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**Manganese Redox Mediation of  $\text{UO}_2$  Stability and Uranium Fate in the Subsurface:  
Molecular and Meter Scale Dynamics**

**Final Report**

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**Abstract:**

One strategy to remediate U contamination in the subsurface is the immobilization of U via injection of an electron donor, e.g., acetate, which leads to stimulation of the bioreduction of U(VI), the more mobile form of U, to U(IV), the less mobile form. This process is inevitably accompanied by the sequential reductive dissolution of Mn and Fe oxides and often continuing into sulfate-reducing conditions. When these reducing zones, which accumulate U(IV), experience oxidizing conditions, reduced Fe and Mn can be reoxidized forming Fe and Mn oxides that, along with  $\text{O}_2$ , can impact the stability of U(IV).

The focus of our project has been to investigate (i) the effects of Mn(II) on the dissolution of  $\text{UO}_2$  under both reducing and oxidizing conditions, (ii) the oxidative dissolution of  $\text{UO}_2$  by soluble Mn(III), (iii) the fate of U once it is oxidized by  $\text{MnO}_2$  in both laboratory and field settings, and (iv) the effects of groundwater constituents on the coupled Mn(II)/U(IV) oxidation process. Additionally, studies of the interaction of Se, found at the DOE site at Rifle, CO, and Mn cycling were initiated to understand if observed seasonal fluctuations of Se and Mn are directly linked and whether any such linkages can affect the stability of U(IV).

## **Summary of Results:**

### ***Effects of Mn(II) on UO<sub>2</sub> Dissolution in Reducing and Oxidizing Conditions***

An experimental study was performed to evaluate the effect of Mn(II) on UO<sub>2</sub> dissolution in reducing and oxidizing conditions. We previously reported the effects of Ca(II) and Zn(II) on UO<sub>2</sub> dissolution rates and showed that these divalent cations exert inhibitory effects in both reducing and oxidizing conditions. The inhibition could be attributed to adsorption and secondary precipitation. However, the effects of redox sensitive cations, such as Mn(II), on UO<sub>2</sub> dissolution were not fully understood. The effects of Mn(II) on UO<sub>2</sub> dissolution kinetics were investigated using batch and continuously stirred-tank reactors (CSTR) at different dissolved oxygen conditions and Mn(II) loadings.

Under anoxic conditions Mn(II) inhibited UO<sub>2</sub> dissolution, which was probably due to adsorption of Mn(II) and precipitation of MnCO<sub>3</sub> that decreased exposure of U(IV) surface sites to oxidants. In contrast, Mn(II) promoted UO<sub>2</sub> dissolution under oxic conditions through Mn redox cycling. Oxidation of Mn(II) by O<sub>2</sub> produced reactive Mn species, possibly short-lived Mn(III) in solution or at the surface, that oxidatively dissolved the UO<sub>2</sub> more rapidly than could the O<sub>2</sub> alone. At pH 8 the Mn cycling was such that there was no measurable accumulation of particulate Mn oxides. At pH 9 Mn oxides could be produced and accumulate, while they were continuously reduced by UO<sub>2</sub>, with Mn(II) returning to the aqueous phase. With the rapid turnover of Mn in the redox cycle, concentrations of Mn as low as 10 μM could maintain an enhanced UO<sub>2</sub> dissolution rate. The presence of the siderophore desferrioxamine B (a strong Mn(III)-complexing ligand) effectively decoupled the redox interactions of uranium and manganese to suppress the promotional effect of Mn(II).

### ***Kinetics of oxidative UO<sub>2</sub> Dissolution by Soluble Mn(III)***

Laboratory studies investigated the kinetics of oxidative UO<sub>2</sub> dissolution by soluble Mn(III). Mn(III) has been identified as an intermediate species in Mn redox processes and can be a significant form of dissolved Mn at oxic/anoxic interfaces of soil and groundwater environments. Oxidative dissolution of UO<sub>2</sub> by soluble Mn(III) may be an important pathway in Mn-mediated oxidation of UO<sub>2</sub>. The kinetics of oxidative UO<sub>2</sub> dissolution by soluble Mn(III) stabilized with pyrophosphate and desferrioxamine B (DFOB) were quantitatively evaluated in batch experiments at anoxic conditions.

