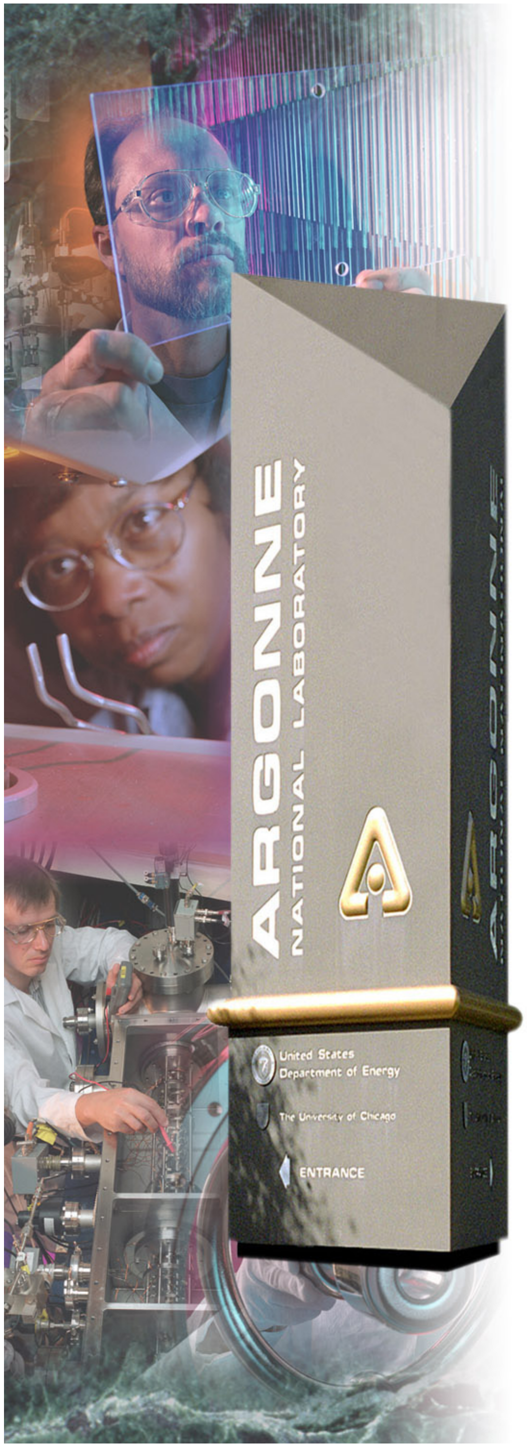


Synchrotron resources for ERSD scientists: Synchrotron-based research at the ALS, APS, NSLS, and SSRL

Ken Kemner

Molecular Environmental Science Group,
Environmental Research Division

NABIR PI Meeting

April 19, 2005

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**

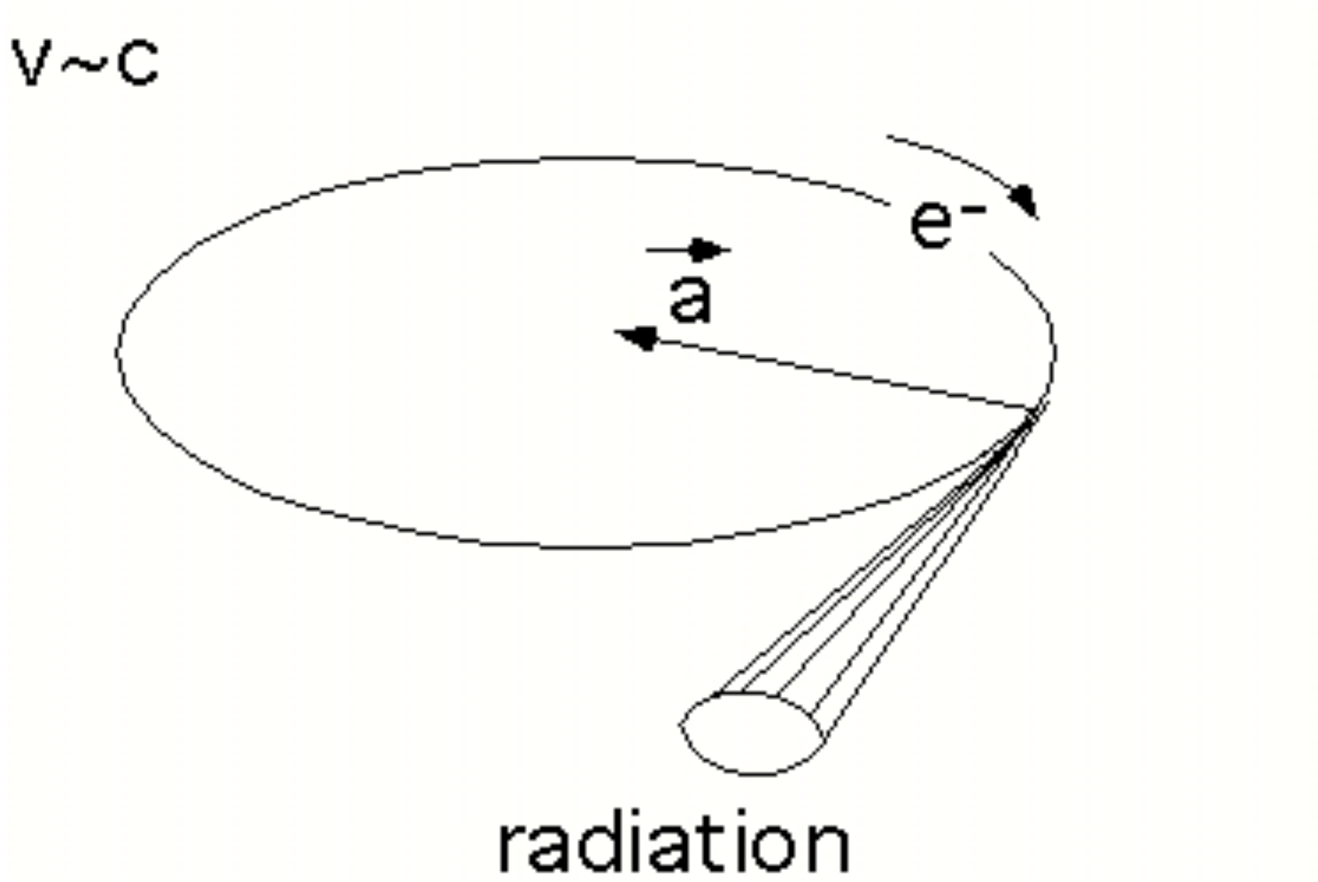
  Advice

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

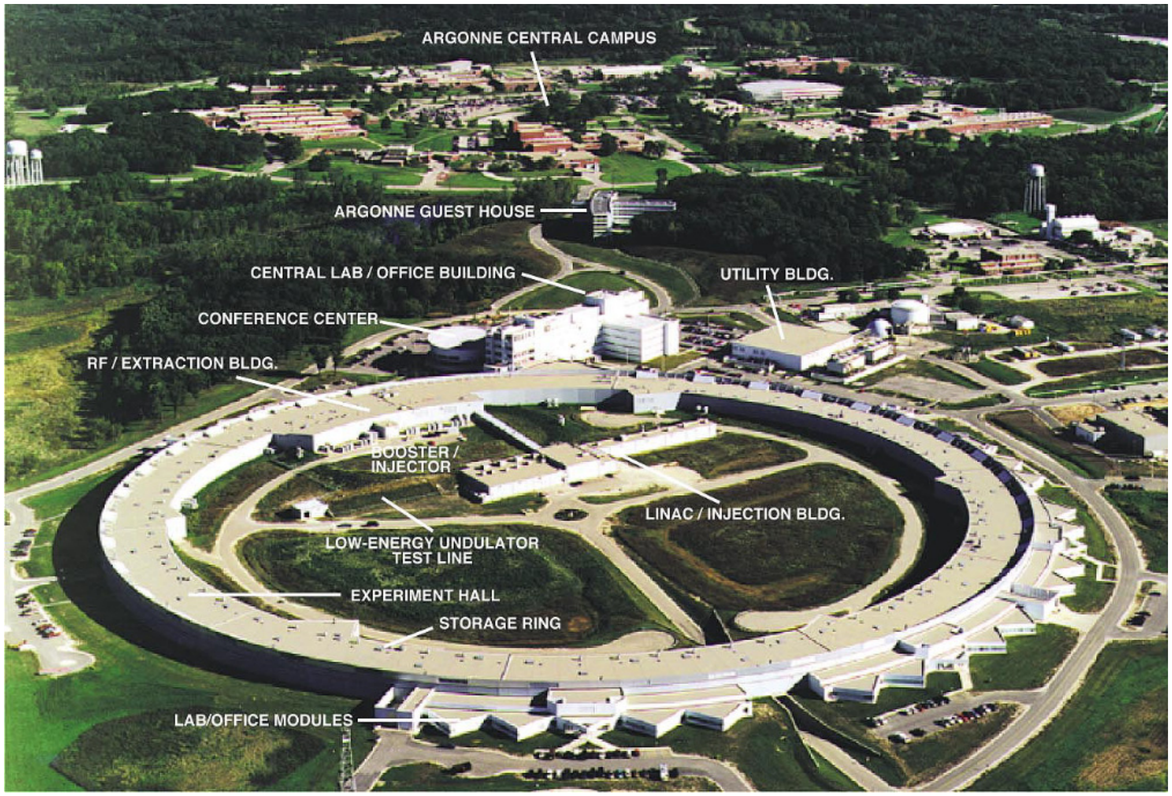
  Collaborator/Coauthor

  - Assist users in collecting data
  - Analyze data and assess results

“X-ray Physics 101”



