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Elucidating Bioreductive Transformations within Physically Complex Media: Impact on the Fate and Transport of Uranium and Chromium

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SUMMARY

In situ stabilization (inclusive of natural attenuation) of toxic metals and radionuclides is an attractive approach for remediating many contaminated DOE sites. By immobilizing toxic metals and radionuclides in place, the removal of contaminated water to the surface for treatment as well as the associated disposal costs are avoided. To enhance *in situ* remediaton, microbiological reductive stabilization of contaminant metals has been, and continues to be, actively explored. It is likely that surface and subsurface microbial activity can alter the redox state of toxic metals and radionuclides, either directly or indirectly, so they are rendered immobile. Furthermore, anaerobic bacterial metabolic products will help to buffer pulses of oxidation, typically from fluxes of nitrate or molecular oxygen, and thus may stabilize reduced contaminants from oxidative mobilization.

Uranium and chromium are two elements of particular concern within the DOE complex that, owing to their abundance and toxicity, appear well suited for biologically mediated reductive stabilization. Subsurface microbial activity can alter the redox state of toxic metals and radionuclides, rending them immobile. Imparting an important criterion on the probability that contaminants will undergo reductive stabilization, however, is the chemical and physical heterogeneity of the media. Our research first examined microbially induced transformation of iron (hydr)oxide minerals and their impact on contaminant attenuation. We revealed that in intricate cascade of geochemical reactions is induced by microbially produced Fe(II), and that during transformation contaminants such as U(VI) can be incorporated into the structure, and a set of Fe(II) bearing solids capable of reducing Cr(VI) and stabilizing resulting Cr(III). We also note, however, that common subsurface constituents such as phosphate can modify iron oxide transformation pathways and thus impact contaminant sequestration—affecting both Cr and U stabilization.

We extended our work to explore factors controlling the sequestration of uranium in the subsurface, with a particular emphasis on mineralogic and geochemical complexity. We reveal that one of the primary factors controlling uranium reduction, via both biological and chemical pathways, is the aqueous speciation of U(VI). Specifically, ternary calcium-uranyl-carbonato complexes stabilize U(VI) relative to reduction. However, countering the lack of reduction, we note a novel sequestration pathway in which the U(VI), as the uranate ion, is incorporated into the structure of transformation iron oxides; magnetite and goethite, both products of Fe(II) induced transformation of ferrihydrite, harbor appreciable quantities of uranium. In sum, our

results provide important information on predicting and potentially controlling the migration of chromium and uranium within the DOE complex.

RESEARCH OBJECTIVES

The goal of this research is to quantify bioreductive transformations controlling uranium and chromium sequestration, with a specific emphasis on variations in reactive components, inclusive of bacteria. Our work has sought to answer specific questions relevant to the success of the ERSP mission. Can uranium and chromium be stabilized with respect to transport through reductive stimulation within natural media? What spatial variation in degree and mechanisms/pathways of reductive stabilization exist? Our specific objectives of this research were to determine: (1) the impact of geochemical heterogeneity on metal reduction, (2) alterations in mineral reactivity with changes in surface composition, (3) the stability of reaction products, and (4) a comprehensive kinetic reaction model for uranium and chromium reduction.

RESEARCH ADVANCEMENT AND IMPLICATIONS

The fate and transport of radionuclides such as uranium and heavy metals such as chromium are dictated in part by biogeochemical transformations of the contaminant and phases comprising the environmental matrix. Ferric (hydr)oxides, for example, are ubiquitous components of surface and subsurface environments that have critical controls on biogeochemical cycles of carbon and most trace elements, and thus biogeochemical transformations of iron (hydr)oxides have direct impacts on contaminant cycling. We have therefore been investigating the biogeochemical controls on the fate and transport of uranium in chromium with a particular emphasis on transformation of iron phases within subsurface environment. Our studies encompass increasing complexity within the chemical/mineralogical, biological, and physical realms while continuing to seek molecular-level detail on operating biogeochemical processes. Specifically, we have conducted a series of experiments ranging from static-flow systems with a single mineral phase to hydrodynamic column experiments having the full suite of biological and chemical heterogeneity observed within subsurface environments. In sum, our studies provide revealing details on the biogeochemical factors exerting dominant impacts on contaminant fate.