The Mn(III)-PP complex was a potent oxidant that induced rapid UO<sub>2</sub> dissolution at a rate higher than by a comparable concentration of dissolved O<sub>2</sub>. However, the Mn(III)-DFOB complex was not able to induce oxidative dissolution of UO<sub>2</sub>. The ability of Mn(III) complexes to oxidize UO<sub>2</sub> was probably determined by whether the coordination of Mn(III) with ligands allowed the attachment of the complexes to the UO<sub>2</sub> surface to facilitate electron transfer. Systematic investigation into the kinetics of UO<sub>2</sub> oxidative dissolution by the Mn(III)-PP complex suggested that Mn(III) could directly oxidize UO<sub>2</sub> without involving particulate Mn species (e.g., MnO<sub>2</sub>). The expected 2:1 reaction stoichiometry between Mn(III) and UO<sub>2</sub> was observed. The reactivity of soluble Mn(III) in oxidizing UO<sub>2</sub> was higher at lower ratios of pyrophosphate to Mn(III) and lower pH, which is probably related to differences in the ligand-to-metal ratio and/or protonation

states of the Mn(III)-pyrophosphate complexes. Disproportionation of Mn(III)-PP occurred at pH 9.0, and the oxidation of  $\text{UO}_2$  was then driven by both  $\text{MnO}_2$  and soluble Mn(III). Kinetic models were derived that provided excellent fits of the experimental results.

### *The fate of U oxidized by $\text{MnO}_2$*

*Uranium(VI) adsorption to  $\text{MnO}_2$ .* The equilibrium and mechanisms of U(VI) adsorption to synthetic and biogenic Mn oxides were determined as a function of aqueous composition. Batch equilibrium experiments were integrated with X-ray absorption spectroscopy measurements to yield a model for adsorption that could predict the macroscopic adsorption behavior of uranium using reactions that were consistent with the molecular-scale structure of the adsorbed U(VI). Chemically-synthesized  $\text{MnO}_2$  was prepared at WUSTL and biogenic  $\text{MnO}_2$  was prepared at OHSU. Careful purification of biogenic  $\text{MnO}_2$  from the biomass residual was performed. Adsorption experiments were performed over a broad range of pH, three dissolved inorganic carbon concentrations, and two different U(VI) loadings. U LIII-edge extended X-ray absorption spectroscopy fine structure (EXAFS) spectra were collected and analyzed at the Stanford Synchrotron Radiation Lightsource (SSRL)

Equilibrium U(VI) adsorption was strongly influenced by the solution chemistry. With increasing pH in the acidic region, the extent of adsorption increased dramatically. The presence of dissolved inorganic carbon decreased adsorption at pH values above neutral because of the formation of stable dissolved U(VI)-carbonate complexes. Compared with its synthetic analog, biogenic  $\text{MnO}_2$  appeared to be a weaker sorbent for U(VI). The adsorption edge for syn- $\text{MnO}_2$  occurred at lower pH than for the bio- $\text{MnO}_2$ , suggesting a lower sorption affinity of bio- $\text{MnO}_2$ . The ratio of the adsorption capacities correlated remarkably well with the ratio of the specific surface areas of the two  $\text{MnO}_2$  materials.

Equilibrium U(VI) adsorption was successfully modeled over a broad range of solution compositions with a surface complexation model that included inner-sphere monodentate and bidentate surface complexes and a ternary uranyl-carbonato surface complex. The pH-dependence of the monodentate versus bidentate surface complex were consistent with EXAFS measurements. Further, the EXAFS measurements suggested the need for the ternary surface complex whose inclusion then improved the fit of the model to the data.

In the process of developing the surface complexation model for the U(VI)- $\text{MnO}_2$  system, questions regarding the most appropriate way to include bidentate surface complexes in surface complexation models arose. Further examination revealed inconsistencies and even incorrect uses of some models and a large gap between the state-of-the-art modeling practices developed by theoreticians and the actual applications of surface complexation models by practitioners evaluating adsorption. A critical review article was written and published in *Environmental Science & Technology* to help resolve confusion and to bridge the gap between practitioners and theoreticians.