Aerial view of the Advanced Photon Source

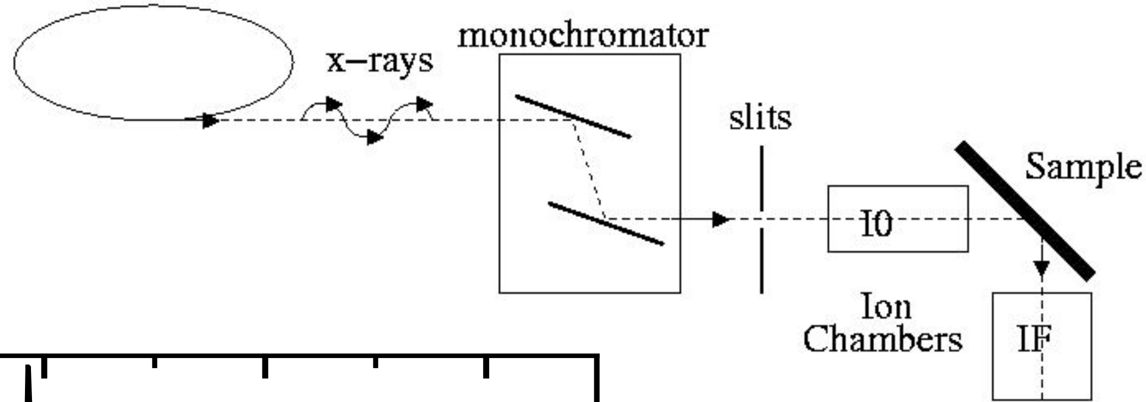


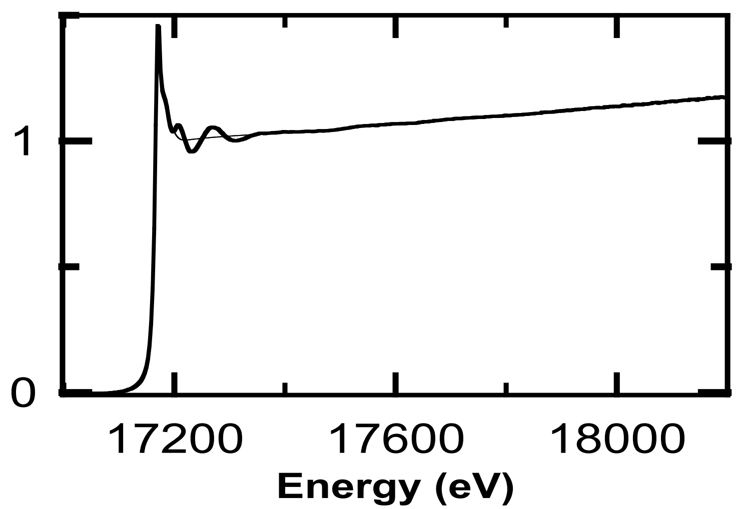
Techniques available at Synchrotrons

- **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

ALS, APS, NSLS, SSRL





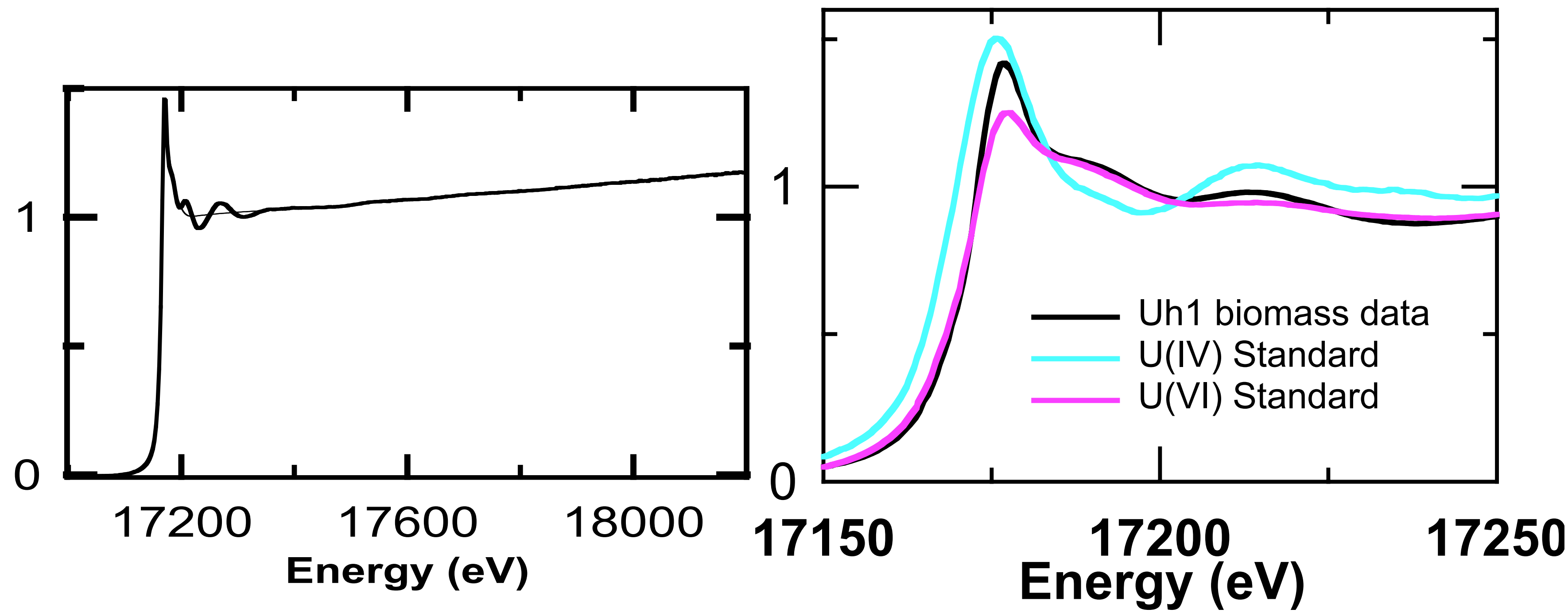
- **Attenuation of x-rays**

  $$I_t = I_0 e^{-\mu(E)\cdot x}$$

- **Absorption coefficient**

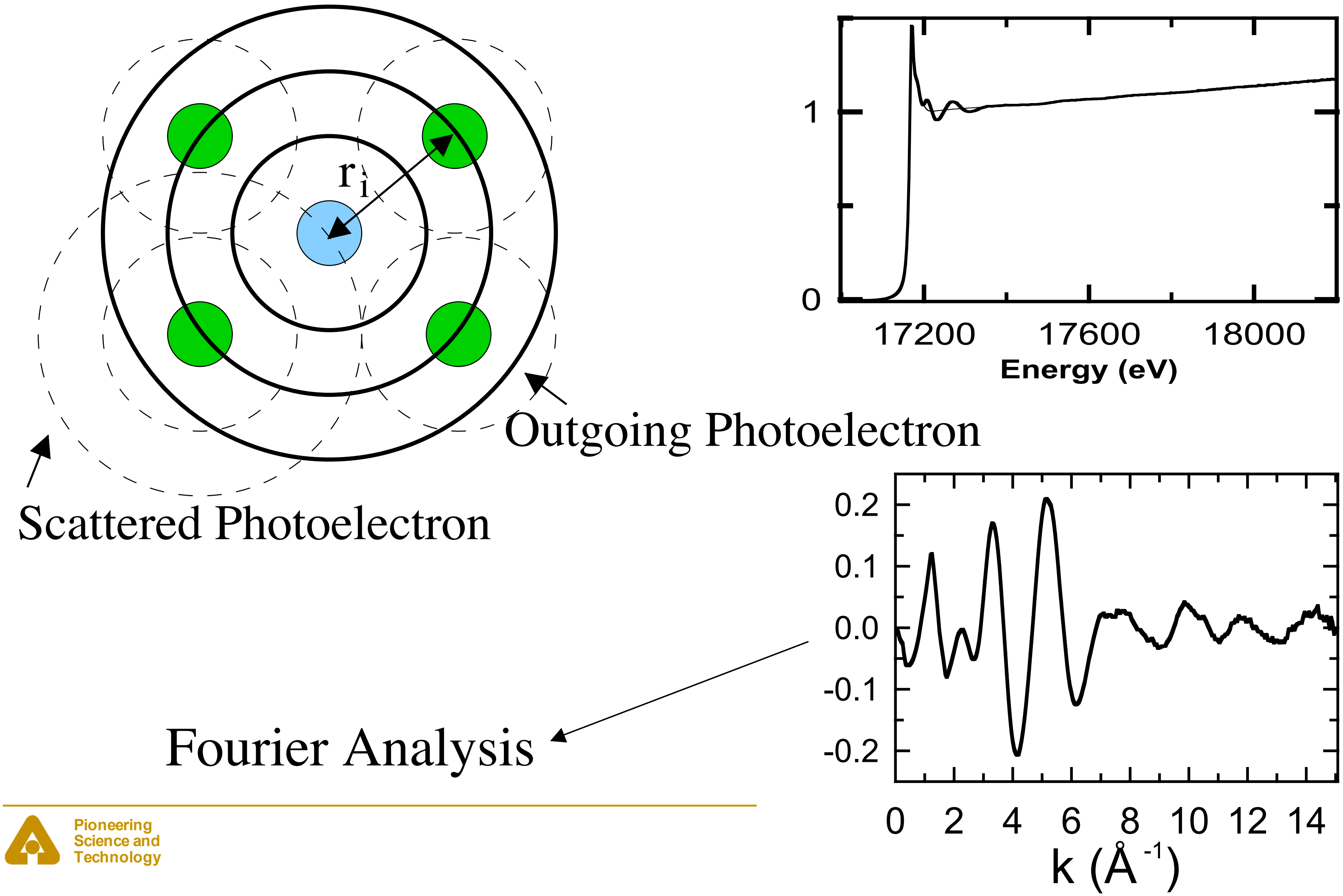
  $$\mu(E) \propto I_f/I_0$$

X-ray Absorption Near Edge Structure-(XANES)

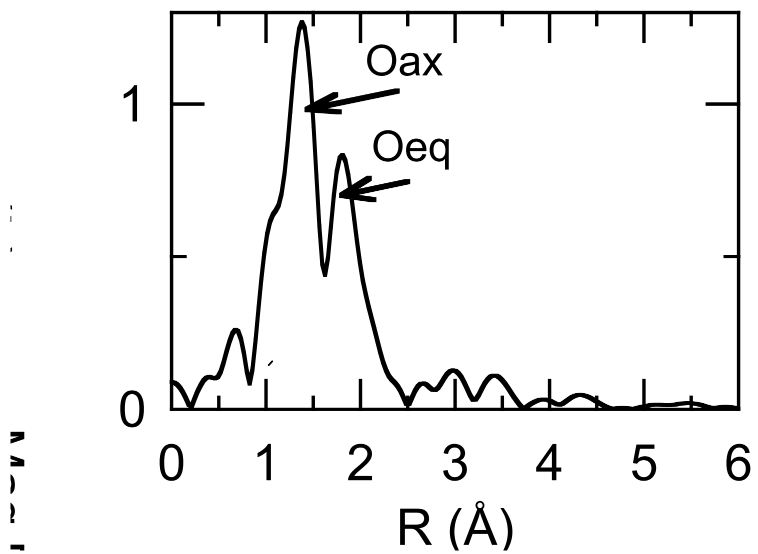


