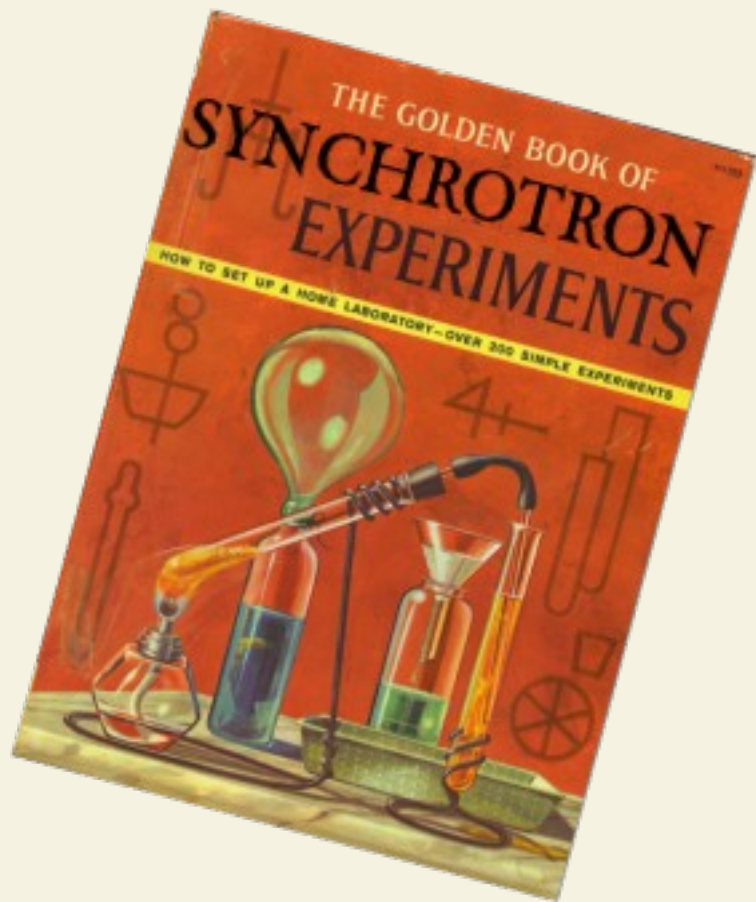


A Synchrotron Spectroscopy Primer



*Being a brief guide to
 χ -ray absorption and
 χ -ray fluorescence
spectroscopies for girls
and boys of all ages.*