*Physical and Chemical Factors Controlling the Redox Interaction of  $\text{UO}_2$ - $\text{MnO}_2$ .* Laboratory studies were performed to investigate the physical and chemical factors controlling the interaction between  $\text{UO}_2$  and  $\text{MnO}_2$ . Because both  $\text{MnO}_2$  and  $\text{UO}_2$  are insoluble at

environmentally relevant conditions, the degree to which physical contact was necessary for  $\text{UO}_2$  oxidation was unknown. A well-mixed multi-chamber reactor with a permeable membrane was used to eliminate direct contact of the two minerals while still allowing transport of aqueous species. The oxidation of  $\text{UO}_2$  was not significantly enhanced if  $\text{MnO}_2$  was physically separated from it. Complete mixing of  $\text{MnO}_2$  with  $\text{UO}_2$  led to a much greater extent and rate of U oxidation. Effective oxidation of  $\text{UO}_2$  by  $\text{MnO}_2$  requires physical contact or close proximity. When direct contact is not possible, the reaction slowly progresses through release of soluble U(IV) with its adsorption and oxidation on  $\text{MnO}_2$ .

Continuously stirred-tank reactors (CSTR) were used to quantitatively examine the rates of  $\text{MnO}_2$ -mediated  $\text{UO}_2$  dissolution and the effects of chemical factors (mixing ratio and carbonate concentration) on the dissolution rates.  $\text{MnO}_2$  dramatically promoted the  $\text{UO}_2$  dissolution, but the degree of promotion leveled off when the  $\text{MnO}_2$ : $\text{UO}_2$  ratio exceeded a certain value.  $\text{UO}_2$  oxidation by  $\text{MnO}_2$  was faster at higher carbonate concentrations. Substantial amounts of U(VI) were retained on  $\text{MnO}_2$  surfaces through adsorption. The amounts of U(VI) adsorbed on  $\text{MnO}_2$  were inversely related to  $\text{UO}_2$  dissolution rates, suggesting that the U(VI) product could passivate  $\text{MnO}_2$  surfaces. The release of Mn into the effluent was less than what would be expected based on the measured U release and the stoichiometry of the reaction, which indicates that the fate of Mn and the changes of its oxidation states were more complex than initially anticipated. Based on grain-to-grain contact, electron transfer, and surface speciation, a conceptual model was proposed to predict the oxidation rate of  $\text{UO}_2$  by  $\text{MnO}_2$ . The model is applicable to broader water chemistry conditions and may be relevant to other redox processes involving two poorly soluble minerals.

### ***Effects of groundwater constituents***

*Iron and sulfate reducing conditions.* We have shown that, in a laboratory setting, biogenic  $\text{MnO}_2$  plays a role in the immobilization of uranium via sorption processes but does not appear to play an important role in U(IV) oxidation. The next step was to evaluate these findings in natural sediments in order to verify that they still hold within the complex subsurface environment.

We carried out column experiments with sediment from the Old Rifle site, Colorado. The columns were amended with anoxic Rifle Artificial Groundwater (RAGW) with or without sulfate and included  $50\mu\text{M}$  U(VI) and  $5\text{mM}$  acetate. In the absence of sulfate, the columns remained in an iron-reducing metabolic regime. In contrast, when sulfate was included, the columns eventually reached sulfate-reducing conditions.

The columns accumulated 250-300 ppm of U during the reduction phase. Interestingly, despite previous results showing that Mn(II) oxidation took place in untreated sediments in the presence of Mn(II) and  $\text{O}_2$ , there was no evidence of Mn(II) oxidation in pre-reduced (under iron- or sulfate-reducing conditions) sediments in the presence of U(IV). This suggests that either reducing conditions preclude Mn(II) oxidation even when  $\text{O}_2$  is added or the presence of U(IV) inhibits Mn(II) oxidation. We hypothesize that the former is true because we have shown extensive Mn(II) oxidation by *Bacillus* SG-1 spores in the presence of U(IV) (Plathe et al., 2013).

