Mesoscale Biotransformation of Uranium: Influences of Organic Carbon Supply Rates and Sediment Oxides

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Introduction & Objectives

Remediation and long-term stewardship of uranium-contaminated sediments and groundwaters are critical problems at a number of DOE facilities and mining sites. Some remediation strategies based on in-situ bioreduction of U are potentially effective in significantly decreasing U concentrations in groundwaters. However, a number of basic processes require understanding in order to identify conditions more conducive to success of reduction-based U stabilization. Our current research targets several of these issues including: (1) effects of organic carbon (OC) forms and supply rates on stability of bioreduced U, (2) the roles of Fe(III)- and Mn(III,IV)-oxides as potential U oxidants in sediments, and (3) microbial community changes in relation to U redox changes. These issues were identified in our previous study on U bioreduction and reoxidation (Wan et al., 2005). Most of our studies are being conducted on historically U-contaminated sediments from Area 2 of the Field Research Center, Oak Ridge National Laboratory, in flow-through columns simulating in-situ field remediation.

Approaches

Redox transformations of U are being tested in new FRC2 sediment columns supplied with OC at rates of 0, 16, 55, 160, and 550 mmol (kg sediment)$^{-1}$ year^{-1}. These 200 mm long columns are being infused with either lactate or acetate in synthetic groundwater (neutral salts), with OC concentrations of 0, 3, 10, 30, and 100 mM, at an average pore water velocity of 300 mm year^{-1} (Fig. 1). The current set of columns have been running for over 400 days.

Analyses of effluents (U, major ions including carbonate/bicarbonate, OC), sediment redox status (X-ray absorption near edge structure (XANES) spectroscopy of Mn, Fe, and U, and Pt redox electrodes), and chemical extractions of sediments are being obtained to quantify geochemical changes.

We employed a high-density 16S DNA microarray (Phylochip) to determine the structure and population dynamics of the resulting microbial communities. 16S rRNA gene amplicons were labeled and hybridized to the Phylochip, which is capable of measuring the relative abundance of nearly 9,000 Bacteria and Archaea.

Geochemical and microbiological information obtained during the course of this study is being used to develop an integrated understanding of biogeochemical responses to a range of OC supply rates.

Figure 1. Columns of FRC Area 2 sediment (total U = 257 mg kg^{-1} = 1.08 mmol kg^{-1}) in N_2 glovebox. The columns are being supplied with either lactate or acetate, at OC concentrations from 0 to 100 mM.

Results

Redox potential profiles

Redox potential profiles within columns showed lowering of Eh proportional to the OC supply rate (Fig. 2). The columns infused with OC at 160 and 550 mmol (kg sediment)$^{-1}$ year^{-1} (30 and 100 mM OC in influent) were Fe-reducing throughout, whereas the 16 and 55 mmol OC (kg sediment)$^{-1}$ year^{-1} (3 and 10 mM OC in influent) columns were only reducing at their inlet region.

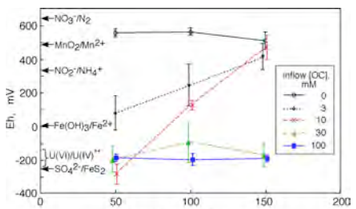

Figure 2. Profiles of redox potentials measured by Pt electrodes (mV relative to standard H electrode).

Effluent carbonate and uranium

The effluent U concentrations show complex but very reproducible dependence on the OC supply rate and mineralization (Fig. 3), consistent with OC oxidation having dual impacts of driving reduction of U as well as formation of U(VI)-carbonato complexes (Fig. 4). This portion of our study is also showing that lactate and acetate have the same geochemical impact on effluent U concentrations (and all other measured chemical species), when compared on the basis of OC supply rate.

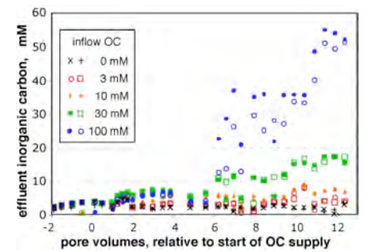

Figure 3. Concentrations of inorganic carbon (bi-carbonate) measured in effluents from columns supplied with different OC concentrations (acetate).

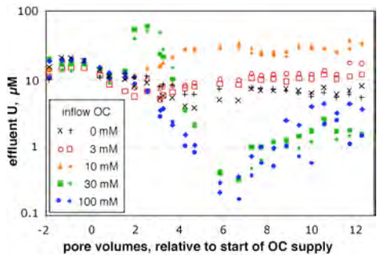

Figure 4. Uranium concentrations in effluents from columns with different OC supply rates (acetate, duplicate columns). At OC supply rates that are insufficient for establishing reducing conditions, more U(VI) is mobilized through carbonato complexes. Some U(VI) mobilization also results under reducing conditions through the same mechanism.

Mn, Fe, and U oxidation states

Previously, we identified several factors that point to a residual reactive Fe(III) fraction in sediments that likely serves as the terminal electron acceptor for U reoxidation. Micro- XANES spectroscopy is being used to determine distributions of Mn, Fe, and U oxidation states in sediments at various stages of OC-stimulated bioreduction (Fig. 5, 6).

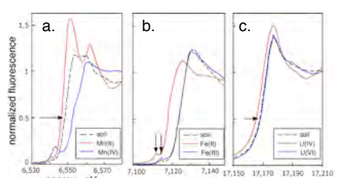

Figure 5. XANES spectra of original FRC2 sediment and end member oxidation state standards for **(a.)** Mn, **(b.)** Fe, and **(c.)** U.