Iron (Hydr)oxide Transformation Pathways

Iron (hydr)oxides are ubiquitous in the environment with contents ranging from one to several hundred g kg^{-1} in aerobic soils (Cornell and Schwertmann, 1996). A spectrum of iron (hydr)oxides exists in the environment, having a diverse range of crystallinities and subsequent reactivities and exerting a pronounced influence on contaminant sequestration. The thermodynamic stability of iron (hydr)oxides is a function of crystal structure and particle size, which ultimately controls the solubility of the (hydr)oxide phases. Solubility of iron (hydr)oxides generally increases from ferrihydrite ($K_{so}=10^{-39}$) to goethite ($K_{so}=10^{-41}$) to hematite ($K_{so}=10^{-43}$) at circumneutral pH. Given the greater abundance but lower surface area of more crystalline iron (hydr)oxides in the environment, microbial reduction of phases such as goethite and hematite may substantially contribute to the long-term potential for Fe(II) generation, sequestration, and associated biogeochemical cycles. Furthermore, they may undergo intense degradation through reductive dissolution or biotransformation, thus altering the reactive components of a system.

In addition to their importance as terminal electron acceptors, the fate of many nutrients and metals is dictated, in part, by iron (hydr)oxide formation and transformations. For instance, the reductive dissolution of iron (hydr)oxides by dissimilatory iron-reducing bacteria may either enhance (release of sorbed ions) or diminish (reductive immobilization via redox active metabolites) contaminant fate and transport within subsurface environments. Due to the strong reducing capacity of ferrous Fe, the fate of Fe(II) following dissimilatory iron reduction will have a profound bearing on metal cycles, including Cr (Fendorf et al., 2000; Wielinga et al., 2001; Hansel et al., 2003b). And secondary mineralization pathways of Fe(II) following dissimilatory iron reduction of ferrihydrite are controlled, in large part, by the supply rate and concentration of Fe(II) in solution (Fredrickson et al., 1998; Benner et al., 2002; Zachara et al., 2002; Hansel et al., 2003a).

We have previously observed the rapid and near complete conversion of ferrihydrite to goethite (minor product) and magnetite (major product; $[Fe^{2+}]>0.4$ mM) under advective flow in an artificial groundwater medium supplemented with 3 mM lactate (Benner et al., 2002; Hansel et al., 2003a). The addition of merely 40 μM ferrous Fe to ferrihydrite results in near complete (90%) conversion to goethite and lepidocrocite within 2 h. As such, the persistence of iron (hydr)oxides in the environment may stem from a microbially generated ferrous Fe-catalzyed

Oswald ripening process. Thus, even in relatively young systems, the predominant substrates available for dissimilatory iron reduction may instead be more crystalline (thermodynamically stable) iron (hydr)oxides such as goethite and hematite. Accordingly, we recently compared the reducing capacity and Fe(II) sequestration mechanisms of goethite and hematite to ferrihydrite under advective flow within a medium mimicking that of natural groundwater supplemented with organic carbon.

Microbial reduction of ferrihydrite, goethite, and hematite was investigated using a number of columns performed in two main experimental studies. The first study consisted of a series of ferrihydrite, goethite, and hematite columns (1 column per oxide) that were reacted for 16 d and the aqueous chemistry and exported cells were monitored daily within both the effluent and side ports. The microbial cell distribution (numbers and surface organization) associated with the solid-phase and secondary mineral phases were determined exclusively at the termination of the experiment following 16 d of reaction. A second set of column experiments was performed where 5 smaller columns for each iron (hydr)oxide were run simultaneously and terminated at varying time points. This series of columns was conducted to check for reproducibility, determine the influence of initial Fe(III) concentration, and to observe temporal variation in microbial distribution on the iron (hydr)oxide surfaces.

Introduction of dissolved organic carbon upon flow initiation results in the onset of dissimilatory iron reduction of all three Fe phases (ferrihydrite, goethite, and hematite). While the initial surface area normalized rates are similar (ca. 10^{-11} moles Fe(II) m^{-2} g^{-1}), the total amount of Fe(III) reduced over time along with the mechanisms and extent of Fe(II) sequestration differ among the three iron (hydr)oxide substrates. Following 16 d of reaction, the amount of Fe(III) reduced within the ferrihydrite, goethite, and hematite columns is 25, 5, and 1%, respectively. While 83% of the Fe(II) produced in the ferrihydrite system is retained within the solid-phase, merely 17% is retained within both the goethite and hematite columns. Magnetite precipitation is responsible for the majority of Fe(II) sequestration within ferrihydrite, yet magnetite was not detected in either the goethite or hematite systems. Instead, Fe(II) may be sequestered as localized spinel-like (magnetite) domains within surface hydrated layers (ca. 1 nm thick) on goethite and hematite or by electron delocalization within the bulk phase. The decreased solubility of goethite and hematite relative to ferrihydrite, resulting in lower $Fe(III)_{aq}$ and bacterially-generated $Fe(II)_{aq}$ concentrations, may hinder magnetite precipitation.

