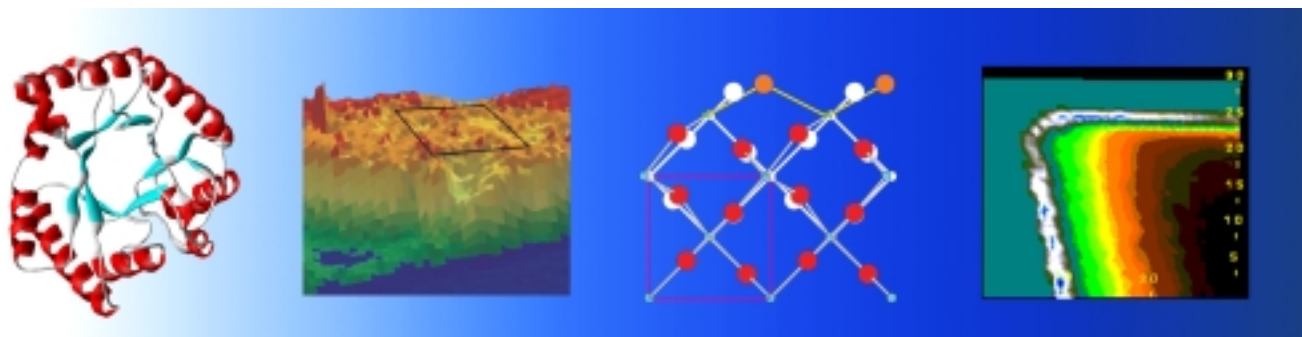


# Workshop 3: Environmental Science

Paul Fenter, organizer

Tuesday, October 9, 2001  
8:30 am–Noon & 1:30–5:00 pm



Many of the technical challenges that are inherent to advances in environmental science are ideally addressed by the unique properties of third-generation x-ray synchrotron sources. This workshop highlights recent developments spanning a diverse range of environmental phenomena (e.g., mineral-water interface structure and reactivity, actinide chemistry, groundwater contaminants, biogeochemistry, etc.) through direct structural and spectroscopic measurements at the APS. Presentations will reveal many of the interrelationships between these complex phenomena and the technical advances that make these measurements possible.

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| 8:30–9:30 am     | <b>Structure and Reactivity of <math>\alpha</math>-<math>\text{Al}_2\text{O}_3</math> (0001) and (1-102) Surfaces</b><br>T.P. Trainor, <i>The University of Chicago (GSE-CARS)</i> |
| 9:00–9:30 am     | <b><i>In Situ</i> X-ray Reflectivity Study of the Water-Muscovite (001) Interface</b><br>L. Cheng, <i>Argonne National Laboratory</i>  |
| 9:30–10:00 am    | <b>From the Still to Soils and Swamps: The (001) Surface of Muscovite in Salt and Natural Organic Matter Solutions</b><br>K.L. Nagy, <i>University of Colorado</i>                 |
| 10:00–10:30 am   | <b>Refreshments</b>  |
| 10:30–11:00 am   | <b>X-ray Microprobe Studies of Cs and Cr Adsorption in Hanford Sediments</b><br>Steve Heald, <i>Pacific Northwest National Laboratory</i>  |
| 11:00–11:30 am   | <b>Geochemistry of Cr in the Hanford Vadose Zone: Chemical Speciation Near Field to the SX Tank Farm</b><br>Samuel J. Traina, <i>The Ohio State University</i>                     |
| 11:30 am–1:30 pm | <b>Lunch</b>   |
| 1:30–2:00 pm     | <b>A Bent-crystal Optic for Resolving Fluorescence X-rays in Mixed Actinide Systems</b><br>A.J. Kropf, <i>Argonne National Laboratory</i>  |
| 2:00–2:30 pm     | <b>New Experiments Probing Metal Ion Speciation in Solution</b><br>L. Soderholm, <i>Argonne National Laboratory</i>  |
| 2:30–3:00 pm     | <b>Microprobe XAFS Studies with Sorbed Plutonium on Tuff</b><br>Martine C. Duff, <i>Westinghouse Savannah River Company</i>  |

3:00–3:30 pm	<b>Refreshments</b>
3:30–4:00 pm	<b>XAFS Investigations of Interactions of U(VI) with Minerals and Microbes</b> S.D. Kelly, <i>Argonne National Laboratory</i>
4:00–4:30 pm	<b>Opportunities for Environmental Science Research at the APS</b> Stephen R. Sutton, <i>The University of Chicago, (CARS)</i>