- **Position or shape of absorption edge often depends on valence state of absorbing atoms**

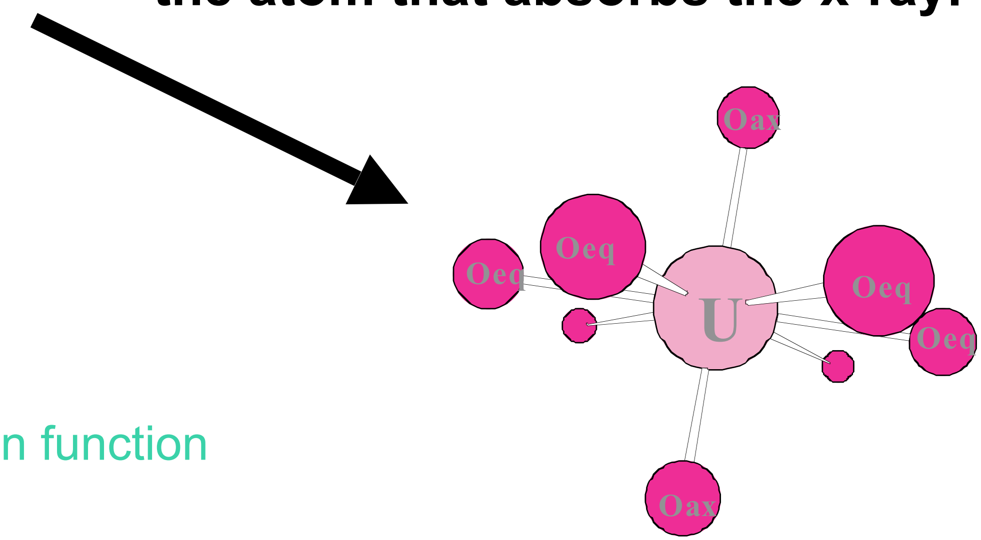
Extended X-ray Absorption Fine Structure- (EXAFS)



Fourier Transform of $\chi(k)$

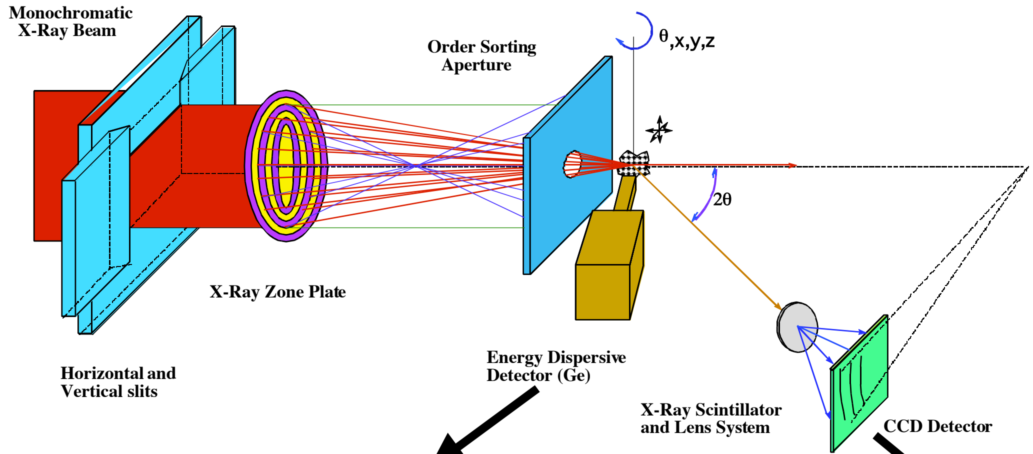


We can use XAFS to determine atomic structure surrounding the atom that absorbs the x-ray.



- Like an atomic radial distribution function
  - Distance
  - Number
  - Type
  - Structural disorder

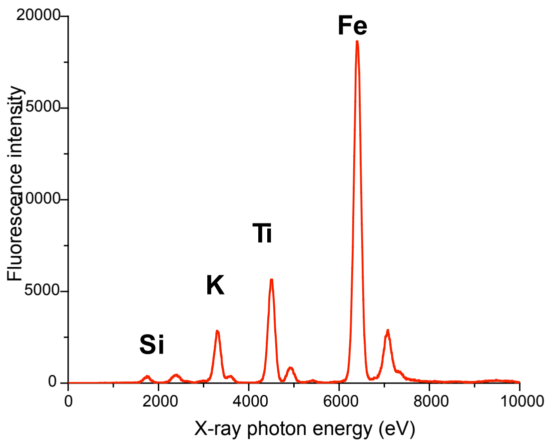
X-ray Microscopy:



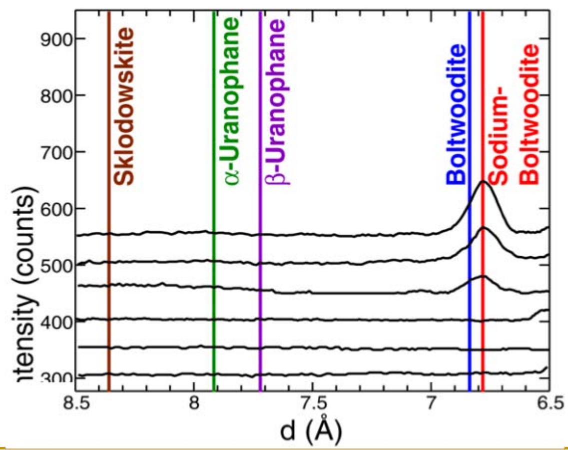
Spatially resolve information provided by x-rays.