The above observation stems from results showing no difference in the concentration of U in the effluent from columns treated with Mn(II) and O<sub>2</sub> or only O<sub>2</sub>. Additionally, the influent and effluent Mn(II) concentrations were similar, indicating no Mn(II) oxidation and precipitation. Because there was no detectable Mn(II) oxidation, we focused on the micro-scale characterization of U(IV) oxidation for U(IV) formed under iron-reducing or sulfate-reducing conditions.

The U concentration in the effluent was significantly different for the columns prepared under iron- and sulfate-reducing conditions. The iron-reducing columns, when treated with 5% O<sub>2</sub>, released about 60 μM U for 7 days and about 10 μM U from 7 to 14 days. This corresponded to a release of about 280 ppm of U. In contrast, the sulfate-reducing columns only released about 10 μM for 20 days. This corresponded to about a 20 ppm release. This suggests that U(IV) is more stable under sulfate-reducing conditions than under iron-reducing conditions. Because most of the U was lost from the iron-reducing system, we focused on the sulfate-reducing columns before and after oxidation to gain insight into the role of minerals associated with U(IV) in precluding oxidation and release.

Based on extensive SEM characterization of the pre-oxidation sample, we identified three types of U-rich areas: U is (a) associated with Fe/S-rich coatings on grains, (b) associated with Fe-rich but S-poor coatings on grains and (c) present in stand-alone U-rich aggregates. Interestingly, in the post-oxidation sample, U was found primarily in the presence of Fe/S or just S. This suggests that stand-alone aggregates of U are lost through oxidation and that Fe/S and S have redox buffering capacity that may explain the discrepancy between the iron- and the sulfate-reducing columns.

Additionally, in almost every case, there is a strong association of U with Ca. In practically every instance (pre- or post-oxidation), wherever U was present, Ca was found in association, albeit at a much lower atomic percent than U. This suggests sorption of Ca onto UO<sub>2</sub> as was shown in UO<sub>2</sub> incubated *in situ* in Rifle groundwater (manuscript in preparation).

In order to better characterize this association at the nanometer scale, we used FIB-SEM to extract lamellae from the sediment thin sections and image them using STEM. We obtained lamellae from area identified as U rich from SEM.

The pre-oxidation sample showed extensive accumulation of U. The atomic percent in U-rich areas varied between ~20-55%. U was found as aggregates approximately 100 nm that diffract as UO<sub>2</sub>. Additionally, U was found in association with magnetite. The U aggregate morphology was prevalent in the sample and there were only sparse examples of U in association with Fe and S.

The post-oxidation sample primarily showed the association of U with magnetite and to a lesser extent, its association with Fe and S containing regions. U was often found embedded in a matrix of magnetite.

These findings show that the oxidation of U(IV) as UO<sub>2</sub> is buffered by the presence of magnetite. This is a surprising finding. The expectation was to find U associated primarily with iron sulfide minerals such as mackinawite, as has been shown in the past (Bargar et al., 2013). These results

highlight the importance of magnetite as a redox buffer for uraninite and the association of  $\text{UO}_2$  with magnetite in the pre-oxidation sample. This is consistent with our previous findings if one considers that this work was focused on areas where high concentrations of U were concentrated. These areas would typically contain more  $\text{UO}_2$  while areas containing mackinawite and sulfate-reducing biofilms would typically include non-crystalline U(IV). The latter areas would include more diffuse concentrations of U due to the association of non-crystalline U(IV) with extracellular polymeric substances and would be less prominent in a study (such as this one) where the focus was on U hotspots.

Overall, this work shows the importance of magnetite in the formation of  $\text{UO}_2$  in sediments and its role of buffering U oxidation to a certain extent. It is also clear that the presence of mackinawite in this sample was important in consuming  $\text{O}_2$  and indirectly protecting  $\text{UO}_2$  from oxidation.