Manganese(III,IV) oxides were completely reduced to Mn(II) in sediments infused with ≥ 16 mmol OC (kg sediment)$^{-1}$ year^{-1} (Fig. 6a). Iron oxidation states changed very little relative to its initial condition of 88% Fe(III) under even the highest injected OC concentrations (Fig. 6b). In sediments supplied with 160 and 550 mmol OC (kg sediment)$^{-1}$ year^{-1}, rapid U reduction was followed by a transient reoxidation period, before stabilizing in predominantly reduce states (Fig. 6c). Even at this late stage, about 20% of the U remained as U(VI). The measured rapid and complete Mn reduction, and very little reduction of a much larger Fe(III) inventory support our hypothesis (Wan et al., 2005) that a reactive Fe(III) fraction is responsible for U(IV) reoxidation under reducing conditions.

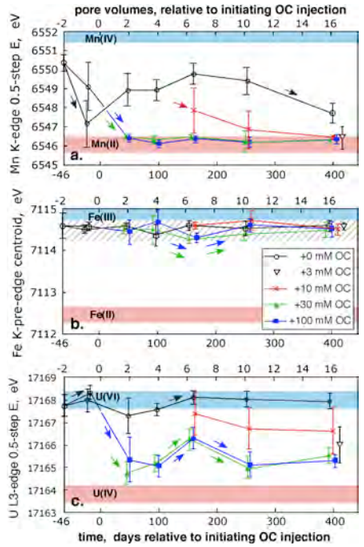

Figure 6. Time trends of average X-ray absorption energies for **(a.)** Mn K-edge half step height, **(b.)** Fe K-edge pre-edge peak centroid, and **(c.)** U L_{III}-edge half step height in sediment columns. Energies of corresponding end member oxidation states are shown as horizontal bands. The diagonally slashed band in the Fe graph indicates the range of energy shift possible if only the citrate-dithionite extractable Fe is reduced. Arrows indicate where energy differences between 2 adjacent time points (or relative to the initial sediment in cases where intermediate time measurements were not obtained) are significantly different at $p \leq 0.001$.

Microbial Community Analyses*

Comparison of the resulting microbial communities indicates that OC supply rate is the primary determinant of the bacterial community structure. The secondary determinant of community structure is sampling time point, which in the 30 and 100 mM OC treatments corresponds to phases of net U-reduction (T1) and a later phase of U(IV) reoxidation and U(VI) remobilization (T2). All of the communities cluster according to OC supply rate and time point with the exception of the column receiving 30 mM OC lactate.

Phylochip analysis showed an increase in the number of operational taxonomic units detected between the U-reduction and U-remobilization phases in all columns except those receiving high OC lactate supply (100 mM and 30 mM OC equivalents). Known U-reducing bacteria such as *Anaeromyxobacter dehalogenans*, *Desulfovibrio desulfuricans*, *Geobacter metallireducens*, *Pseudomonas putida* and *Geothrix fermentans* were detected in all columns by Phylochip analysis. Although the dynamics of these U-reducing bacteria differed depending on the form of OC supplied and the supply rate, our data indicate that U-reducing bacteria were present in each column during the phase of U(IV) reoxidation and U(VI) remobilization and in some cases showed an increase in relative abundance between the two phases.

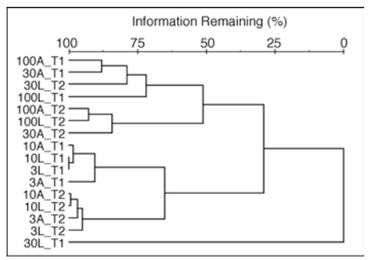

Figure 7. Hierarchical cluster analysis of Phylochip data. Samples are coded by OC supply rate (100, 30, 10 and 3 mM), OC supply form (L=Lactate, A=Acetate), and sampling time point (T1= 5.5 pore volumes OC supply, T2= 12 pore volumes OC supply).

*More detailed information on microbial community analyses is presented in Rebecca Daly et al., ERSP 2007 poster.

Implications to the Field

- Low OC supply rates mobilize more U(VI) than no OC supply because aqueous U(VI) carbonato complexes are formed without U reduction.
- Excessively high OC supply rates also mobilize U(VI) through the same complexation reaction until extensive U reduction is achieved.
- The geochemical responses (redox potentials, U reduction, effluent chemistry) to lactate and acetate were practically identical on a per mole OC basis.
- Manganese reduction to Mn(II) occurs rapidly and thoroughly during OC supply.
- The very large inventory of Fe(III) in these sediments remained largely unreduced, even at the highest OC supply rates.
- Rapid initial U reduction in sediments receiving high OC supply rates were followed by reoxidation, reproducing results from our previous study.
- Sufficient Fe(III) remained in all sediments to permit U(IV) reoxidation under reducing conditions.
- OC supply rate has a greater effect on bacterial community structure than the form of OC supplied.
- Known U-reducing bacteria were detected in all columns, at both sampling time points.

Recent Publications

- Zheng, et al. 2003. Influence of calcium carbonate on U(VI) sorption to soils. *Environ. Sci. Technol.*, *37*, 5603-5608.
- Tokunaga, et al. 2004. Hexavalent uranium diffusion in soils. *Environ. Sci. Technol.*, *38*, 3056-3062.
- Wan, et al. 2005. Reoxidation of bioreduced uranium under reducing conditions. *Environ. Sci. Technol.*, *39*, 6162-6169.
- Tokunaga, et al. 2005. Uranium reduction in sediments. *Environmental Science Technology*, *39*, 7077-7083.
- Brodie, et al. 2006. Bacterial population dynamics during U reduction and reoxidation. *Appl. Environ. Microb.*, *72*, 6288-98.

Acknowledgments

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