Resolution is dependent on the size of the x-ray probe.

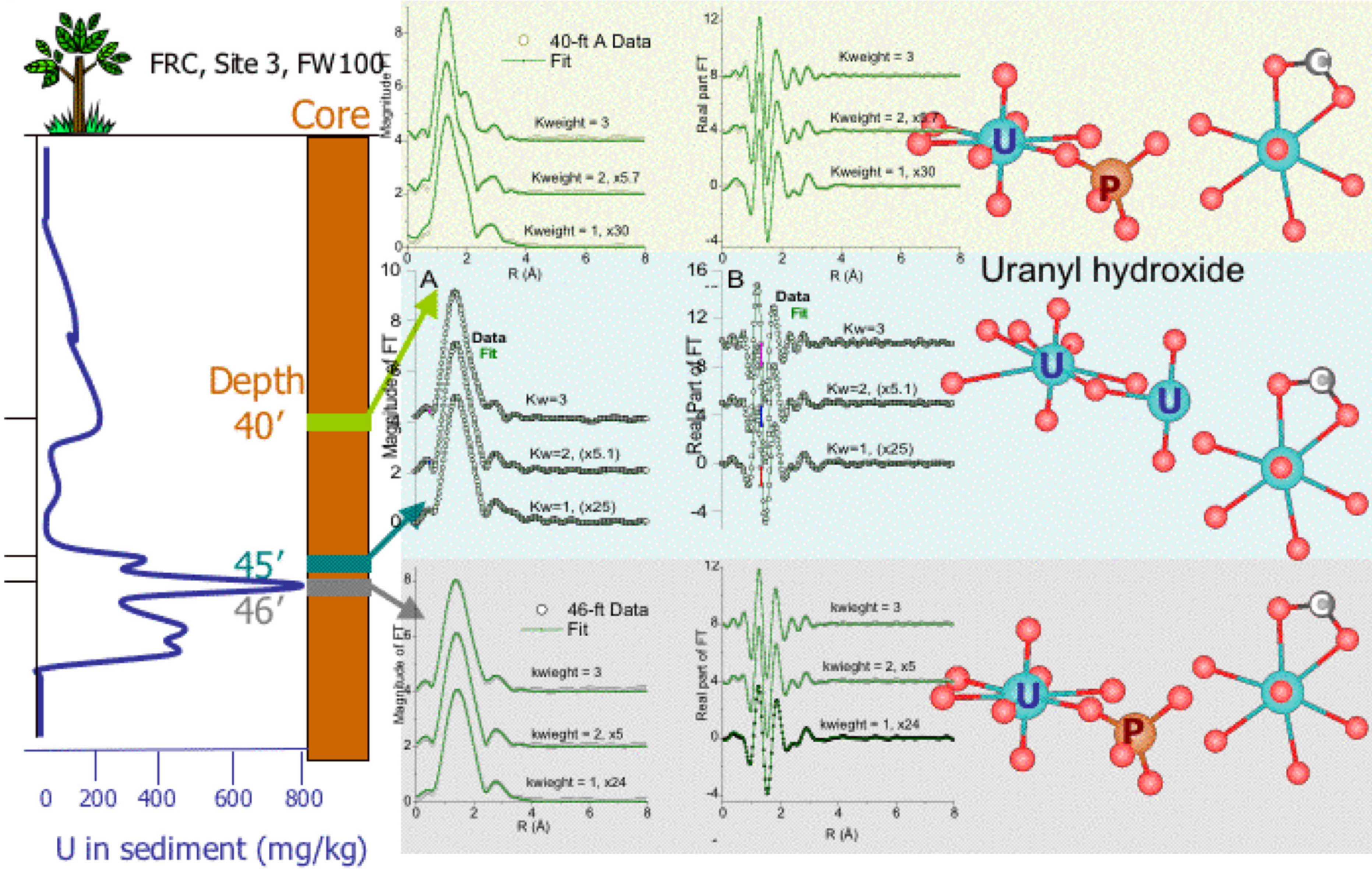
X-ray fluorescence (Elemental analysis)



X-ray scattering (Crystal phase analysis)



XAFS investigation of depth dependence on U speciation at the FRC - *Kelly, Kemner, Watson, Jardine, Phillips (ANL, ORNL)*



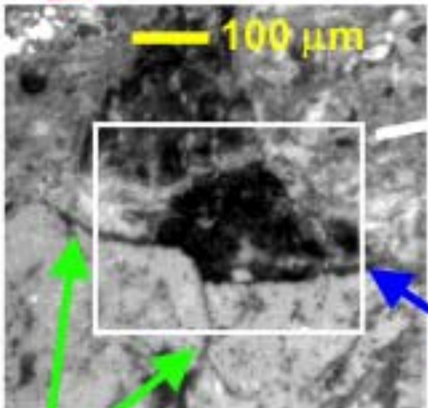
Heterogeneous Plutonium Sorption on Yucca Mtn. Tuff

M.C. Duff, D.B. Hunter, S.R. Sutton, I.R. Triay, D.T. Vaniman, S.J. Chipera
P.M. Bertsch, G.S.-MacCarthy, D.T. Reed

