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 oblique corner sites in the tunnels. This work strengthens the scientific basis using bacterial Mn oxidation for enhanced attenuation of U(VI).

References and Acknowledgments:

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

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

Mn bio-oxides show a progressive evolution of structure in the region of 7-10 Å (highlighted). The sharp positive node at ~8 Å, 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 XRD: presence of U(VI) alters structure. At low U(VI), the Mn bio-oxides resemble a poorly crystalline hexagonal layered manganese initially with a prominent 7.5 Å basal plane peak. Increasing U(VI) leads to the expansion of the basal plane spacing toward 9.8 Å, which is characteristic of both hydrated layer manganates and tunnel manganates such as todorokite. Diffuse scattering at 3.25 Å and 1.9 Å, which are expanded, hydrated layer manganates and tunnel manganates such as the basal plane peak. 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 (Oeq removed) are dominated by scattering from carbonate ternary ligands and Mn at 3.3 Å, indicative of bilaterate ternary surface complexes on Mn bio-oxides. At higher U(VI) (e.g., sample G) strong 2nd-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 (todorokite corner complex, illustrated below) provided reasonable fit results.

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.

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.

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).

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.