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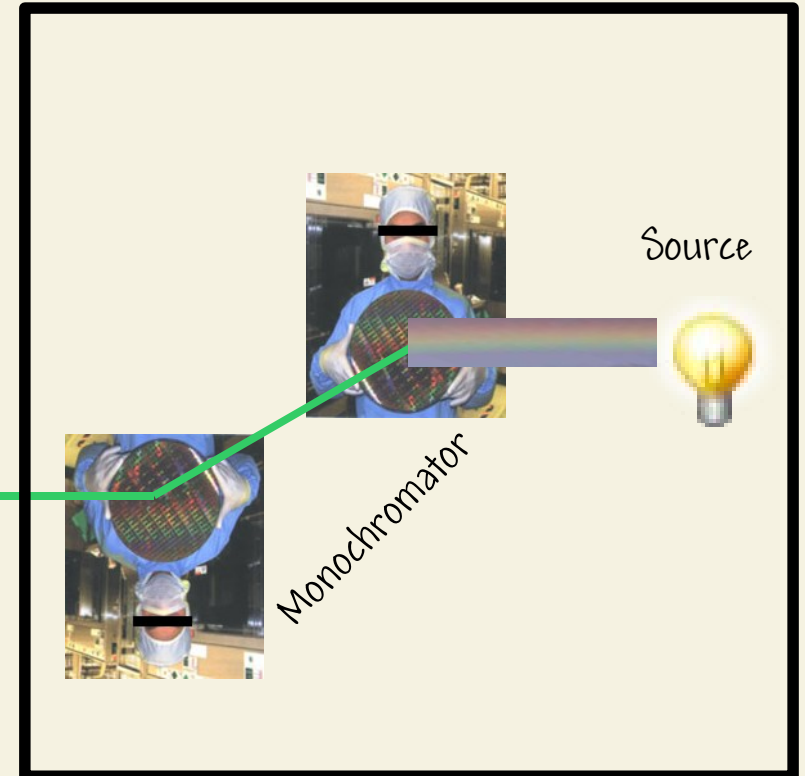
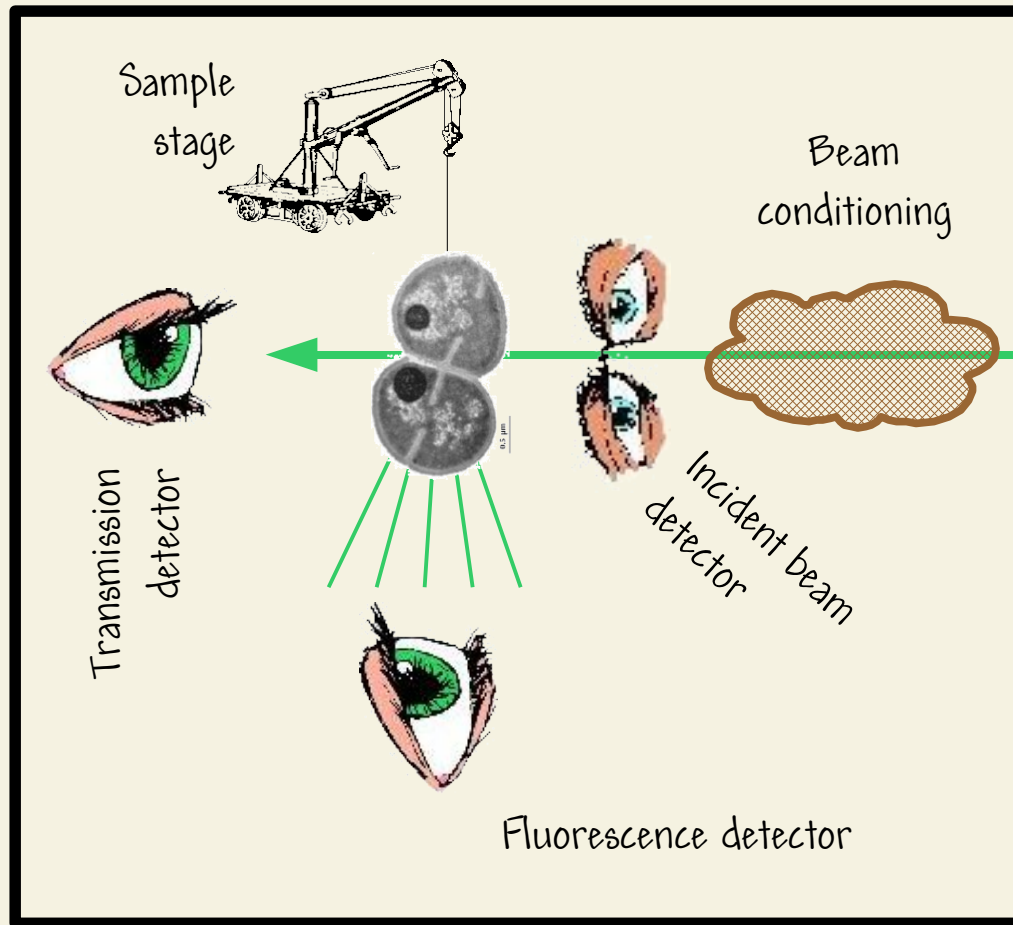
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Making and detecting x-rays for spectroscopy

Experimental hutch



Optical Enclosure

of course

Source =



~ The sample stage is usually an XY or XYR stage but might also be:

~ Electrochemistry cell

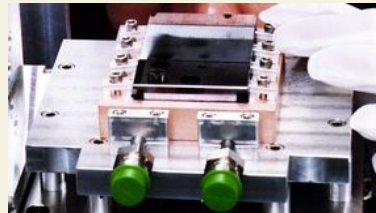
~ Cryostat or furnace

~ High pressure cell

~ Chemical reaction cell

~ etc.....