The University of Georgia
Savannah River Ecology Laboratory

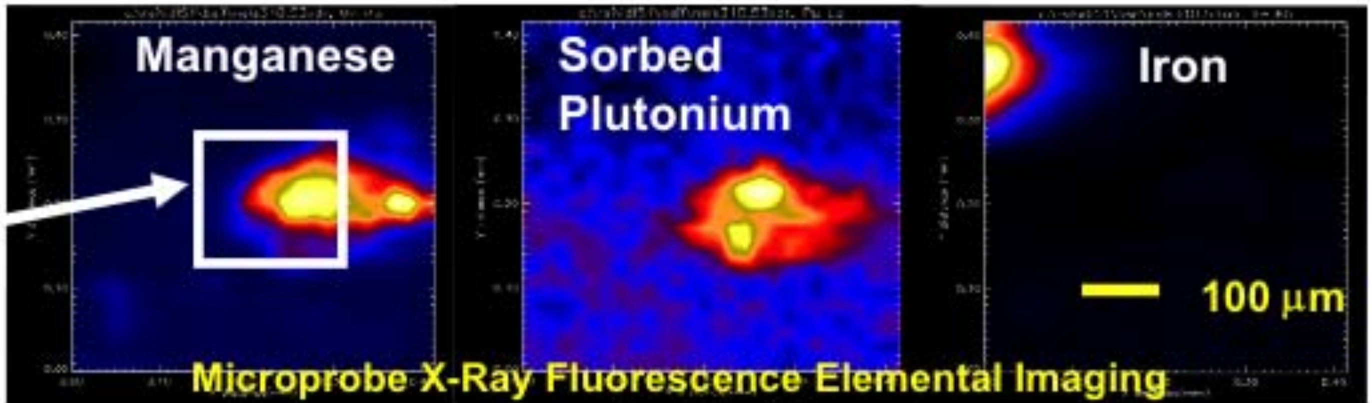
GeoSoilEnviroCARS

Fe oxide



Mn-rich Area

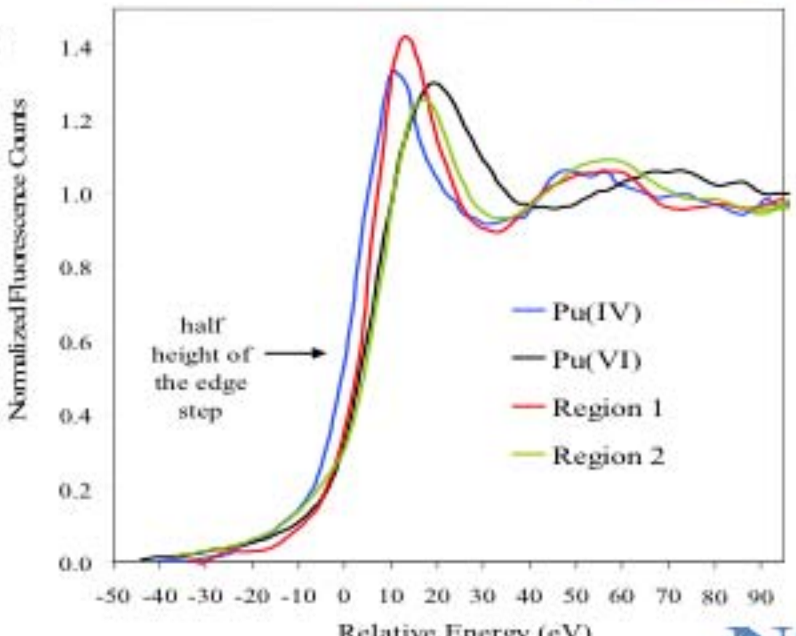
Fractures in tuff



Concentration

Low  High

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



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

Enviro. Sci. & Tech. 33 (1999) 2163

WSRC-MS-2003-00603

NSLS National Synchrotron Light Source **Beamline X26A**

Uranium Speciation in Contaminated Hanford Sediments

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

Leakage at Tank BX-102

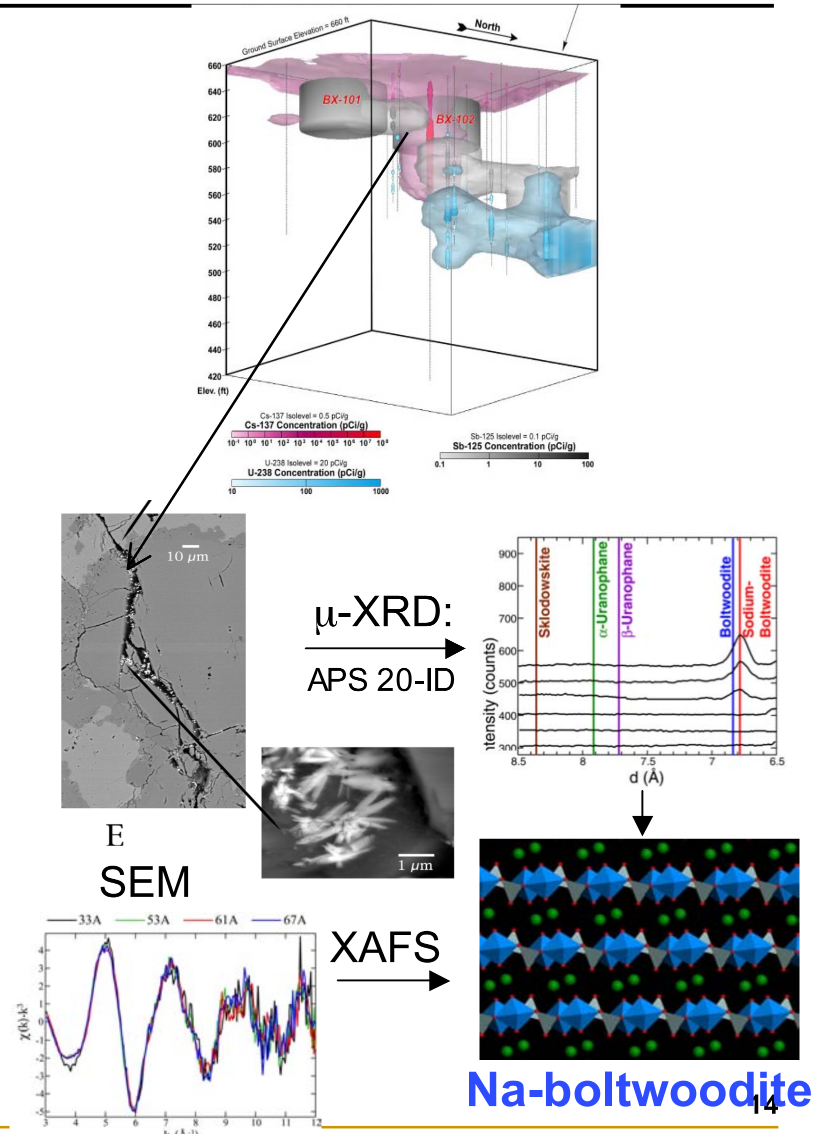
What is the speciation of uranium in the contaminated vadose zone? Is it adsorbed onto mineral surfaces or precipitated as a solid phase?

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.**

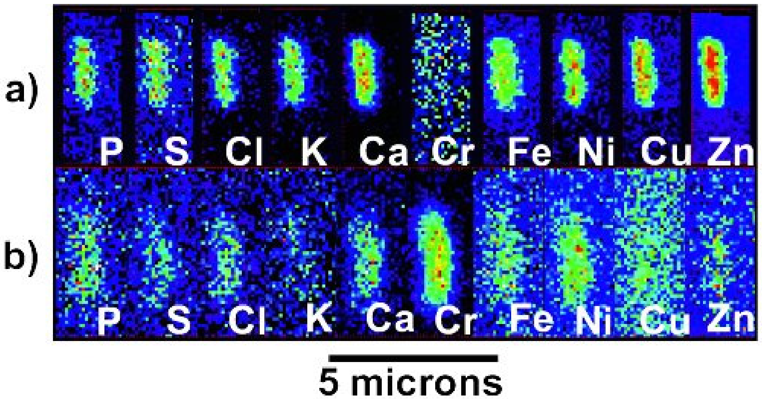
(Catalano *et al.*, *Environ. Sci. Technol. 38*, 2822, 2004)

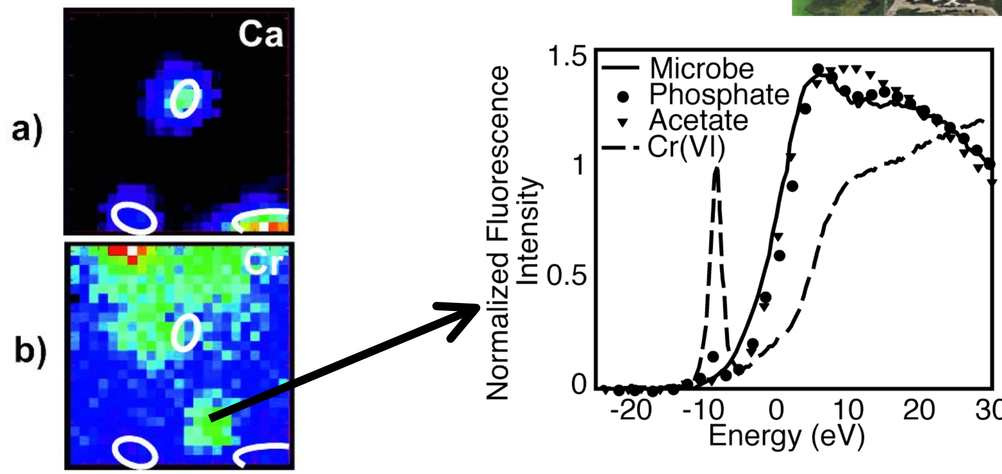


BX-102 Slant Bore Hole,
SSRL BL 11-2

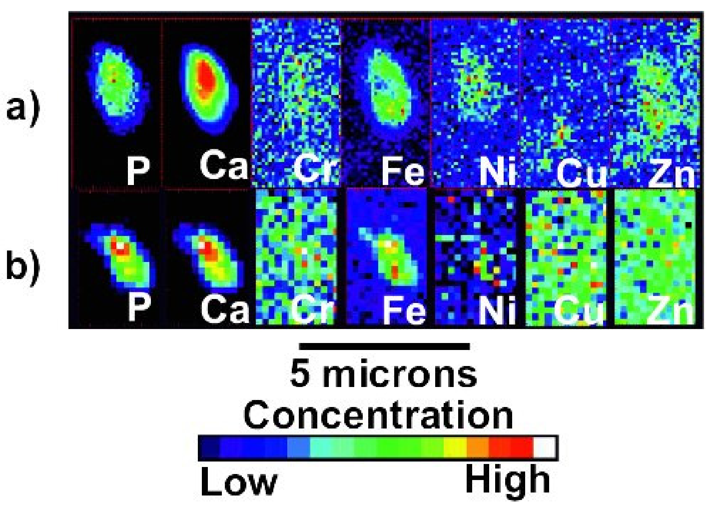
X-ray micro(spectro)scopy investigations of Cr reduction by planktonic and surface-adhered bacteria

Planktonic Cells





Surface-adhered Cells

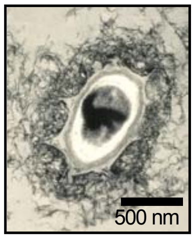


- -Surface-adhered *P. fluorescens* resistant to toxic effects of Cr(VI)- apatite precipitation
- -Active microbial response not needed for Cr reduction
- -XRF microsocpy can infer metabolic activity
- -Elemental and Chemical analysis of single bacterial cells
- -150 nm spatial resolution

Kemner, Kelly, Lai, Maser, O'Loughlin, Sholto-Douglas, Cai, Schneegurt, Kulpa, Nealson, *SCIENCE*, **306** 686-687, 2004.

