



# Environmental Remediation Science at the Stanford Synchrotron Radiation Laboratory



## Science: Basis for In-Situ Stabilization of U(VI) Using Bacteriogenic Mn Oxides

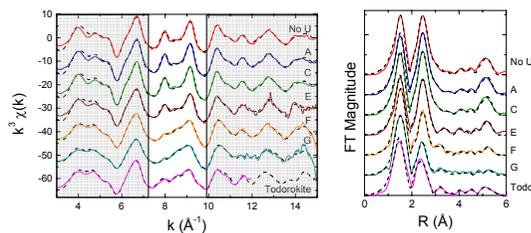
Natural Mn oxide colloids and grain coatings are ubiquitous in the environment and have extremely high sorptive capacities for heavy metals, including U(VI). Mn(II) is a common ground water solute, which is bacterially oxidized to Mn(VI) oxide under microaerophilic conditions. In-situ stimulation of Mn oxide production provides a potential route to enhanced attenuation of ground water U(VI). We have used extended x-ray absorption fine structure (EXAFS) spectroscopy and synchrotron-based *in-situ* x-ray diffraction (SR-XRD) to probe the structural mechanisms of uranium binding by manganese oxides produced by *Bacillus* sp., strain SG-1. These results indicate that U(VI) is structurally bound within tunnel-structured Mn oxides.

**Experimental:** Mn bio-oxides were produced by adding aliquots of Mn(II) and U(VI) to suspensions of *Bacillus* sp. SG-1 spores. Mn(II) concentration was kept at approximately 10µM, whereas the ratio of U:Mn varied between samples from 0.1 to 100. All samples were buffered at pH 7.8 with HEPES.

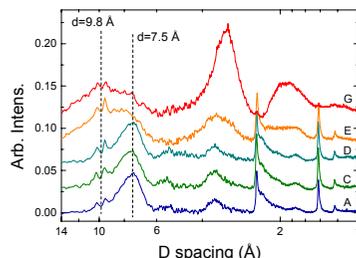
| Sample    | U(VI) Additions | Mole percent U(VI) in oxide | Mn(II) Oxidized |
|-----------|-----------------|-----------------------------|-----------------|
| No Uranyl | N/A             | N/A                         | 99.5 %          |
| A         | 50 nM           | 0.02 %                      | 99.2 %          |
| B         | 100 nM          | 0.02 %                      | 99.2 %          |
| C         | 500 nM          | 0.31 %                      | 99.4 %          |
| D         | 1 µM            | 0.28 %                      | 99.2 %          |
| E         | 4 µM            | 2.6 %                       | 92.9 %          |
| F         | 10 µM           | 9.2 %                       | 77.9 %          |
| G         | 20 µM           | 32 %                        | 36.8 %          |

### Mn EXAFS: presence of U(VI) alters structure.

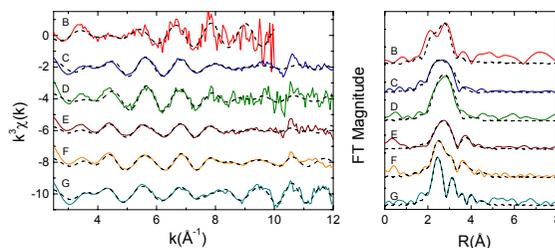
Mn bio-oxides show a progressive evolution of structure in the region of 7-10 Å<sup>-1</sup> (highlighted). The sharp positive node at ~8 Å<sup>-1</sup>, which is present at low U(VI) (e.g., sample A), indicates a hexagonal layered Mn oxide. With increasing U(VI), this feature disappears. The resulting spectral shape is characteristic of todorokite, a tunnel-structured Mn oxide. Fits to the EXAFS show that the out-of-plane bending of the layers increases from about 4% (flat layers) at low U(VI) to >20° (layers bent into tunnels) at high U(VI).



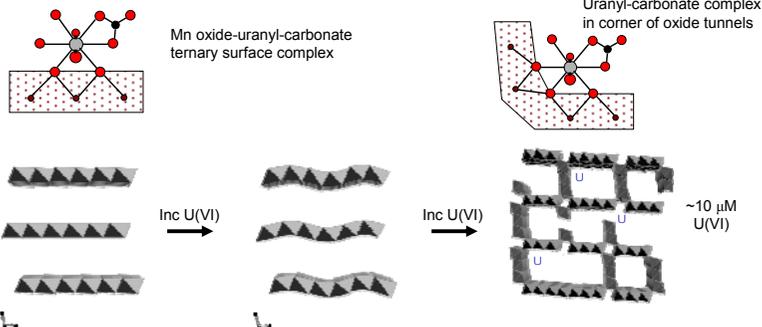
**In-situ SR-XRD: presence of U(VI) alters structure.** At low U(VI), the Mn bio-oxides resembles a poorly crystalline hexagonal layered manganese initially with a prominent 7.5 Å basal plane peak. Increasing U(VI) leads to basal peak broadening and an increase of the basal plane spacing toward 9.8 Å, which is characteristic of both expanded, hydrated layer manganates and tunnel manganates such as todorokite. Diffuse scattering at 3.25 Å and 1.9 Å, which are consistent with a todorokite-like tunnel structure containing U, become intense as U(VI) increases. Particle size is estimated to be ~ 1.2 nm based on the 9.8 Å peak width.