Monochromator =

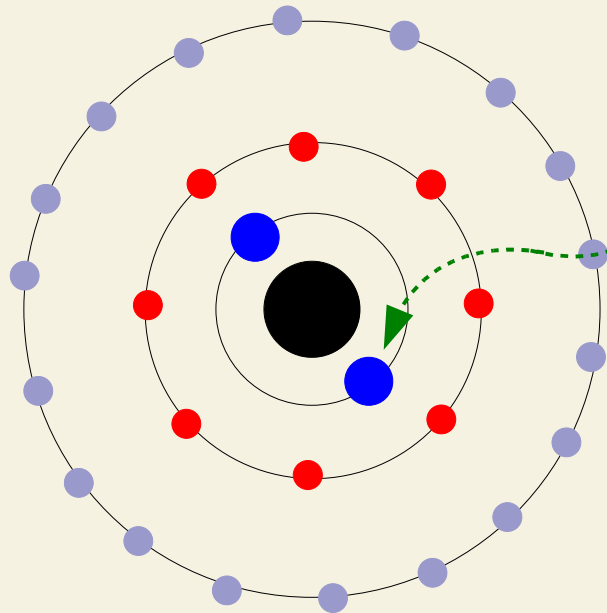


Detector =



The sample can be almost anything!

When a photon meets an electron



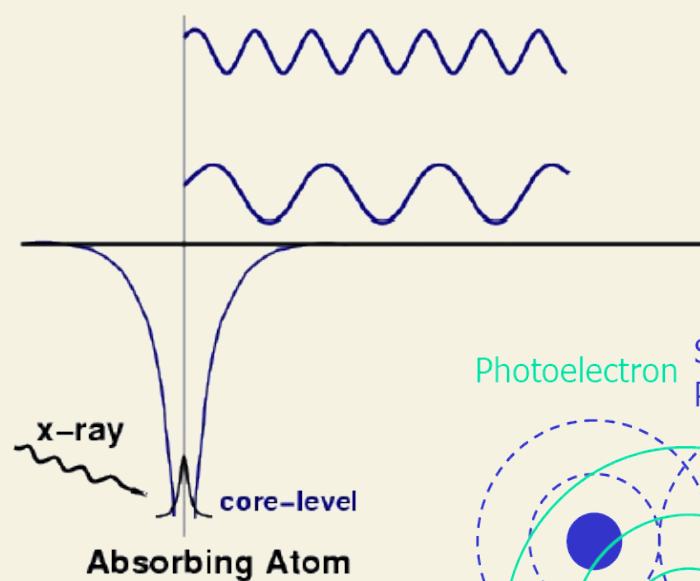
K edge ● 1s electrons

L edges ● 2s, 2p electrons

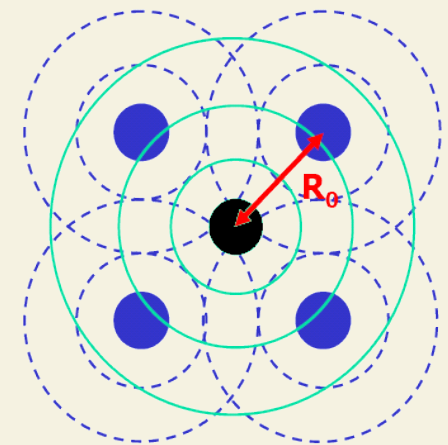
M edges ● 3s, 3p, 3d electrons

X-ray Absorption

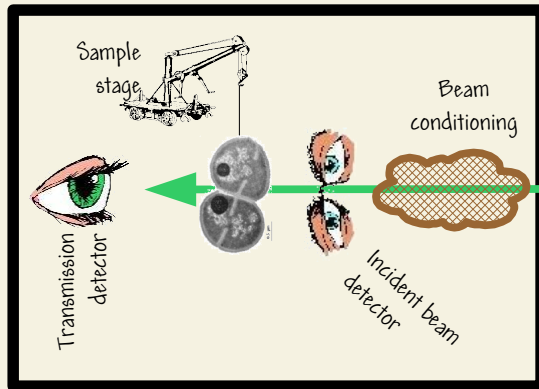
photo-electron $\lambda \sim (E - E_0)^{-1/2}$