Chemical Dynamics of Environmental Bacteriogenic Mn-Oxide Nanoparticles

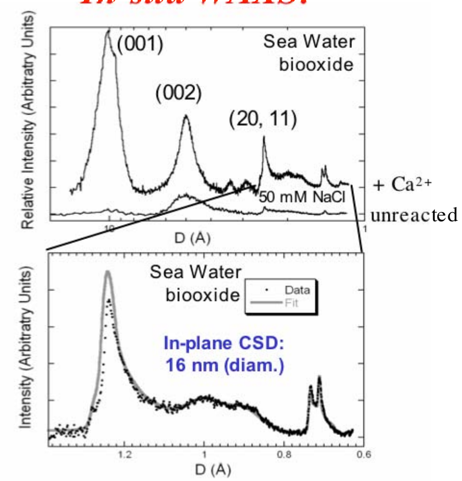
J.R. Bargar, S.W. Webb (SSRL), and B.M. Tebo (OHSU)

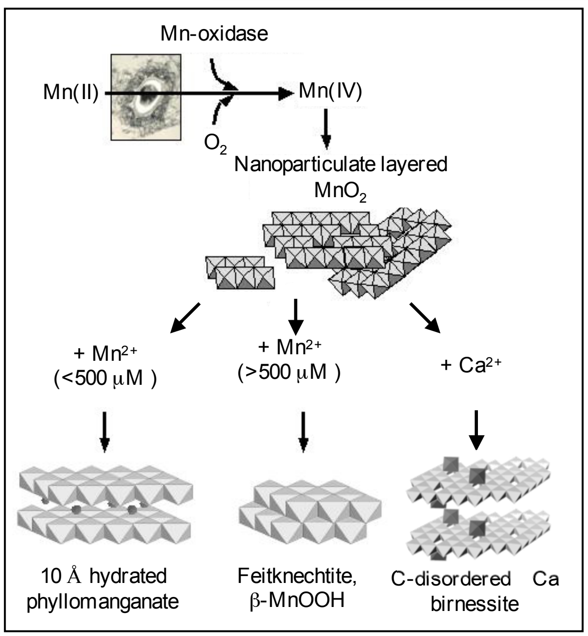


Mn-oxides encrusting cells of Bacillus SG-1

nanoparticles < 16 nm

In-situ WAXS:





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.

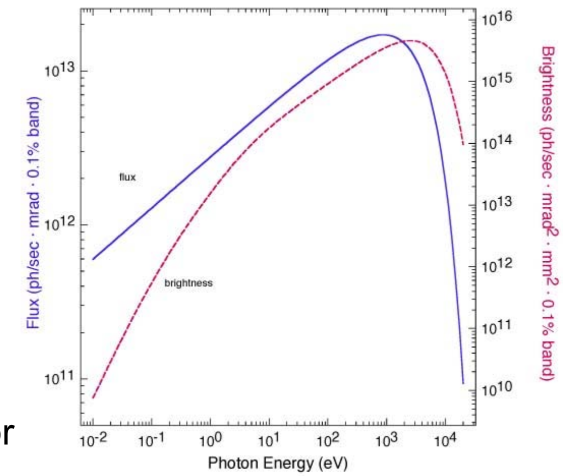
Transformations greatly enhance coupling to local elemental cycles and may be exploited by microorganisms.

J.R. Bargar et al (2005) *Am. Mineral.* 90, p. 143.; Webb et al (2005), *Am. Mineral.* (in press); Webb et al (2005) *Geomicrobiology J.* (in press).

Infrared Spectroscopy

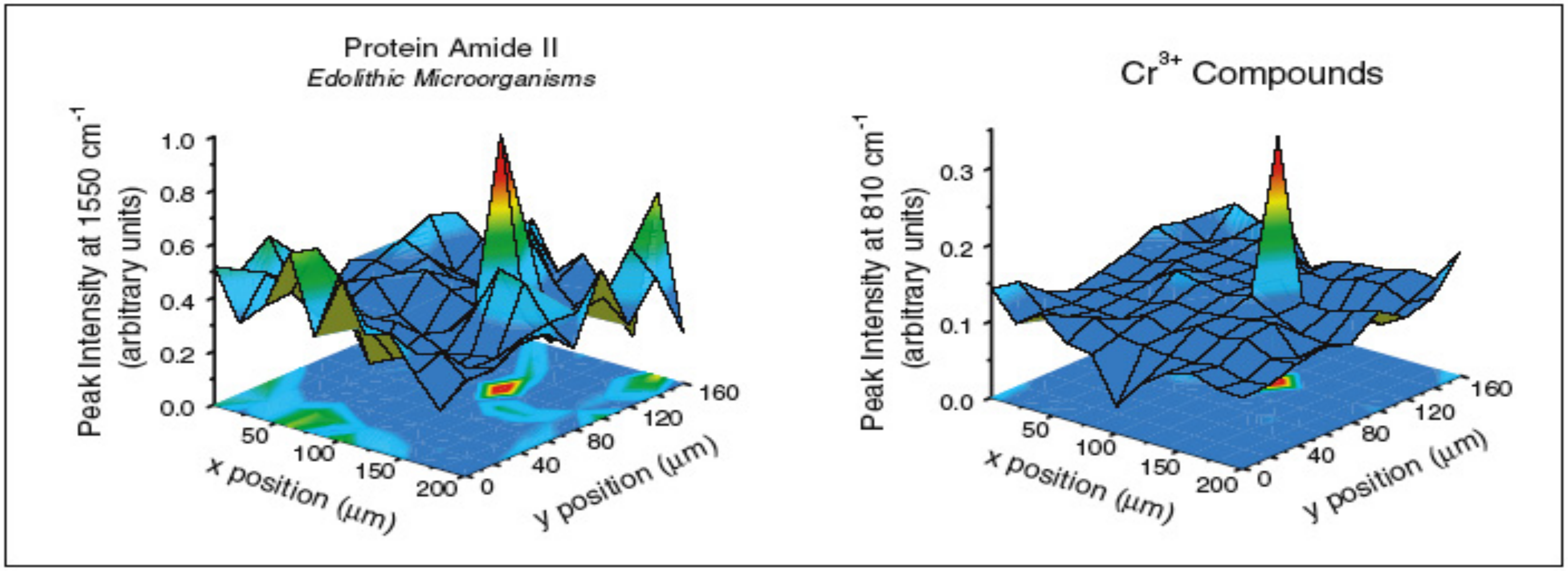
- Provides state-of-the-art Fourier transform infrared (FTIR) spectromicroscopy in the mid-IR region (0.01 eV to 1 eV).
- Produces 2-D spectral maps of IR absorption, with up to a few microns resolution;
- Analysis of the absorption signatures permits identification of chemical compounds present. IR 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.

IR 1.4.3



Flux and brightness curves for bend magnet.

IR Example

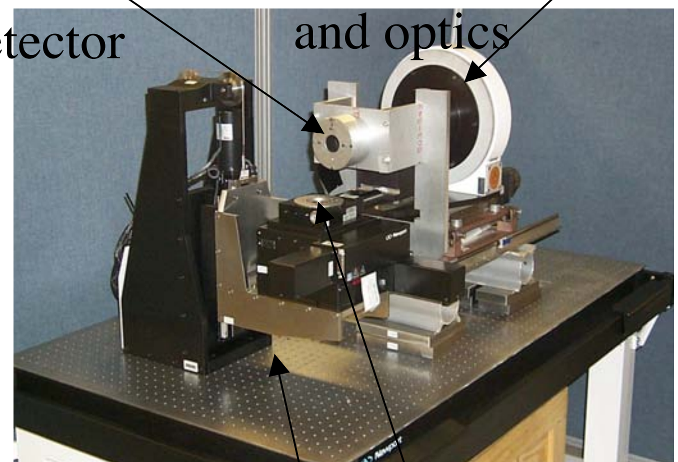


Conversion of Cr(VI) to Cr(III) on a magnetite surface and in the presence of microbes and toluene.