Nevertheless, following an initial, more rapid reduction period, the three Fe (hydr)oxides support similar aqueous ferrous iron concentrations, bacterial populations, and microbial Fe(III) reduction rates. A decline in microbial reduction rates and further Fe(II) retention in the solid-phase correlates with the initial degree of phase disorder (high energy sites). As such, sustained microbial reduction of 2-line ferrihydrite, goethite, and hematite appears to be controlled, in large part, by changes in surface energy, which is influenced by microbial reduction and secondary Fe(II) sequestration processes regardless of structural order (crystallinity) and surface area.

Surface Modifications to Iron (Hydr)oxide Mineralization

Owing to its high surface area and intrinsic reactivity, ferrihydrite, a short-range order ferric hydroxide common to soils and sediments, serves as a dominant sink for numerous metals in subsurface environments and is consider the primary Fe-phase for microbial metabolism (Fredrickson et al, 1998). However, ferrihydrite may be a short-lived intermediate within such systems and its fleeting presence will have profound impacts on metal biogeochemical cycles (Benner et al., 2002; Hansel et al., 2003; Zachara et al., 2002). Introduction of Fe(II) by reductive dissolution of Fe(III) minerals, for example, converts ferrihydrite to Fe phases varying in their retention and reducing capacity (Fendorf et al., 2000). Thus, the fate of numerous (in)organic ions, along with the decomposition of organic matter, is dictated by the Fe(II)-induced secondary mineralization of ferrihydrite. While Fe(II) concentration is the master variable dictating secondary mineralization pathways following reductive dissolution of ferrihydrite, our studies reveal that the kinetics of conversion and ultimate mineral assemblage are a function of competing mineralization pathways influenced by pH and stabilizing ligands.

Natural environments often include numerous organic and inorganic constituents that may appreciably alter the reactivity of iron (hydr)oxides relative to pristine synthetic analogs, which are frequently used in laboratory experiment. Many oxyanions (e.g. phosphate and arsenate) interact strongly with iron (hydr)oxides via surface complexation and may therefore affect Fe(III) reducibility, stability, and mineralization pathways. A systematic study examining modifications in surface composition on microbially mediated iron transformations was lacking. Accordingly, we investigated the impact of surface-associated oxyanions at varying coverages,

using phosphate as a model constituent, on the extent of ferrihydrite reduction and resulting biomineralization pathway under static- and dynamic-flow conditions.

We conducted batch and column studies examining ferrihydrite bioreductive transformation with a systematic variation in phosphate surface coverage. Ferrihydrite was reacted with PO_4^{3-} at concentrations from 10 μM to 2000 μM in synthetic groundwater medium for three days. Phosphate adsorption was well described by the Langmuir equation, and the monolayer sorption (Γ) was 0.28 g P Kg^{-1} solids (or 797 mmole P Kg^{-1} ferrihydrite). Batch reactions were performed with synthetic groundwater medium and ferrihydrite-coated sand. Phosphate was coated to various degrees (50 and 100 % of the adsorption maximum, Γ_{max}) on the ferrihydrite-coated sand. The role of phosphate on secondary mineralization was investigated by inoculation with *S. putrefaciens* to a cell density of ~ 10^8 mL^{-1} (biotic) or by reacting 0.2 or 2 mM ferrous sulfate (abiotic) with the (P-)Fe-coated sand for 7 d. Flow experiments were conducted in columns (3.8 cm diameter (ID)) with 4 sampling ports located at 1.7, 5, 8.3, and 11.7 cm along the flow-path. Ferrihydrite-coated sand was coated with phosphate to Γ_{max}, washed once in synthetic groundwater medium, and then inoculated with *S. putrefaciens* to a cell density of ~ 8 x 10^8 g^{-1}. The flow rate was maintained at 373 mL d^{-1} (2.9 pore volumes) upward through the column.

An inverse correlation between ferrous iron production and surface-associated phosphate illustrates how strongly sorbing oxyanions stabilize the structure of ferrihydrite toward dissimilatory Fe reduction. Additionally, the extent of ferrihydrite reduction being modified, the transformation pathway is also vastly different in the presence of phosphate. A four-fold decrease in the extent of ferrihydrite transformation is observed in the presence of phosphate at maximum surface coverage, correlating well with the corresponding decrease in Fe(II) production. The most notable difference in the secondary iron phases is the apparent inhibition of goethite. Magnetite and green rust formation, albeit not the proportion, is in concurrence with previous studies performed in a minimal growth medium (Glasauer et al., 2003) but differs from the secondary phases formed (i.e. vivianite and siderite) under condition where the growth medium is optimized to achieve more rapid rates of reduction (Fredrickson et al., 1998).

