Biotic-Abiotic Pathways: A New Paradigm for Uranium Reduction in Sediments

Uranium, one of the most common radioactive elements on Earth, makes its presence felt in many ways. It is the primary fuel for U.S. civilian nuclear energy and is a major groundwater contaminant at sites across the US – in fact, more than 15 large and persistent uranium-contaminated aquifers are present in the western U.S. alone. Cleanup of groundwater resources is an economic, societal, and legal imperative, but the estimated cost of this effort is several billion dollars. In addition, uranium is likely to remain an important energy source worldwide. The reactions that control uranium behavior in aquifers occur at the molecular scale. They are hosted in chemically and physically complex assemblages of reactive nanoscale minerals, microbial cells, and biofilms that reside within pores between sediment grains and as grain coatings. Knowledge of these molecular-scale processes can provide breakthrough cost-saving and efficiency-boosting insights in uranium clean-up and ore extraction technologies.

Uranium is also important to the study of Earth's oceans and atmosphere across deep geological time because the relative abundance of natural uranium isotopes recorded in the rock record is sensitive to paleo-oxygen levels.

Uranium redox transitions, *i.e.*, the exchange of electrons between the 4+ and 6+ oxidation states of uranium, are of central importance to these subjects. Uranium present in aquifers as U^{6+}, the *uranyl* cation (UO_2^{2+}) (often complexed by carbonate), is undesirable because it is relatively mobile in groundwater. When present above regulatory concentration thresholds, it is very difficult to clean up. Conversely, U^{4+} is relatively insoluble, especially if it can be stabilized as uraninite (UO_2). For this reason, there is much interest in reducing uranyl to U^{4+} *in situ* in contaminated aquifers. The opposite redox reaction, oxidation to U^{6+}, is desired to extract U^{4+} from uranium deposits. Modern *in situ* leach techniques are designed to extract uranium using liquids that are flushed through ore bodies in a fashion similar to fracking, currently in use for oil and gas recovery.

Wherever metal redox transformations occur in low-temperature (<100° C) sediments, one is almost certain to find bacteria and organic matter. Indeed, bacteria often drive metal redox cycling in aquifers. Energy is released when elements change oxidation states, and bacteria have developed metabolic systems to harvest this energy. For example, metal reducing bacteria (MRB) can reduce Fe^{3+} (present in iron oxide minerals) to Fe^{2+} and U^{6+} to U^{4+}. Sulfate reducing bacteria (SRB) reduce S^{6+} (sulfate, present in groundwater) to S^{2-} (sulfide); some SRB have the ability to reduce U^{6+}. These redox transformations are coupled to the oxidation of organic matter, which releases the electrons that end up on the metal redox partner.

Bioremediation. There is much interest in stimulating natural subsurface bacteria to reduce uranyl to UO_2 in order to mitigate mobile uranium contamination in impacted aquifers. A Lawrence Berkeley National Laboratory (LBNL) team funded by the U.S. DOE Office of Biological and Environmental Research (BER) has tested this strategy at the Old Rifle site, a uranium-contaminated site in Rifle, CO (Figure 1). This location provides an accessible and easily instrumented geochemical proxy for other contaminated aquifers in the western U.S. The LBNL team added acetate (vinegar) – a non-toxic organic substrate for bacterial growth – to the aquifer to biostimulate MRB and SRB growth and ecological dynamics in the aquifer. A group of researchers from SSRL, led by John Bargar (senior scientist at SSRL) and funded by the same DOE-BER program, worked alongside the LBNL team to understand the molecular scale reaction pathways traversed by uranium after acetate was added to the aquifer.

Such knowledge has great value to uranium remediation and ore extraction technologies, but has been quite difficult to obtain. The concentration of uranium in contaminated western U.S. aquifers is generally less than 1 mg/kg, which is below the detection limit for analysis by x-ray absorption spectroscopy (XAS), an important technique for studying metal contaminants in sediments. In addition, due to the complexity of flow paths in aquifers, there is no way to know in advance the best locations to drill for samples. And drilling is expensive; it is not possible to "oversample" the aquifer.

Figure 1. Old Rifle, CO field site (lower left-hand corner) next to the Colorado River.

A biological-abiotic uranium reduction pathway. To study uranium reduction mechanisms in the Old Rifle aquifer, it was necessary to develop innovative approaches that simultaneously addressed these challenges. Bargar's team adopted a novel approach that used existing wells in the aquifer to host *in situ* reactors filled with freshly harvested aquifer sediments, in which uranium reduction could be studied. To hydrologically and biogeochemically connect the reactors to the aquifer – an essential step to insure the study sampled aquifer processes – groundwater from the wells was continually pumped through the reactors. A small amount of additional uranium was amended to the reactors at concentrations representative of values found at contaminated sites in the region. Because the reactors were installed in existing wells, it was easy to harvest them and forensically analyze the sediments using synchrotron techniques.

