrently on both sites. Manganese (III, IV) oxides are among the most powerful naturally occurring oxidants and may promote oxidative dissolution of uraninite ($UO_{2,cr}$) and TcO_2, even under anaerobic conditions. Thermodynamic calculations predict, and batch laboratory experiments confirm, manganese oxides oxidize UO_2 and TcO_2 under a broad range of solution conditions. Yet the rate this solid–solid redox reaction occurs is poorly known. Initial characterization focused on oxidation of a dissolved organic (oxalate) by Mn oxides. Oxalate oxidation by Nsutite (γ-$Mn^{IV}O_2$), Birnessite (δ-$Mn^{IV}O_2$), Manganite (γ-$Mn^{III}OOH$), and Hausmannite ($Mn^{II}Mn^{III}Mn^{III}O_4$) is well described by a 2nd-order kinetic model, which accounts for aqueous speciation and Mn sorption (treated as equilibrium reactions), changing surface area as solids are reductively dissolved (kinetic reactions), and the electron transfer reaction (kinetic). For these minerals, generation of Mn^{2+} as reaction progresses has little impact on reaction rate and extent. By contrast, oxalate oxidation by Bixbyite ($Mn^{III}Mn^{III}O_3$) exhibits a decrease in rate of reaction as Mn^{2+} is generated, and cannot be described by a single 2nd-order kinetic expression. Rate inhibition is removed when alternate sites for Mn^{2+} sorption are included, and rate of oxalate loss is described by a single 2nd-order expression. Thermodynamic calculations predict the propensity for oxalate oxidation follows the order Hausmannite > Bixbyite > Manganite > Birnessite > Nsutite. Kinetic data follow the order Manganite > Hausmannite > Birnessite > Bixbyite > Nsutite. Rate constants for oxalate oxidation by various Mn oxides span several orders of magnitude. Reaction network and rate parameters identified from batch systems described results from continuous flow experiments. Results provide baseline characterization of the reactivity of Mn oxides for future experiments investigating the reactivity of UO_2 with the same Mn oxides.