Synchrotron resources for ERSD scientists: Synchrotron-based research at the ALS, APS, NSLS, and SSRL

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Argonne National Laboratory

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Outline

• Goals of program
• Synchrotron radiation and how you can use it
  - Technique tutorials
  - Examples from the four synchrotrons
• Introduce the people
• How to choose a synchrotron/beam line/scientific collaborator
• Upcoming X-ray “schools”
Goals of Program

- In response to feedback from scientists funded by the ERSD and in response to the ENVIROSYNCH white paper that provided recommendations for improving access to research facilities and productivity in the field of Molecular Environmental Science, ERSD has decided to:
  - Improve infrastructure of beam lines at the ALS, APS, NSLS, & SSRL
  - Provide support to scientists at the DOE labs with synchrotrons who will facilitate the use of synchrotrons by ERSD-funded scientists

Advice
- Assist users in navigating the General User Proposal process
- Assist users in choosing appropriate synchrotron and/or technique given the problem to be addressed

Collaborator/Coauthor
- Assist users in collecting data
- Analyze data and assess results
“X-ray Physics 101”

\[ v \sim c \]

\[ a \]

\[ e^- \]

radiation
Aerial view of the Advanced Photon Source
Techniques available at Synchrotrons

• X-ray absorption spectroscopy (XAS, XAFS, EXAFS, XANES, XRF, circular dichroism)
• X-ray scattering (Diffraction, X-ray standing waves)
• X-ray microscopy (STXM, XRF mapping, microdiffraction, microspectroscopy)
• X-ray tomography
• Infrared spectroscopy
• Ultraviolet spectroscopy
• Protein crystallography
X-ray-Absorption Fine Structure Spectroscopy (XAFS) Spectroscopy

- Attenuation of x-rays
  \[ I_t = I_0 e^{-\mu(E) \cdot x} \]

- Absorption coefficient
  \[ \mu(E) \propto \frac{I_t}{I_0} \]

ALS, APS, NSLS, SSRL

\[ \text{Energy (eV)} \]

\[ \begin{array}{c}
17200 \\
17600 \\
18000 \\
\end{array} \]
**X-ray Absorption Near Edge Structure-(XANES)**

- Position or shape of absorption edge often depends on valence state of absorbing atoms.
Extended X-ray Absorption Fine Structure (EXAFS)

Scattered Photoelectron

Outgoing Photoelectron

Fourier Analysis
Fourier Transform of $\chi(k)$

We can use XAFS to determine atomic structure surrounding the atom that absorbs the x-ray.

- Like an atomic radial distribution function
  - Distance
  - Number
  - Type
  - Structural disorder
X-ray Microscopy:

Spatially resolve information provided by x-rays.
Resolution is dependent on the size of the x-ray probe.

X-ray fluorescence
(Elemental analysis)

X-ray scattering
(Crystal phase analysis)

Order Sorting
x,y,z

Fe

Ti

Si

0 2000 4000 6000 8000 10000
X-ray photon energy (eV)

Fluorescence intensity

9000
8000
7000
6000
5000
4000
3000
2000
1000

Sklodowskite
α-Uranophane
β-Uranophane
Boltwoodite
Sodium-Boltwoodite

Intensity (counts)
d (Å)

8.5 8 7.5 7 6.5
XAFS investigation of depth dependence on U speciation at the FRC - Kelly, Kemner, Watson, Jardine, Phillips (ANL, ORNL)
Heterogeneous Plutonium Sorption on Yucca Mtn. Tuff

P.M. Bertsch, G.S.-MacCarthy, D.T. Reed

Microprobe X-Ray Fluorescence Elemental Imaging

Fe oxide

Manganese
Sorbed Plutonium
Iron

100 µm

Mn-rich Area

Fractures in tuff

Micro-Pu-XANES studies indicate Pu(V) is oxidized to Pu(VI) in some regions and sorbed as Pu(V) in others

Low
High

Micro-XRF imaging reveals Pu(V) sorption on tuff rock occurs preferentially on Mn oxide rich areas and not on Fe oxide rich areas


Los Alamos National Laboratory

NSLS Beamline X26A
Uranium Speciation in Contaminated Hanford Sediments

J. Catalano, G. Brown (Stanford University), and J. Zachara (PNNL)

Leakage at Tank BX-102

What is the speciation of uranium in the contaminated vadose zone? Is it adsorbed onto mineral surfaces or precipitated as a solid phase?

Conclusion from EXAFS and μ-XRD: Na-boltwoodite is dominant U-containing phase.

Why is this information important?

• Na-boltwoodite is much less soluble than other uranophane minerals in Hanford porewater. U release will be slow in comparison to adsorbed U.
• Provides scientifically credible basis for models of future U migration. Stakeholders and regulators have lauded this scientifically sound and rigorous approach.