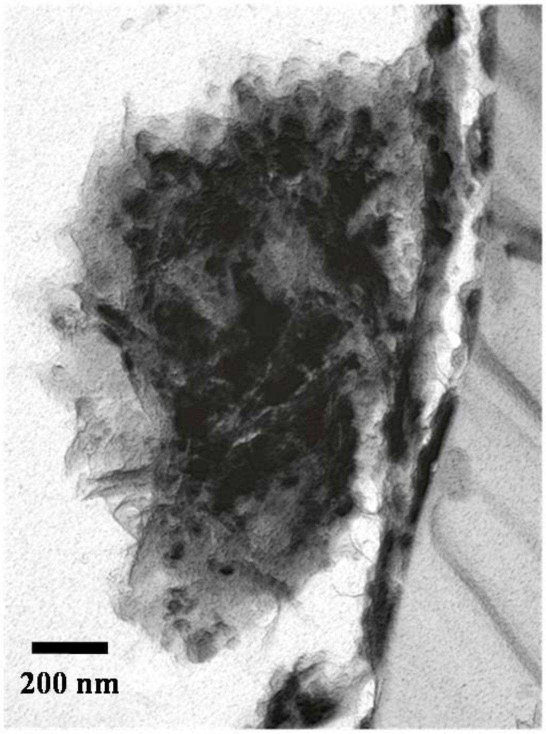

Figure 2. Bright-field TEM image of a clump platy FeS nano-minerals on a sediment grain surface. U^{4+} is present throughout this clump.

Prior to this study it was generally thought that uranyl would be reduced to U^{4+} in the aquifer by enzymes on bacterial cells, producing UO_2. Bacterial reduction of Fe^{3+} and sulfate produces iron sulfide (FeS) (Figure 2), which also can reduce uranyl to U^{4+}. While both pathways (*i.e.*, biological reduction by enzymes and abiotic reduction by FeS) have been proposed, neither had been confirmed to occur in an aquifer. The research team used x-ray imaging at SSRL Beam Lines 10-2 and 2-3 to measure the micron-scale distribution of uranium in the aquifer sediments and to determine if it was closely associated with iron oxides or iron sulfides. Most of the U^{4+} was found to be associated with FeS (Figure 3), suggesting that FeS was supplying electrons to reduce U^{6+} to U^{4+}. The team also used SSRL Beam Line 11-2 to perform XAS measurements to characterize the local molecular structure around U^{4+} at very low concentrations. These measurements showed that the dominant U^{4+} products were bound to biopolymers; UO_2 was present but only at relatively low concentrations. Electron microscopy and chemical extraction measurements confirmed and enhanced these conclusions.

These results lead to the surprising conclusion that *both* bacterial biomass *and* FeS are required to explain reduction uranyl to U^{4+} in the aquifer. At least some of the electrons required to reduce uranyl are supplied by FeS. However, biomass is required to first form the FeS, and then to chemically bind U^{4+}.

The finding that U^{4+} is complexed by biomass and that UO_2 is a less abundant product indicates that models used to predict uranium redox reactions must be updated to include complex behaviors that often occur in nature. The intimate intermixture of biomass and FeS at the scale of 100s of nanometers (revealed by electron microscopy, Figure 2) fosters reactions that could not be predicted from existing models, assuming purely biological or purely abiotic reactions. Abundant interfaces between these components are crucial reaction centers. These properties are typical of so-called *mesoscale* systems.

On a more practical note, biomass-complexed U^{4+} is less stable than uraninite, and future research in bioremediation should include a focus on ways to modify the speciation of U^{4+} to favor uraninite production. In addition, the Old Rifle site provides a model for biogeochemical reactions that occur in ore deposits. These results suggest that biomass-associated U^{4+} is likely to play important roles in the formation and economic extraction of uranium ores.

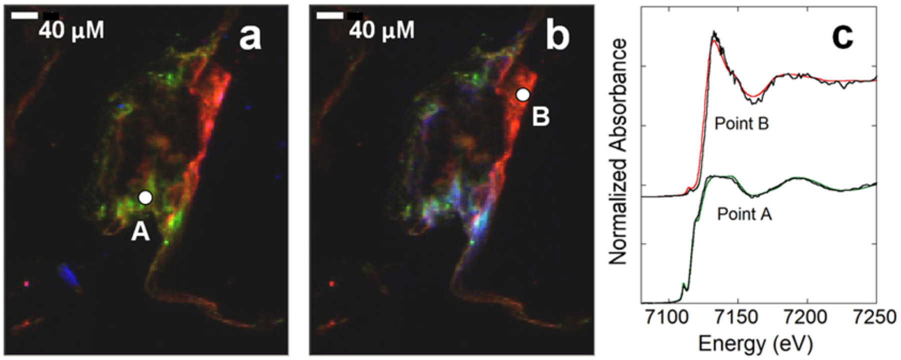

Figure 3. Panel a: Tricolor XAS image of a sediment grain from the Old Rifle aquifer after an acetate biostimulation experiment. Red shows locations where XANES are characteristic of Fe(III) oxides, green areas are characteristic of Fe(II) sulfides, and blue corresponds to Fe-bearing clays. Panel b: Same color scheme as panel a, except blue has been reassigned to show U Lα fluorescence. Note that U is co-located with Fe sulfides. Panel c: Fe K-edge XANES spectra from locations marked A and B in panels a and b. Data are plotted in black. The red spectrum is ferrihydrite, a poorly crystalline Fe^{3+} oxyhydoxide, and the green spectrum is a linear combination of 93% FeS and 7% ferrihydrite. These results illustrate that uranium occurs with FeS and not Fe^{3+} oxides. Reproduced from Reference 1.

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Reference

1. J. R. Bargar, K. H. Williams, K. M. Campbell, P. E. Long, J. E. Stubbs, E. I. Suvorova, J. S. Lezama-Pacheco, D. S. Alessi, M. Stylo, S. M. Webb, J. A. Davis, D. E. Giammar, L. Y. Blue and R. Bernier-Latmani, "Uranium Redox Transition Pathways in Acetate-amended Sediments", *Proc. Natl. Acad. Sci. USA* **110**, 4506 (2013)

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