*Calcium, magnesium and bicarbonate.* We examined the effects of varying  $\text{O}_2$  and selected common groundwater constituents,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ , on the coupled Mn(II)/U(IV) oxidation by a model organism, *Bacillus* sp. strain SG-1, using two different forms of U(IV), biologically produced uraninite (bio- $\text{UO}_2$ ) and monomeric (complexed) U(IV). Briefly, (i) monomeric U(IV) was more susceptible to oxidation by  $\text{O}_2$  and  $\text{MnO}_2$  compared to bio- $\text{UO}_2$ ; (ii) increasing  $\text{O}_2$  levels resulted in more rapid oxidation of both forms of U(IV); and (iii) the presence of  $\text{Ca}^{2+}$  but not  $\text{Mg}^{2+}$  conferred stability to bio- $\text{UO}_2$ . To assess whether increasing  $\text{O}_2$  can lead to different structures and hence different reactivities of biogenic Mn oxides as Mn(II) oxidation rates increased, Extended X-ray Absorption Fine Structure (EXAFS) spectra of the biogenic Mn oxides were collected. Qualitatively, EXAFS indicated that at all levels of  $\text{O}_2$  (0.1-5 %) tested, the local structures of the biogenic Mn oxides were similar to that of  $\delta$ - $\text{MnO}_2$  or hexagonal birnessite. Because the presence of  $\text{Ca}^{2+}$  appeared to decrease the reactivity between biogenic Mn oxides and bio- $\text{UO}_2$ , EXAFS and synchrotron radiation-based XRD (SR-XRD) data were collected to gain insight into possible changes to the structure of the Mn oxides. EXAFS analysis suggested the presence of  $\text{Ca}^{2+}$  (5 mM) promoted a change in the local structure of Mn oxides from one with hexagonal layer order (with no amendment or with the addition of 5 mM  $\text{Mg}^{2+}$ ) to one with orthogonal layer order, a structure reported to have less reactivity. However, based on qualitative analysis of SR-XRD, long-range order of the biogenic Mn oxides was not affected by the presence of either  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . Therefore, it does not appear that changes in the reactivity of biogenic Mn oxides due to structural changes occurred resulting in the lack of an effect of  $\text{Ca}^{2+}$  on the oxidation of bio- $\text{UO}_2$ . Rather the  $\text{Ca}^{2+}$  likely provides greater stability to bio- $\text{UO}_2$ , even during active  $\text{MnO}_2$  formation.

*Vanadium.* Vanadium is commonly found at the DOE site at Rifle, CO as the site was previously both a U and V milling site. Interestingly, U and V can form a relatively immobile phase as uranyl vanadate, e.g.,  $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2$  or  $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2$ . Therefore, once U(IV) is oxidized by  $\text{MnO}_2$ , U(VI) may be associated with  $\text{MnO}_2$  via adsorption or may precipitate through the formation of uranyl vanadate. Initially, the effect of V (0, 10, 100  $\mu\text{M}$ ) on the oxidation of monomeric U(IV) by  $\text{MnO}_2$  and/or  $\text{O}_2$  was examined. In the presence of 100  $\mu\text{M}$  V(V), a decrease in  $\text{HCO}_3^-$ -extractable U(VI) was observed which suggests either (i) less U(VI) was formed or (ii) although U(VI) is formed it became less extractable. X-ray Absorption Near Edge Spectroscopy (XANES) analysis showed the fraction of U(VI) associated with the solid phases

was not significantly different among the conditions tested. This suggested that U(VI) in the form of uranyl vanadate is being produced which is not  $\text{HCO}_3^-$ -extractable. This was further verified by extracting uranyl vanadate solutions aged for various times (2-15 days) with  $\text{HCO}_3^-$ . There was less extractable U(VI) with increasing time of aging, suggesting uranyl vanadate is not susceptible to  $\text{HCO}_3^-$ -extraction and that V does not have any impact of U(IV) oxidation. Formation of the uranyl vanadate was also verified by electron microscopy. EXAFS spectra of the solid phases were collected to investigate the presence of uranyl vanadate, U(VI) sorbed to biogenic  $\text{MnO}_2$ , and possibly other U species and are currently being analyzed.