X-ray micro(spectro)scopy investigations of Cr reduction by planktonic and surface-adhered bacteria

- Surface-adhered *P. fluorescens* resistant to toxic effects of Cr(VI) - apatite precipitation
- Active microbial response not needed for Cr reduction
- XRF microscopy can infer metabolic activity
- Elemental and Chemical analysis of single bacterial cells
- 150 nm spatial resolution

Environmental Mn-containing nanoparticles:
- Created by bacterial oxidation of Mn(II)
- Primary sources/sinks for Mn(II) in the environment.
- Directly impacts global carbon fixation, contaminant and nutrient cycling in soils, electron acceptor for microbial respiration.

What is this material and what are its properties?

In-situ SR-based EXAFS and WAXS:
- Primary biooxide product is nanoparticulate, highly reactive.
- Transforms into other Mn oxide phases in presence of reactants (Mn$^{2+}$, Ca$^{2+}$, etc).
- Transformations are related to thermodynamic stabilities.

Provides basis for predicting/rationalizing environmental occurrence of Mn biooxides.

Transformations greatly enhance coupling to local elemental cycles and may be exploited by microorganisms.

Infrared Spectroscopy

- Provides state-of-the-art Fourier transform infrared (FTIR) spectromicroscopy in the mid-IR region (0.01 eV to 1 eV).

- Produces 2-D spectral maps of IR absorption, with up to a few microns resolution;

- Analysis of the absorption signatures permits identification of chemical compounds present. IR spectroscopy is especially sensitive to vibrations of O-H, C-H, C-O, N-H, and C-N bonds;

- Lock-in beam stabilizer system permits high-resolution imaging of dynamic interactions;

- The low infrared photon energy and beam power density do not detrimentally affect living cells; this beamline is extremely useful for investigating live organisms and their interaction contaminants in geologic materials, over time;

- A specially-designed sample mount provides opportunities to more thoroughly investigate an IR sample using other complementary SR techniques, such as μXAS/μEXAFS.
**Conversion of Cr(VI) to Cr(III) on a magnetite surface and in the presence of microbes and toluene.**

- The mineral/microbe was exposed to chromate and toluene and then monitored over time using IR spectromicroscopy.
- After five days, the images showed a significant decrease in the chromate and toluene at the same positions as the living cells, which were identified by amide absorption bands (Holman et al., 1999)
μTomography 8.3.2

- **Absorption tomography** in the 3-60 keV photon energy range;
- **Recently commissioned**: initial user experiments in progress.
- Well suited to **penetrate geological samples** that are several centimeters wide;
- Permits nondestructive, micro-resolution, **3D characterization** of the interior structure of samples;
- 3D data can be acquired in minutes, which permits the **imaging of flow phenomena and dynamically evolving processes** (such as pore clogging) in real time;
- Expected **resolution 0.5 microns** (resolution of 2 microns has been achieved to date)

**Scintillation detector**

**CCD recorder and optics**

**Sample X, Y positioner**

**Sample rotation**

*LBNL Experts: Liviu Tomutsu and Malcolm Howells*
Microtomography Example

Microtomographic images of geological materials can yield detailed information about the sample matrix and pore network. In this example, the images were used to estimate pore-scale hydrological properties and to test pore-scale simulation models (from Selin et al., 2003, LBNL).
ALS-MES STXM: Versatile, User-friendly, and Efficient

Best spatial resolution (~25 nm)
Wide energy range 80-2160 eV
High energy resolution with EPU Software/data acquisition code

Actinide incorporation into Fe oxides: Lu(III) as Am(III) homologue

Scanning Transmission X-ray Microscope (STXM)


Cluster Map

O K-edge spectra

• Oxygen K-edge spectra collected at every pixel
• Pre-edge features compared to end-member compounds: pure hematite and Lu-hematite model
• Cluster analysis reveals Lu-rich regions

STXM

• ~30 nm resolution
• C, N K-edges
• Mineral thin-sections & biomaterials

Lu expelled as a result of hematite crystallization

Lu-rich regions

Advanced Light Source (ALS) of LBNL

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Envirosynch
A national organization representing environmental science users of U.S. synchrotron sources
www.envirosync.org
How do you choose a synchrotron?

- Location (San Francisco area, Long Island, Chicago)
- Person with whom you are comfortable
- Unique capabilities of beam line at a specific synchrotron
Opportunities to learn even more:

- **NABIR PI Poster Sessions….The Swan?…..**
- **Synchrotron Environmental Science - III (SES-III)**
  - Brookhaven/NSLS-September 19-21, 2005
- **XAFS College**
  - Argonne/APS- July 25-29, 2005
- **Stanford-Berkeley Summer School on Synchrotron Techniques**
  - June 13-17, 2005