- 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)

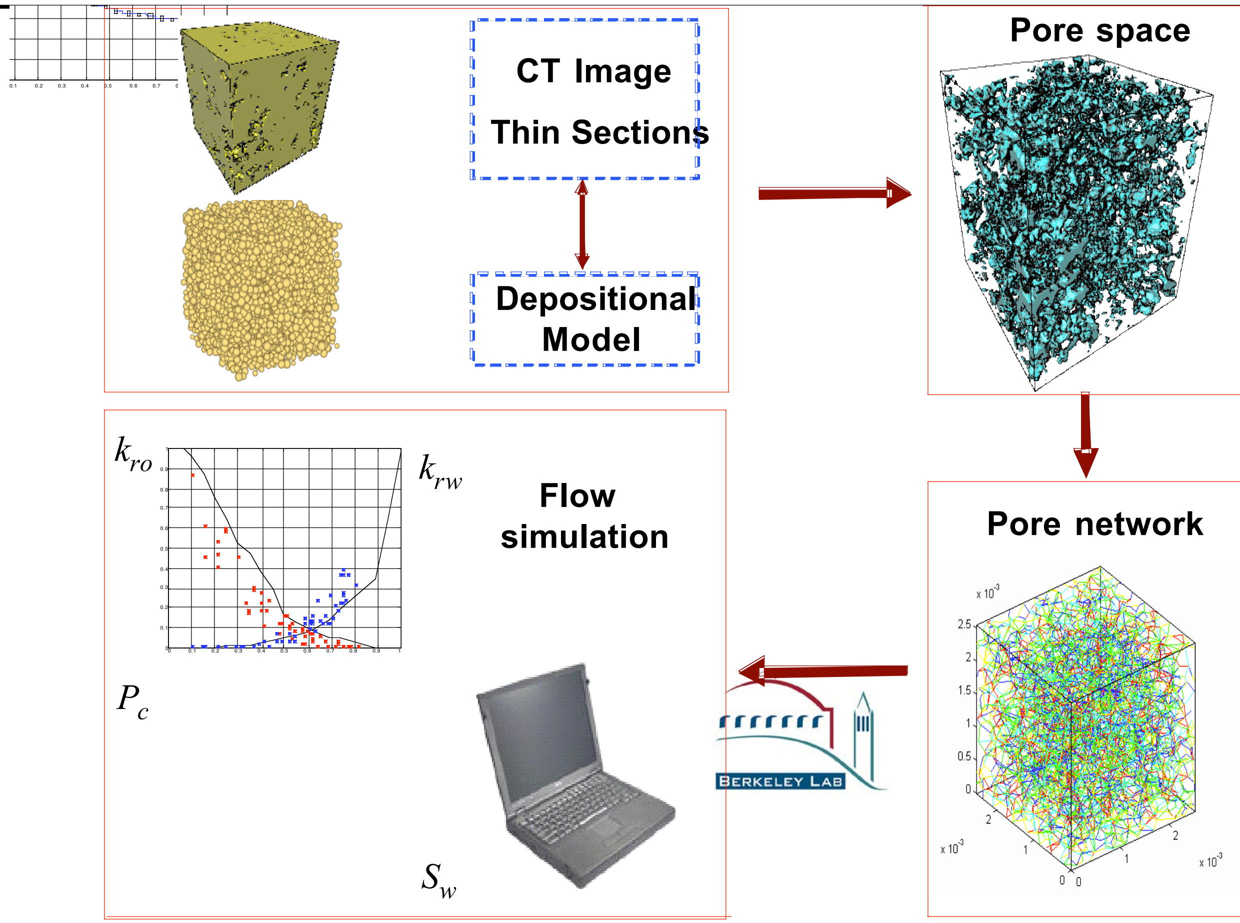
μTomography 8.3.2

- 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)



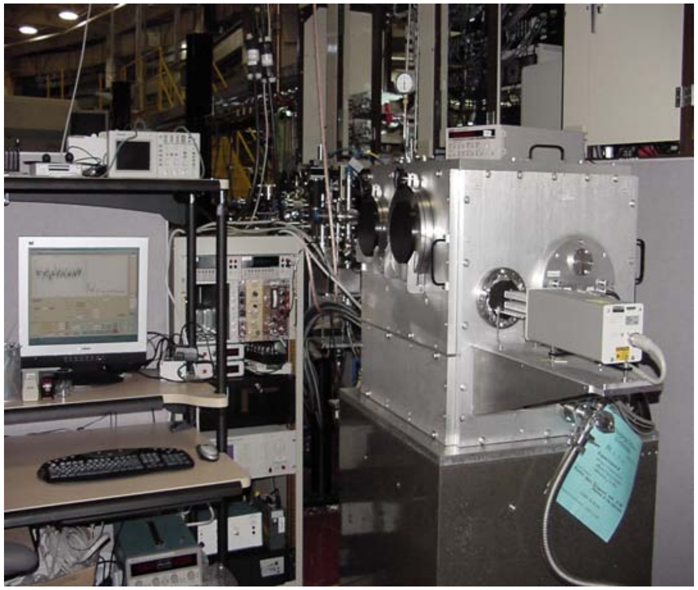
LBNL Experts:
Liviu Tomutsu and Malcolm Howells

Microtomography Example

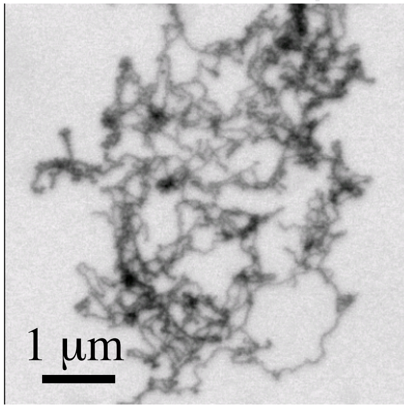


Microtomographic images of geological materials can yield detailed information about the sample matrix and pore network. In this example, the images were used to estimate pore-scale hydrological properties and to test pore-scale simulation models (from Selin et al., 2003, LBNL)

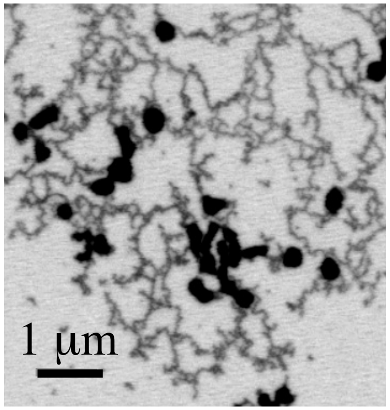
ALS-MES STXM: Versatile, User-friendly, and Efficient

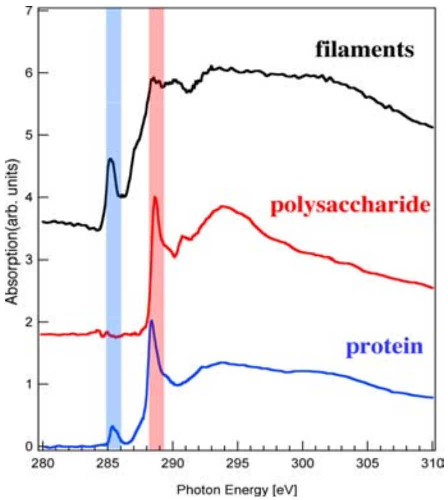


Natural filaments
polysaccharides + proteins



Synthetic filaments
(Fe-Alginate)





Best spatial resolution (~25 nm)

Wide energy range 80-2160 eV

High energy resolution with EPU

Software/data acquisition code

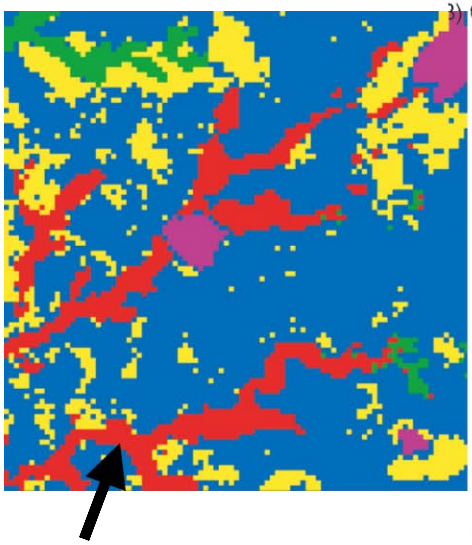
C. Chan, et. al., Science **303**, 1656 (2004)

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

Scanning Transmission X-ray Microscope (STXM)