**U EXAFS: edge- and tunnel sites.** At low U(VI) (samples B, C), residual EXAFS (O<sub>org</sub>, O<sub>eq</sub> removed) are dominated by scattering from carbonate ternary ligands and Mn at 3.3 Å, indicative of bidentate ternary surface complexes on Mn bio-oxides. At higher U(VI) (e.g., sample G) strong 2<sup>nd</sup>-shell structure is present and suggests the existence of additional Mn shells. Potential sites for U(VI) incorporation into a todorokite-like structure were examined and only one site (tridentate corner complex, illustrated below) provided reasonable fit results.



**Conclusions:** At [U(VI)] ≤ 4 µM, U(VI) bonds to edges or surfaces of layered Mn bio-oxides. As U(VI) concentration approaches 10 µM, a structural transition to a nano-crystalline tunnel-structured Mn bio-oxide occurs, and U(VI) is increasingly bound at obtuse corner sites in the tunnels. This work strengthens the scientific basis using bacterial Mn oxidation for enhanced attenuation of U(VI).



**References and Acknowledgments:** This work is published in ES&T 40, 771-777 (2006). This work was supported by DOE-BER ERSD and by NSF-CRAEMS. Facilities at SSRL are supported by DOE-BES, DOE-BER, and NIH-NCRR.

## User Support & Activity

The SSRL Environmental Remediation Science Program supports BER ERSD-funded scientists and their collaborators at SSRL through an integrated approach involving direct hands-on support, technique development, education & outreach, and instrument development.

www-ssrl.slac.stanford.edu/mes/remedi/index.html

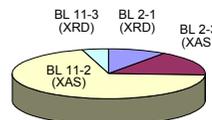
Techniques supported by this program:

- XANES/EXAFS
- In-situ XRD
- Chemical imaging
- µ-XANES/EXAFS
- µ-XRD

Contacts: Sam Webb or John Bargar: samwebb@slac.stanford.edu, bargar@slac.stanford.edu



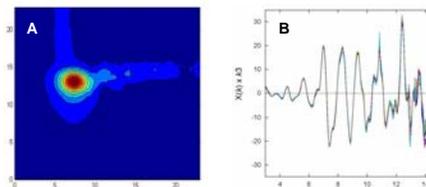
SSRL beam stations used for ERSD Research, normalized to ERSD shifts



Eleven BER-ERSD projects conducted research at four SSRL beam stations in FY 05, using 11% of the total time available at these stations. At BL 11-2, which was the station most frequently utilized by ERSD researchers, 26% of the total station time was used by ERSD projects. Support for these activities is also provided by SSRL (DOE-BES) and by the SSRL SMB program (DOE-BER and NIH-NCRR).

## Hard X-ray Microprobe

We are commissioning a microprobe optimized for µ-XAS, µ-XRD, and µ-XRF measurements on radionuclides of interest to ERSD researchers including U, Np, Pu, Am, and Tc. The facility will also provide experimental capability for other important metals, including Cr, As, Pb, and Sr. µ-EXAFS measurements on a 10 µm-diameter Mo wire (20 KeV) show a high degree of reproducibility and low noise, suggesting that the mechanical stability of the system is adequate for planned measurements.

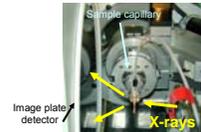


A. 2-D intensity map of beam focus at BL 2-3. Beam dimensions are 2 x 2.3 µm, FWHM. B. 10 successive EXAFS scans (through a fill) at the Mo K-edge (20 KeV), measured in transmission mode from a horizontally-oriented 10 µm thick Mo wire. This test is highly sensitive to vertical beam motion because the cross sectional area of the wire, and thus the transmitted intensity, varies rapidly with vertical beam position.

## In-situ XRD

We are developing capabilities for routine *in-situ* XRD analysis of bacterial minerals as well as other complex and problematic natural samples. Important features of this effort include:

- Image plate or CCD for rapid throughput of samples and texture analysis.
- Transmission or reflection geometries.
- Flow-through capability.



Above: Transmission *in-situ* flow-through diffraction at SSRL BL 11-3



Left: Graphical user interface developed for *in-situ* XRD data reduction at SSRL.

Right: *In-situ* flow-through XRD measurements of manganese oxides (δ-MnO<sub>2</sub>) reacting with Co(II). Note that peak amplitudes and positions evolve with time, providing crucial kinetics information. [Co(II)]=10mM, 4mL/h. Inset: two-dimensional XRD pattern showing nanocrystalline particle size.