## Structure and Reactivity of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) and (1-102) Surfaces

T. P. Trainor<sup>1</sup>, P. J. Eng<sup>1</sup>, A.S. Templeton<sup>2</sup>, and G.E. Brown Jr.<sup>2,3</sup>

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Sorption reactions at mineral surfaces have a significant influence on the transport and chemical speciation of trace metals and metalloids in aquatic systems. The extent of solute partitioning and stability of sorbed species are related to the mode of sorption, which is strongly influenced by the structure and composition of the reactive substrate surface. While the structures of hydrated-oxide surfaces are key in determining the surface reactivity, detailed knowledge of oxide and hydrated oxide surface structures is limited. In this work we have applied the techniques of crystal truncation rod diffraction (CTR) and long-period x-ray standing wave (XSW) measurements to investigate the structure and reactivity of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) and (1-102) surfaces.

*In situ* determination of Pb(II) and Pb(II)/Se(VI) uptake on the (0001) and (1-102) surfaces of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> using the long period XSW technique showed that the (1-102) surface is roughly a factor of two more reactive than the (0001) surface. The interpretation of the reactivity differences is based on the local structure of exposed surface functional groups on the two surfaces. The structural models used in this interpretation are based on the results of CTR measurements of the hydrated surface structures. These measurements show that the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface is oxygen/hydroxyl terminated, with a 53% contracted double Al layer directly below and the surface oxygens are in two-fold coordination with the underlying aluminum. In contrast the best model for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (1-102) surface suggest that the surface is terminated by oxygens which are in single, double, and triple coordination with underlying aluminum.

## *In Situ* X-ray Reflectivity Study of the Water-Muscovite (001) Interface\*

L. Cheng<sup>1</sup>, P. Fenter<sup>1</sup>, K.L. Nagy<sup>2</sup>, M. Schlegel<sup>2</sup>, and N.C. Sturchio<sup>1,3</sup>

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The interaction of water with aluminosilicate minerals is an important process in aqueous environments. However, *in situ* structural studies of these mineral-water interfaces are still very limited. We have performed an *in situ* x-ray reflectivity study of a water-muscovite (001) interface. The high-resolution water oxygen density profile normal to the interface obtained from the best fit to the x-ray reflectivity data shows that the interfacial water interacts with muscovite (001) surface by both adsorbing to the surface at its cation sites and directly hydrating the surface oxygen atoms. In addition, the interfacial water density exhibits an oscillatory in the direction normal to the surface within about a nanometer of the surface, implying partial ordering of the interfacial water.

\*This research was supported by the Geosciences Research Program, Office of Basic Energy Sciences, U. S. Department of Energy.

## **From the Still to Soils and Swamps: The (001) Surface of Muscovite in Salt and Natural Organic Matter Solutions\***

K.L. Nagy<sup>1</sup>, M.L. Schlegel<sup>1</sup>, P. Fenter<sup>2</sup>, N.C. Sturchio<sup>3</sup>, and L. Cheng<sup>2</sup>

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The basal surface of phyllosilicate minerals is a primary surface on which sorption of environmental contaminants, natural organic matter (NOM), and life-sustaining nutrients occurs in nature. While much is known macroscopically about sorption on micas and clays, there is little direct information on the relaxation of the basal surface of these minerals, its effects on sorption mechanisms, and the form of sorbate species. We used x-ray reflectivity measurements of the muscovite(001)-aqueous solution interface in various salt and NOM solutions to characterize fundamental aspects of sorption on this permanently-charged surface at the atomistic scale.

Muscovite sheets reacted with solutions were mounted in a thin film cell, and specular x-ray reflectivity data were collected on the still-wet surfaces at the 12-BM station (BESSRC-CAT, Advanced Photon Source). Reflected x-ray intensity was reproduced on different samples and by reversibly changing the solutions in contact with a single surface. High-resolution (~1.3 Å) data were modeled using atomistic or 'optical' structural models that include surface relaxation, sorbate concentration and position, water structure, and surface roughness.