In contrast to the extent of ferrihydrite mineralization (44 and 59 % transformed) observed in the absence of phosphate, only 10 to 20 % of the ferrihydrite is mineralized in the presence of phosphate. This result supports the premise that phosphate stabilizes the structure of

ferrihydrite by inhibiting reduction, poisons the formation of goethite, and promotes the formation of green rust and vivianite–the latter which forms only at high ferrous iron and phosphate concentrations. The formation of carbonate green rust under biotic conditions in the absence of phosphate is likely a result of the microbial respiration which results in the formation and accumulation of bicarbonate under batch conditions. .

Bioreduction and mineralization pathways of iron (hydr)oxides are influenced by strongly sorbing oxyanions such as phosphate. Our studies illustrate slow respiration on a presumably 'bioavailable' form of Fe(III), even when supplied with an electron donor (lactate) concentration of 3 mM; 'leaner' conditions common to most natural environments would likely exaggerate the limited reduction of phosphated ferrihydrite. Additionally, the absence of goethite and typical lower fraction of crystalline Fe phases in phosphatic soils results from a stabilization of ferrihydrite. Thus, when considering the reactivity of iron phases, it is important to appreciate modifications induced by surface composition such as that noted here for phosphate.

Geochemical Constraints on Uranium Reduction

Dependence on Uranyl Speciation.

In soils and sediments, the oxidized state of uranium (U(VI)) is typically mobile, particularly under conditions conducive to the formation of uranyl-carbonato complexes. While in contrast, the reduced state (U(IV)) forms phases with limited solubility such as uraninite. Like other toxic metals and radionuclides (e.g. Cr, Tc) , the fate and transport of uranium is in part dictated by microbial mediated reduction--which, as noted above, yields the subsequent precipitation U(IV) phases such as uraninite. While biological or biologically mediated reduction of uranium is well demonstrated within isolated and constrained laboratory experiments, factors confounding uranium reduction within natural environments remain unresolved. We have therefore conducted a series of experiments that explore the impact of completing electron acceptors and uranyl species on reductive stabilization of uranium.

A critical factor affecting the mobility and reducibility of uranium is the aqueous speciation of uranyl. Uranyl-carbonate complexes have classically been considered the dominant aqueous species of U(VI); however, recently Ca-UO_2-CO_3 ($CaUO_2(CO_3)_3^{2-}$, $Ca_2UO_2(CO_3)_3$) complexes have been described. We initiated our experiments examining the influence of calcium on uranyl reduction within complex mineralogical assemblages containing

iron coated sands under dynamic flow conditions. Parallel flow systems of ferrihydrite coated sands inoculated with *Shewanella putrefaciens* were investigated, one containing a feed solution 4 mM Ca and the other having no Ca. The presence of dissolved calcium in combination with Fe(III) dramatically limits the extent of dissimilatory uranium reduction. No reduction, and minimal retention, transpires in the presence of Ca while reductive precipitation is so extensive in the absence of Ca that U(VI) never transports more than 5-cm within the flow-field and results in nearly 4000 mg Kg^{-1} of uranium over a 54 d reaction period (and uranyl reduction shows no signs of diminishing). Here, uranium is sequestered near the inlet-flow area via reduction of U(VI) to a less soluble U(IV) precipitate that resides both in periplasmic space and on the outer membrane.

Although a multitude of U(VI) species reside under the conditions evaluated within this study, there are two dominant species, $Ca_2UO_2(CO_3)_3$, $(UO_2)_2CO_3(OH)_3^-$, under the geochemical conditions of this study; a third species, $UO_2(CO_3)_2^{2-}$, resides at appreciable fractions of the total uranium. Considering these three species, reduction reactions coupled with lactate oxidation are described by the stoichiometries of reactions 1 to 3.

$$C_3H_5O_3^- + (UO_2)_2CO_3(OH)_3^- \rightarrow C_2H_3O_2^- + 2HCO_3^- + 2UO_2 + H_2O + H^+ \quad (1)$$

$$^1/_2C_3H_5O_3^- + UO_2(CO_3)_2^{2-} + H_2O \rightarrow {}^1/_2C_2H_3O_2^- + {}^5/_2HCO_3^- + UO_2 + {}^1/_2H^+ \quad (2)$$

$$^1/_2C_3H_5O_3^- + Ca_2UO_2(CO_3)_3 + H_2O + {}^1/_2H^+ \rightarrow {}^1/_2\, C_2H_3O_2^- + {}^7/_2HCO_3^- + UO_2 + 2Ca^{2+} \quad (3)$$