*Selenium.* Selenium, toxic but essential in trace amounts, is an element that can be found at the DOE site at Rifle, CO. We explored the effect of Se, i.e., Se(IV) and Se(VI), on Mn(II) oxidation by the model Mn(II) oxidizing bacterium, *Pseudomonas putida* GB-1. Preliminary work showed that (i) Se(IV) was more toxic to *P. putida* GB-1 than Se(VI) as evidenced by less growth; (ii) both Se(IV) and Se(VI) had inhibitory effects on Mn(II) oxidation by *P. putida* GB-1 with Se(IV) being more inhibitory as compared to Se(VI); and (iii) *P. putida* GB-1 reduced both Se(IV) and Se(VI) to Se(0) based on XANES of the solid phases.



## **Papers and Products Delivered:**

### **Publications:**

1. Wang, Z., Xiong, W., Tebo, B.M. and D.E. Giammar (2014). Oxidative UO<sub>2</sub> dissolution induced by soluble Mn(III), *Environmental Science & Technology*, 48(1): 289-298. dx.doi.org/10.1021/es4037308
2. Wang, Z., Tebo, B.M. and D.E. Giammar (2014). Effects of Mn(II) on UO<sub>2</sub> dissolution under anoxic and oxic conditions, *Environmental Science and Technology*, 48(10): 5546-5554. dx.doi.org/10.1021/es5002067
3. Wang, Z., Lee, S.-W., Kapoor, P., Tebo, B.M., and D.E. Giammar (2013). Uraninite oxidation and dissolution induced by manganese oxide: A redox reaction between two insoluble minerals, *Geochimica et Cosmochimica Acta*, 100(1): 24-40. dx.doi.org/10.1016/j.gca.2012.09.053,
4. Wang, Z., Lee, S.-W., Catalano, J.G., Lezama-Pacheco, J.S., Bargar, J.R., Tebo, B.M. and D.E. Giammar (2013). Adsorption of uranium(VI) to manganese oxides: X-ray absorption spectroscopy and surface complexation modeling, *Environmental Science & Technology*, 47: 850-858. dx.doi.org/10.1021/es304454g
5. Wang, Z. and D.E. Giammar (2013). Mass action expressions for bidentate adsorption in surface complexation modeling: Theory and practice, *Environmental Science & Technology*, 47: 3982-3996. dx.doi.org/10.1021/es305180e
6. Giammar, D.E., Cerrato, J.M., Mehta, V., Wang, Z., Wang, Y., Pepping, T.J., Ulrich, K.-U., Lezama-Pacheco, J.S., and J.R. Bargar (2012). Effect of diffusive transport limitations on UO<sub>2</sub> dissolution, *Water Research*, 46: 6023-6032. 10.1016/j.watres.2012.08.034
7. Plathe, K.L., Lee, S.-W., Tebo, B.M., Bargar, J.R., and R. Bernier-Latmani. (2013) Impact of microbial Mn oxidation on the remobilization of bioreduced U(IV), in *Environmental Science and Technology*, vol. 47, num. 8, p. 3606-3613.
8. Plathe K.L., Suvorova, E.I. and R. Bernier-Latmani (in preparation). Micro-scale characterization of U(IV) oxidation by O<sub>2</sub>. In preparation for *Environmental Science and Technology*.
9. Lee, S.-W., Lezama-Pacheco, J.S., Plathe, K.L., Wang, Z., Giammar, D.E., Bargar, J.R., Bernier-Latmani, R., Tebo, B.M. (In preparation). Effects of oxygen and major groundwater constituents on U(IV) oxidation coupled with MnO<sub>2</sub> formation by *Bacillus* sp. SG-1.
- 10.

### **Conference Presentations:**

1. Giammar, D.E., Wang, Z., Tebo, B.M., and J.G. Catalano, Influence of water chemistry on metal sorption to manganese oxides, *247<sup>th</sup> ACS National Meeting*, March 16-20, 2014, Dallas, Texas.
2. Wang, Z., Xiong, W., Tebo, B., and D. Giammar, Oxidative UO<sub>2</sub> dissolution by soluble Mn(III), *246<sup>th</sup> ACS National Meeting*, September 8-12, 2013 Indianapolis, Indiana.
3. Wang, Z., Lee, S.-W., Wu, W., Tebo, B.M., and D.E. Giammar, Different effects of Mn(II) on UO<sub>2</sub> dissolution kinetics under reducing and oxidizing conditions, *245<sup>th</sup> ACS National Meeting*, April 7-11, 2013, New Orleans, Louisiana.