Model fits for the surface in contact with salt solutions show the density and positions of cations, water, and anions above the surface along with the extent of relaxation of the bulk mica beneath the surface. Model fits for the surface immersed in solutions of calcium chloride and fulvic acids show how the cation contributes to bonding NOM to the surface, and provide constraints on NOM thickness.

\*This work was funded by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. Department of Energy.

## **X-ray Microprobe Studies of Cs and Cr Adsorption in Hanford Sediments**

Steve Heald, Jim McKinley, and John Zachara, *Pacific Northwest National Laboratory, Richland, WA 99352 USA*

Millions of gallons of toxic and radioactive waste are stored at the Hanford site. Some of the waste has leaked into the surrounding soil. Cs is the major radioactive component and Cr is an important toxic element, especially if present as chromate (Cr6+). The x-ray microprobe at the PNC-CAT is well suited for looking at these elements in complex sediments. It can provide 1–5 micron resolution, is more sensitive than x-ray microscopy, and can provide valence information. The Cs is known to concentrate on micaceous minerals, and extensive measurements have been made on Cs exposed micas. The Cs is found to concentrate at cracks and weathered edges, possibly where K is depleted. However, microXAFS measurements comparing areas with high and low Cs concentration showed little structural difference. The Cr studies were made on contaminated sediments from core samples obtained by drilling under leaking tanks. Elemental maps of total Cr and chromate were obtained by imaging at different excitation energies. Results for several different sampling depths will be compared.

## **Geochemistry of Cr in the Hanford Vadose Zone: Chemical Speciation Near Field to the SX Tank Farm**

Samuel J. Traina<sup>1</sup>, Yongtian He<sup>1</sup>, Chia-chen Chen<sup>1</sup>, Jeffrey G. Catalano<sup>2</sup>, Jeffrey A. Warner<sup>2</sup>, Gordon E. Brown, Jr.<sup>2,3</sup>, M. Newville<sup>4</sup>, Steven R. Sutton<sup>4,5</sup>, Calvin C. Ainsworth<sup>6</sup>, and John M. Zachara<sup>6</sup>

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Chromium is a common constituent of the many of the high-level waste storage tanks at the DOE's Hanford site. Indeed millimolar concentrations of dissolved chromium (as Cr(VI)) were present in the REDOX wastes contained within the SX Tank Farm. These wastes were highly corrosive, self-boiling, hyper alkaline fluids that induced containment failure of the single-walled storage tanks and release of Cr-containing fluids into the underlying vadose zone. Indeed total Cr concentrations as great as 37,000 ppm have been identified in the underlying sediments. Unfortunately the soils and sediments present at the Hanford site are alkaline and the sorption of Cr(VI) to geoparticles is not expected to be significant. However, under sufficiently alkaline conditions structural Fe(II) can be released from sediment solids, resulting in the abiotic reduction of Cr(VI) to Cr(III) and precipitation of Cr(III)-containing phases. Our model laboratory experiments provide synchrotron based evidence for the homogeneous and heterogeneous reduction of Cr(VI) by sedimentary Fe(II) under hyperalkaline conditions. More importantly, Cr XANES spectra obtained from sedimentary material collected from within the contaminant plume beneath SX-108 provides evidence for some reduction of Cr(VI) to Cr(III). Nevertheless the majority of the Cr in the field samples is present as Cr(VI) and the quantity of water extractable Cr in these samples directly correlates to percent of Cr present as Cr(VI). Thus Cr present beneath the SX Tank Farm still represents a potential environmental hazard.

## **A Bent-crystal Optic for Resolving Fluorescence X-rays in Mixed Actinide Systems**

A.J. Kropf, *Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA*

A highly strained silicon crystal in the Laue geometry has been used as a large-area fluorescence analyzer for x-ray absorption spectroscopy. With an energy resolution of better than 160 eV, this instrument is capable of resolving the  $L\alpha$  fluorescence lines for neighboring actinide elements, while covering  $\sim 0.1$  sr solid angle. XAFS spectra from several mixed actinide samples will be presented, comparing the spectra obtained using different detectors. Large gains in the signal to background ratio will be demonstrated for the x-ray absorption spectra of small quantities of Pu in the presence of Np, and Np in the presence of U. In a more typical environmental system, such as U in the presence of Sr, similar gains may also be achieved.