Rate data for the various systems conform reasonably well to a pseudo-first order kinetic expression dependent on the total U(VI) concentration and having an observed (or overall) rate coefficient representing various factors.

$$-{}^{d[U(VI)]}/_{dt} = k_{obs}[U(VI)]$$

The observed rate coefficient, k_{obs}, for U(VI) reduction in the absence of Ca is the fraction of total uranium residing in the carbonato complex. With the exception of systems with ferrihydrite, which acts as a competing electron acceptor, the averaged k_1 value ($k_1 = k_{obs}/K_p$, where K_p is the proportion of carbonato species and is equal to 1 in the absence of Ca) is 1.18 x 10^{-2} h^{-1}, giving the following operative rate expression.

$$-{}^{d[U(VI)]}/_{dt} = k_1[(UO_2)_x(CO_3)_y]$$

In Ca-bearing solutions, the rate expression becomes more convoluted and would be described by an observed rate coefficient encompassing the initial proportion of the U-carbonato complex,

its rate of regeneration, and the rate of Ca ternary complex reduction. The rate expression for the reduction of U(VI) is therefore

$$-{}^{d[U(VI)]}/_{dt} = k_1[(UO_2)_x(CO_3)_y] + k_2[Ca_2UO_2(CO_3)_3] + k_1k_3[Ca_2UO_2(CO_3)_3]$$

The decrease in rate coefficient with increased Ca concentrations (Figure 4) indicates that $k_1 >> k_3$, leading to the simplification

$$-{}^{d[U(VI)]}/_{dt} = (k_2 + k_3)[Ca_2UO_2(CO_3)_3]$$

Decreasing rate coefficients with increased Ca concentrations described in Table 4 thus represent the combined contributions of k_2 and k_3 and increased proportions (effective concentration) of the Ca ternary complex. The observed rate coefficient would be proportional to $k_{2,3}$ (where $k_{2,3} = k_2 + k_3$), with the proportionality coefficient (K_p) again being the fraction of total uranium residing in the ternary complex (K_p = -1.15[Ca]+0.97) and can be described as ln $k_{2\text{-}3}$ = 30.5[$Ca_2UO_2(CO_3)_3$] - 7.18.

Impact of Competing Substrates. In most natural environments, a multitude of metabolic substrates are present simultaneously. Organisms that can utilize uranium as a metabolic substrate for respiration also may have the ability to use a variety of other oxidized substrates as electron acceptors. Thus, these substrates are, in effect, competing for electrons that are being passed through the electron transport chain during respiration. To assess the feasibility of *in situ* immobilization of uranium in subsurface environments and to understand the cycling of uranium, it is necessary to discern the chemical and/or biological conditions dictating which terminal electron acceptor(s) will be utilized.

Iron(III) phases may impose severe competition on U(VI) for bacterial respiratory reduction (Weilinga et al, 2001). We observe, however, that within batch reactors having nutrient-rich media (10 mM lactate) both *Shewanella alga* and *S. putrefaciens* utilize the two electron acceptors simultaneously, coupling oxidation of lactate with the reduction of both U(VI) and Fe(III). Interestingly, these two microbes do not systematically change their preference towards these two substrates over the course of reaction. Instead, *S. alga* transfers approximately 31% of electrons to U(VI) and 69% of electrons to Fe(III); *S. putrefaciens* transfer 39% to U(VI) and 61% to Fe(III). These ratios, 31/69 and 39/61, do not substantially change as metabolic activity progresses (Figure 3c,d). This suggests that the microbial populations of *S. alga* and *S. putrefaciens* do not have, or are unable to express, a preference towards one of these oxidized

substrates. Further, *S. alga* and *S. putrefaciens* appear to benefit from the presence of two electron acceptors. Analysis of metabolic capacity of the microbial populations suggests that *S. alga* and *S. putrefaciens* are able to oxidize more lactate, transfer more electrons, and conserve more energy when both U(VI) and Fe(III) are available as electron acceptors under nutrient-rich conditions.

Our results illustrate the impact biofilms and their associated gradients have on utilization of metabolic substrates during respiration. Both *S. alga* and *S. putrefaciens* exude extensive exopolysaccharides and rapidly form biofilms, resulting in steep chemical gradients that limit bacterial metabolic activity. When ferrihydrite is present, aggregates form around the particles providing cells deep in the aggregates with an electron acceptor. It is therefore clear, that bacterial growth and biofilm formation can have important effects on substrate availability that can dramatically impact metabolic pathways when more than one substrate is available.

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