Photoelectron Scattered Photoelectron

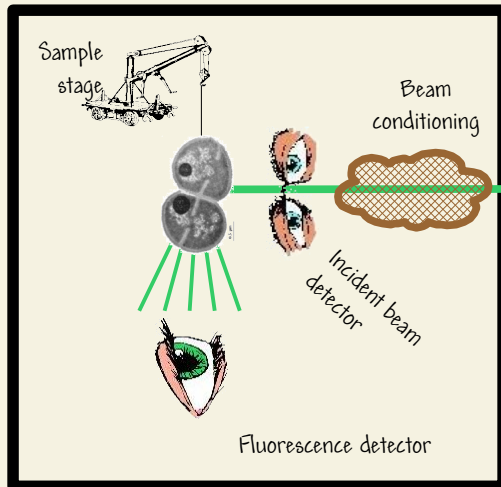
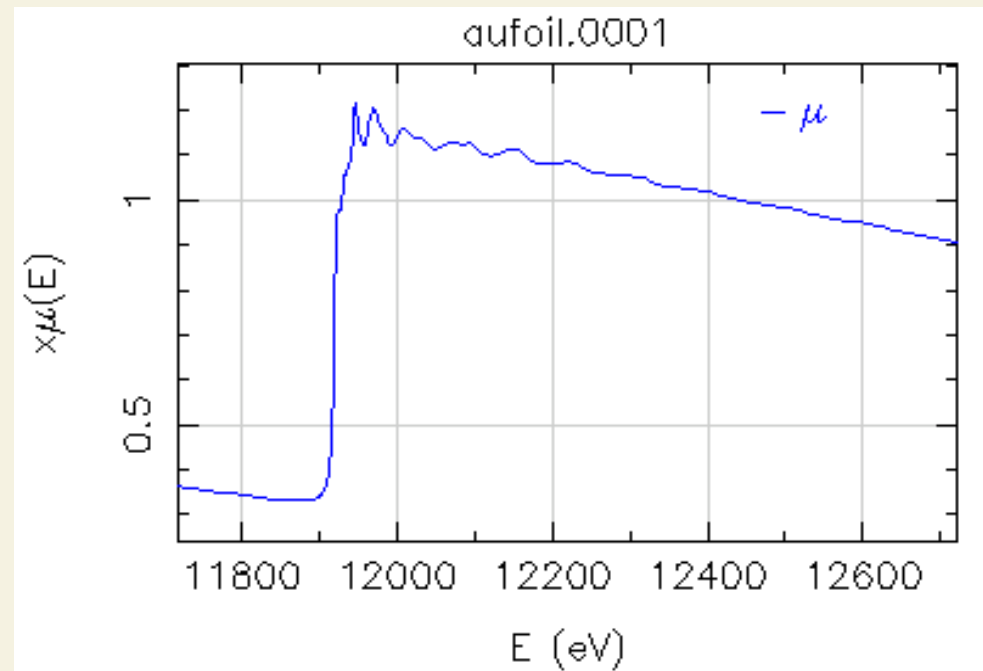


Absorption spectra



TRANSMISSION GEOMETRY

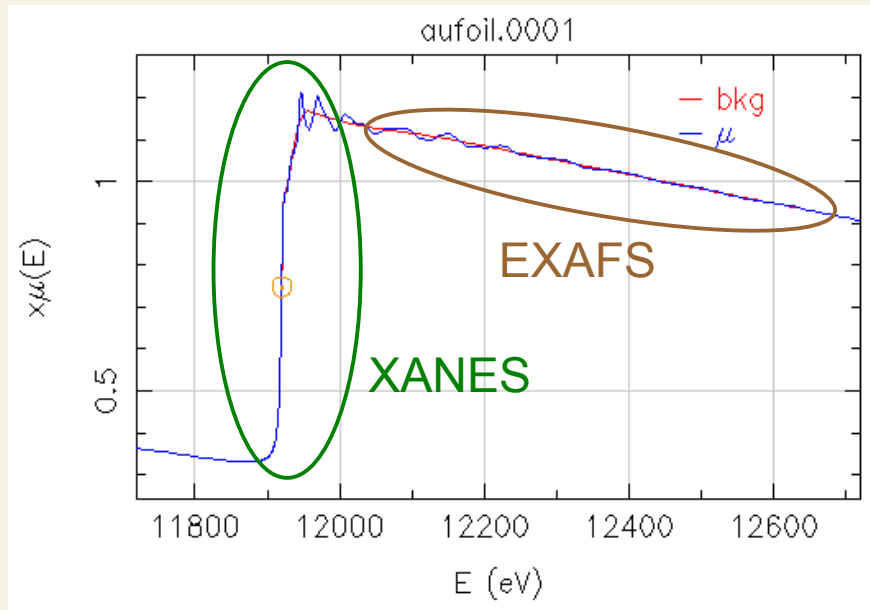
DIRECT MEASURE OF ABSORPTION CROSS-SECTION