## **New Experiments Probing Metal Ion Speciation in Solution\***

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A detailed knowledge about the speciation of redox-active metal ions in complex samples, such as those found naturally in the environment, can be very difficult to obtain. Although there are several methods available for estimating oxidation states, coordination numbers and aggregation in complex systems, these estimations often rely on

assumptions tested under much simpler conditions. We have recently developed novel in-situ spectroscopic and scattering techniques that are ideally suited for probing single-ion and aggregate speciation in complex systems. The spectroscopic experiments involve controlling the potential on a chemical system during the acquisition of x-ray absorption data. By varying the potential in a controlled manner, the speciation of a selected metal-ion can be probed as a function of the applied potential. The scattering experiments involve the use of high-energy scattering to probe the atomic structures of aggregates and colloids in solution.

\*This work has benefited from use of the Actinide Facility and the Advanced Photon Source and is supported by the U.S. DOE OBES, Chemical Sciences, under contract W-31-109-ENG-38.

### **Microprobe XAFS Studies with Sorbed Plutonium on Tuff**

Martine C. Duff<sup>a\*</sup>, Douglas B. Hunter,<sup>a</sup> Matthew Newville<sup>b</sup>, Stephen R. Sutton<sup>b</sup>, Peter Eng<sup>b</sup>, Mark L. Rivers,<sup>b</sup> Ines R. Triay<sup>c</sup>, and David T. Vaniman<sup>d</sup>

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The chemical and bonding environment of sorbed species at the rock-water interface provides information on its potential transport behavior in geologic systems. Due to prior limitations in spatial ( $\mu\text{m}$ -scale) analytical speciation techniques, research has generally emphasized the bulk spectroscopic characterization of sorbed contaminants in monomineralic environments. These studies provide valuable fundamental information on sorption processes but they do not provide information on the behavior of contaminants with heterogeneous surfaces, where multiple sites with unique chemical constituents, bonding environments and high surface free energies can exist.

To investigate sorption at heterogeneous environments on the microscopic scale, we studied the local structure of sorbed plutonium (Pu) [added as Pu(V)] on zeolitic tuff rock with microprobe x-ray absorption fine-structure (micro-XAFS) and x-ray fluorescence (micro-XRF) spectroscopic techniques at the GSECARS sector 13. Using a focused  $4 \times 7 \mu\text{m}^2$  beam, spectra were acquired at Pu-enriched regions on Mn oxide-smectite assemblages. Interpretations of the XAFS spectra show a variety of local structural environments for sorbed Pu. The absence of Pu in the second coordination shell indicates surface precipitation or polymerization of Pu did not occur. These findings suggest Pu sorption on Mn oxide-smectite assemblages involves multiple bonding environments and occurs via an inner sphere mechanism.

### **XAFS Investigations of Interactions of U(VI) with Minerals and Microbes**

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Understanding the fate of heavy-metal and radioactive contaminants such as uranium in the environment is of fundamental importance in the development and evaluation of effective remediation and sequestration strategies. In addition to the minerals commonly found in soils, bacteria and the extracellular material associated with them are thought to play a key role in determining a contaminant's speciation and thus its mobility in the subsurface. We have performed a number of x-ray absorption spectroscopy measurements to investigate the interactions between metals, minerals, and microbes. Such experiments include studies of the oxidation state and local environment of U (1) adsorbed to *Bacillus subtilis* cell walls as a function of pH; (2) exposed to green rusts in an anaerobic environment; and (3) near bio-oxidizing *Dechlorosoma suillum* in an anaerobic environment containing hydrated iron oxide. The x-ray absorption near edge structure (XANES) spectra of  $\text{UO}_3$ ,  $\text{UO}_2$ , and U (1) adsorbed to *B. subtilis*; (2) in a GR suspension; and (3) in bio-oxidized *D. suillum* clearly show that U(VI) is reduced to U(IV) by GR but not during the bio-oxidizing processes of *D. suillum* or during absorption to *B. subtilis* cell walls. These results as well as the U EXAFS results will be presented.

### **Opportunities for Environmental Science Research at the APS**

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The Advanced Photon Source offers opportunities for a wide range of environmental science research using x-ray techniques such as x-ray fluorescence microprobe, microtomography, x-ray absorption fine structure spectroscopy, surface scattering, standing waves and microcrystal diffraction. This presentation will review capabilities of beam lines currently in use in this field and will describe mechanisms for gaining access for experiments. A new sector dedicated to environmental science research is also in the planning stages.