M. Lerotic, C. Jacobsen, T. Schafer and S. Vogt

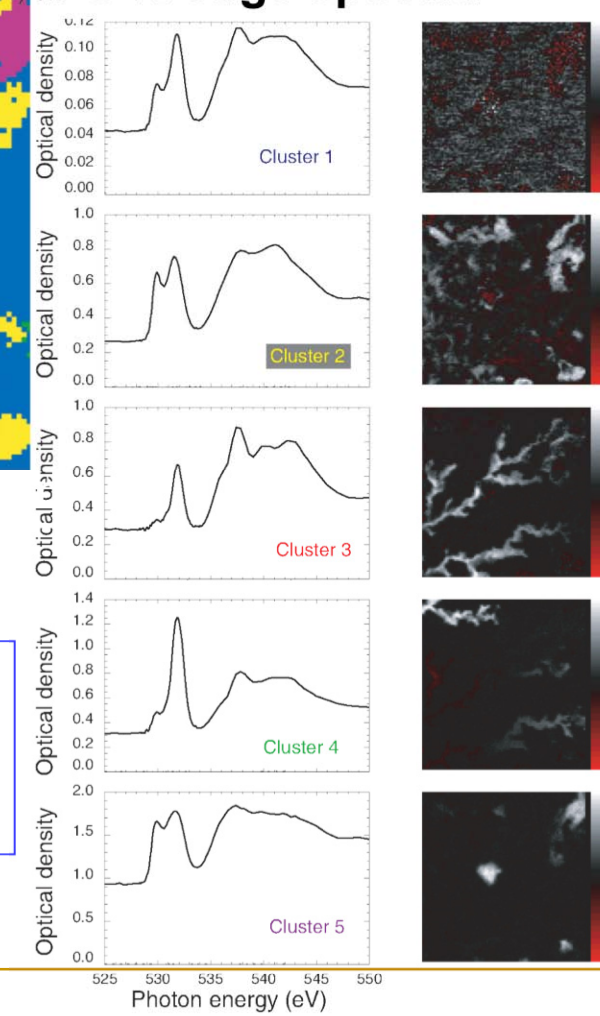
Cluster Map



Lu-rich regions

Lu expelled as a result of hematite crystallization

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**

<u>STXM</u>

•~30 nm resolution

•C, N K-edges

•Mineral thin-sections & biomaterials

Ultramicroscopy **100** (1-2), pp. 35-57 (2004)

Advanced Light Source (ALS) of LBNL

- LBNL Team: **David Shuh, Susan Hubbard, Glenn Waychunas, Hoi-Ying Holman, Liviu Tomutsa**
- **http://esd.lbl.gov/ALS_environmental/index.html**

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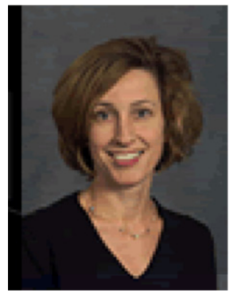
Gawaychunas @lbl.gov

510-486-6160



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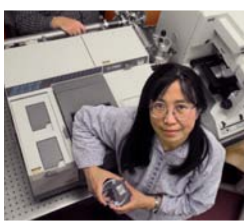

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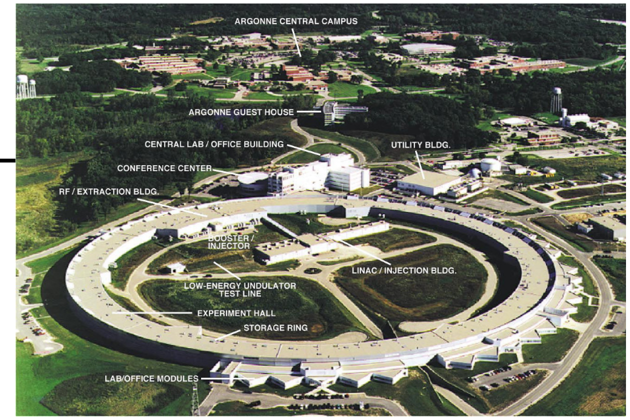
Advanced Photon Source



Molecular Environmental Science Group

Argonne National Laboratory

http://www.mesg.anl.gov/

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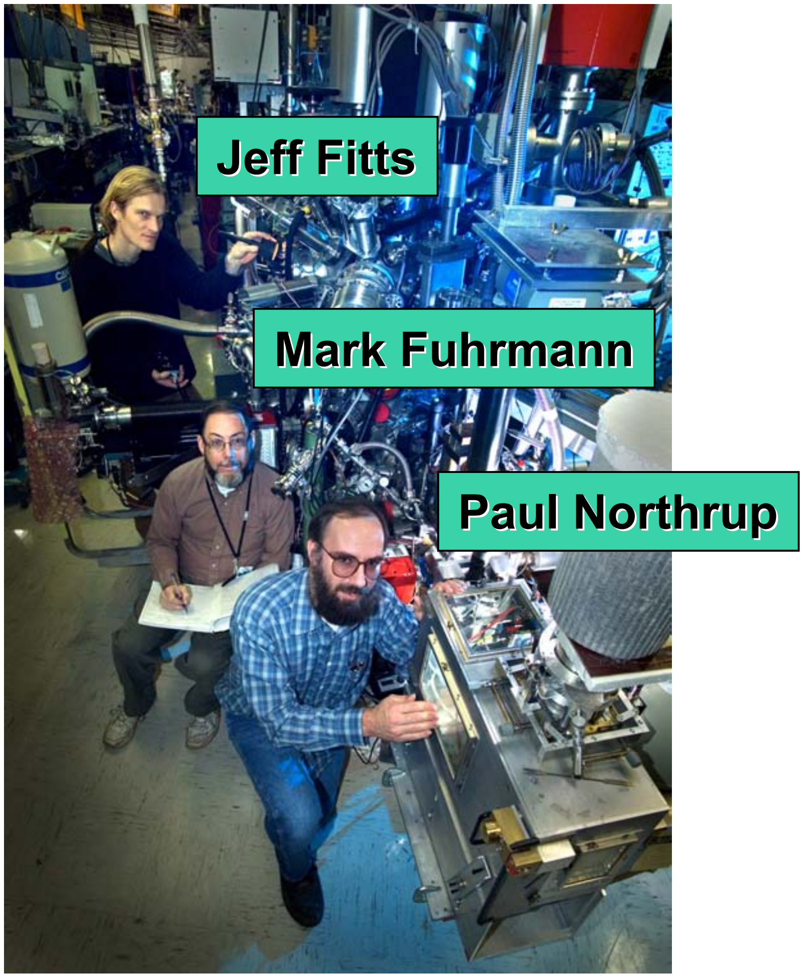
EnviroSuite at the NSLS http://www.bnl.gov/envirosuite/

Beamline X15B at the NSLS



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John

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

Envirosynch

A national organization representing environmental science users of U.S. synchrotron sources

www.envirosync.org

National Synchrotron Light Source
Brookhaven National Laboratory, Upton, NY 11973
Home Page: http://nslsweb.nsls.bnl.gov
Beamline Specifications Page:
http://nslsweb.nsls.bnl.gov/nsls/beamlines/beaminfo.htm

Beamline	Techniques	Beam Characteristics	Contact
U2B	IR spectroscopy, microspectroscopy	Bend, 50-4000 cm^{-1}, 3-10 μm	Lisa Miller lmiller@bnl.gov 631-344-2091
U7A	XAFS, XPS	Bend, 180-1200 eV	Daniel Fischer dfischer@bnl.gov 631-344-5177
U10B	IR microspectroscopy	Bend, 50-4000 cm^{-1}, 3-10 μm	Lisa Miller lmiller@bnl.gov 631-344-2091
X1A1	Soft X-ray imaging and XANES	Undulator, 250-400 eV, 30-50 nm spot	Chris Jacobsen Chris.Jacobsen@stonybrook.edu 631-344-7570
X1A2	Soft X-ray imaging and XANES	Undulator, 350-900 eV, 30-50 nm spot	Chris Jacobsen Chris.Jacobsen@stonybrook.edu 631-344-7570
X3B1	Powder diffraction, XAFS	Bend, 6-30 KeV, mm spot	Peter Stephens pstephens@sunysb.edu 631-632-8156
X7A	Powder diffraction	Bend, 4-45 KeV, mm spot	Thomas Vogt tvogt@bnl.gov 631-344-3731
X11A	XAFS	Bend, 4.5-35 KeV, mm spot	Lisa Tranquada ltran@bnl.gov 631-344-7731
X19A	XAFS	Bend, 2-8 KeV, mm spot	Wolfgang Caliebe caliebe@bnl.gov 631-344-4744
X23A2	XAFS, DAFS, XRD	Bend, 4.7-30 KeV, mm spot	Joseph Woicik woicik@bnl.gov 631-344-5236
X26A	μXRF, μXAFS, μXRD	Bend, 3-30 KeV, 7-10 μm spot	Tony Lanzirotti lanzirotti@bnl.gov 631-344-5626
X18B	XAFS	Bend, 5.7-40 KeV, mm spot	Syed Khalid khalid@bnl.gov 631-344-7496
X23B	XAFS, XRD	Bend, 3-10.5 KeV, mm spot	Lisa Tranquada ltran@bnl.gov 631-344-7731
X27A	Tomography	Bend, 8-40 KeV, 3 μm spot	Keith Jones kwj@bnl.gov 631-344-4588

DAFS = Diffraction Anomalous Fine Structure Spectroscopy
XAFS = X-ray Absorption Fine Structure Spectroscopy
XANES = X-ray Absorption Near-Edge Structure Spectroscopy
XPS = X-ray Photoelectron Spectroscopy
XRD = X-ray Diffraction
XRF = X-ray Fluorescence

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