FLUORESCENCE GEOMETRY

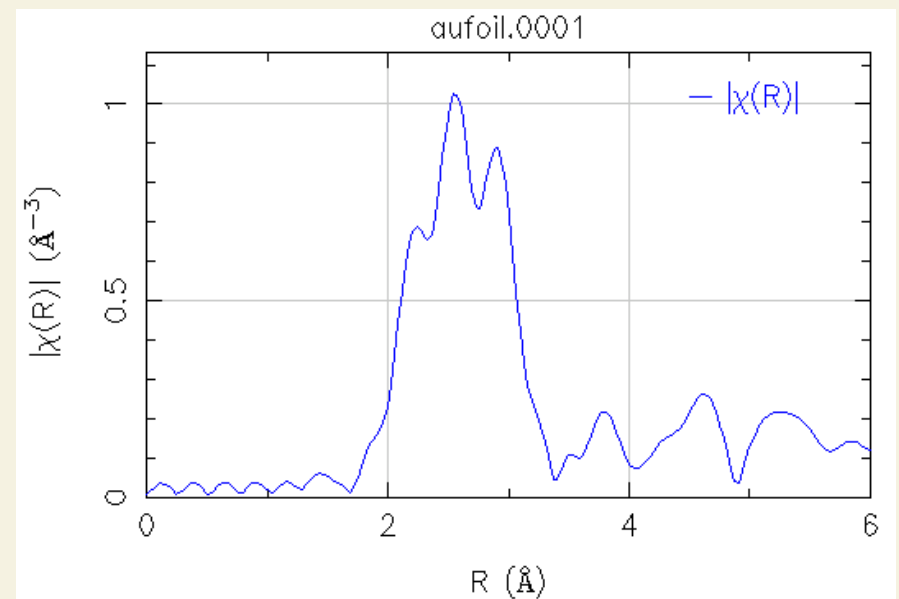
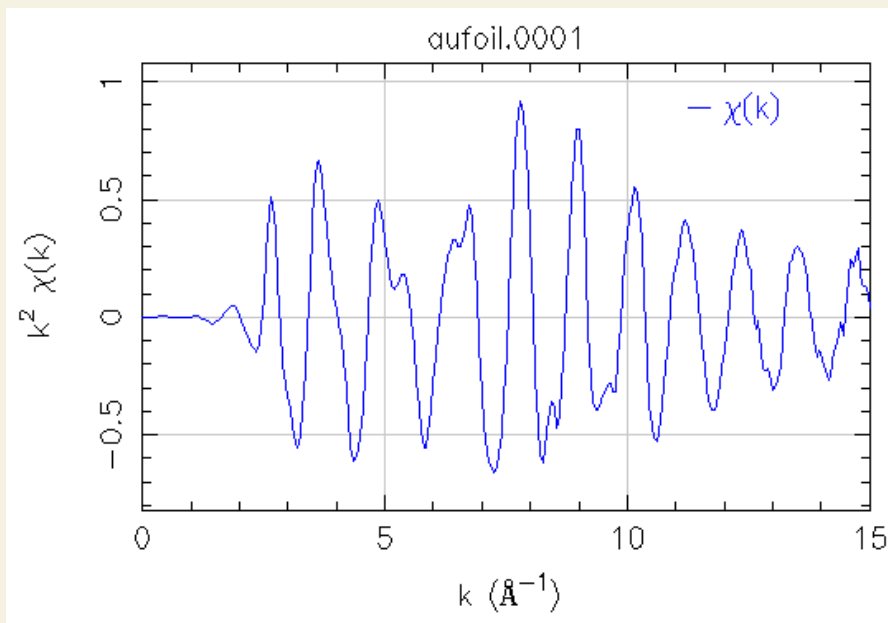
SECONDARY PHOTON PRODUCTION PROPORTIONAL TO ABSORPTION CROSS-SECTION