4. Lee, S.-W., Plathe, K.L., Bernier-Latmani, R., and Tebo, B.M. Effects of common groundwater constituents on coupled Mn(II)/U(IV) oxidation. Presented at OHSU Research Week, May 7-10, 2012, Portland, Oregon, United States.
5. Wang, Z., Lee, S.-W., Tebo, B.M., and D.E. Giammar, Oxidative dissolution of uraninite in the presence of manganese oxide, *2012 Goldschmidt Conference*, June 24-29, 2012, Montreal, Canada.
6. Plathe, K.L., Lee, S.-W., Wang, Z., Giammar, D.E., Tebo, B.M., Bargar, J.R. and R. Bernier-Latmani. Impact of biological Mn(II) oxidation on the persistence of U(IV). Presented at 2012 Goldschmidt Conference, June 24-29, 2012, Montreal, Canada.
7. Lee, S.-W.; Plathe, K.L.; Wang, Z.; Lezama-Pacheco, J.S.; Bargar, J.R.; Giammar, D.E.; Bernier-Latmani, R.; and Tebo, B.M. Effects of common groundwater constituents of coupled Mn(II)/U(IV) oxidation by *Bacillus* sp. SG-1. Presented at 2012 Goldschmidt Conference, June 24-29, 2012, Montreal, Canada.
8. Giammar, D.E. Influence of aqueous geochemistry on the oxidative dissolution of uraninite. Presented at the International Workshop 'Uranium Biogeochemistry: transformations and applications' in Monte Verità, Ascona, Switzerland, March 11-16, 2012 (organized by Rizlan Bernier-Latmani and Stephan Kraemer).
9. Wang, Z., Lee, S.-W., Tebo, B.M., and D.E. Giammar, Uranium(VI) adsorption to manganese oxides at conditions relevant to contaminated subsurface environments, 242<sup>nd</sup> American Chemical Society National Meeting, GEOC9, August 28 – September 1, 2011, Denver, Colorado.
10. Tebo, B.M., Lee, S.-W., Wang, Z., D.E. Giammar, K.L. Plathe, R. Bernier-Latmani, J.R. Bargar, K.H. Williams, P.E. Long. Manganese oxidation in the subsurface and its impact on uranium immobilization: what Mn can do for U, Department of Energy Subsurface Biogeoscience Research, PI Meeting, Washington, D.C., April 26-28, 2011.
11. Wang Z., Kapoor P., Giammar D.E., Effects of manganese oxide on the oxidative dissolution of uraninite, The 17th Annual Mid-American Environmental Engineering Conference (MAEEC), The University of Missouri, Columbia, Missouri, United States, Oct. 2011.
12. Plathe, K.L., Lee, S.W., Lezama-Pacheco, J.S., Tebo, B.M., Bargar, J.R. and R. Bernier-Latmani Fate of uranium during microbially-driven Mn(II) oxidation. Presented at the International Workshop on Uranium Biogeochemistry: Transformations and applications, March 11-16, 2012, Monte Verita, Ascona, Switzerland.
13. Plathe, K.L., Lee, S., Lezama-Pacheco, J.S., Tebo, B.M., Bargar, J.R., Bernier-Latmani, R. Fate of U(IV) during Microbially-Driven Mn(II) Oxidation in Sediments. The 21st Goldschmidt Conference, Prague, Czech Republic, Aug. 2011.
14. Tebo, B.M., Giammar, D.E., Bernier-Latmani, R., Bargar, J., Long, P., Plathe, K., Lee, S.-W., Wang, Z., Williams, K.H. (2011). Interactions of U and Mn oxides and biogeochemical cycling of redox-sensitive elements during water table rise and fall at the Rifle IFRC. Rifle IFRC Planning Meeting, Carmel, CA, March 8-11, 2011.