Analyzing the absorption spectrum



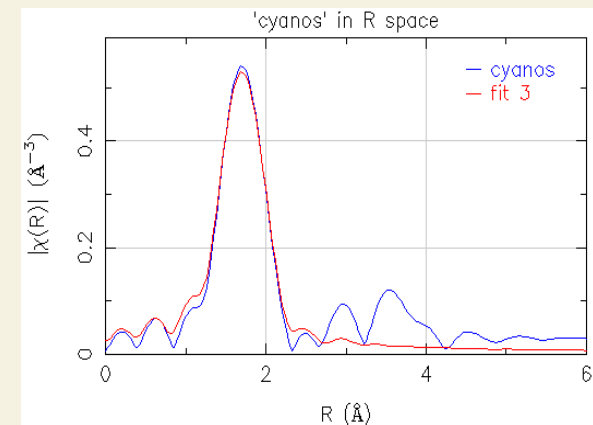
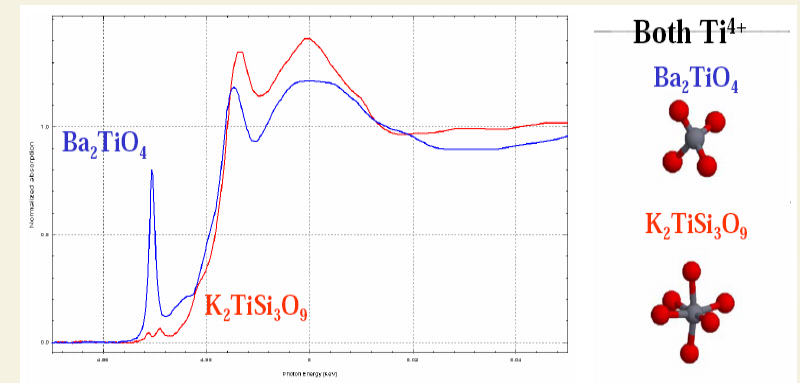
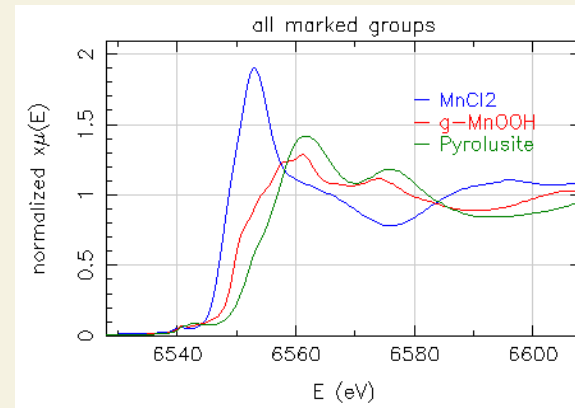
EXAFS Data Processing

- Fit a spline to approximate the background
- Isolate wiggles, convert to wavenumber
- Fourier transform to obtain a function related to a radial distribution function

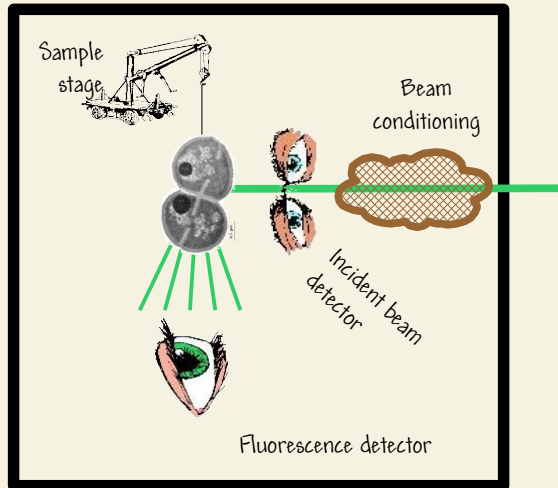


What do we learn from the absorption spectrum?

- ~ Chemical state of the absorber
- ~ Oxidation state
- ~ Coordination chemistry
- ~ Details of the coordination environment
- ~ Species of neighbors
- ~ Number of neighbors
- ~ Distances to neighbors
- ~ No assumption of periodicity or symmetry
- ~ Generally non-destructive experiment with modest sample preparation requirements

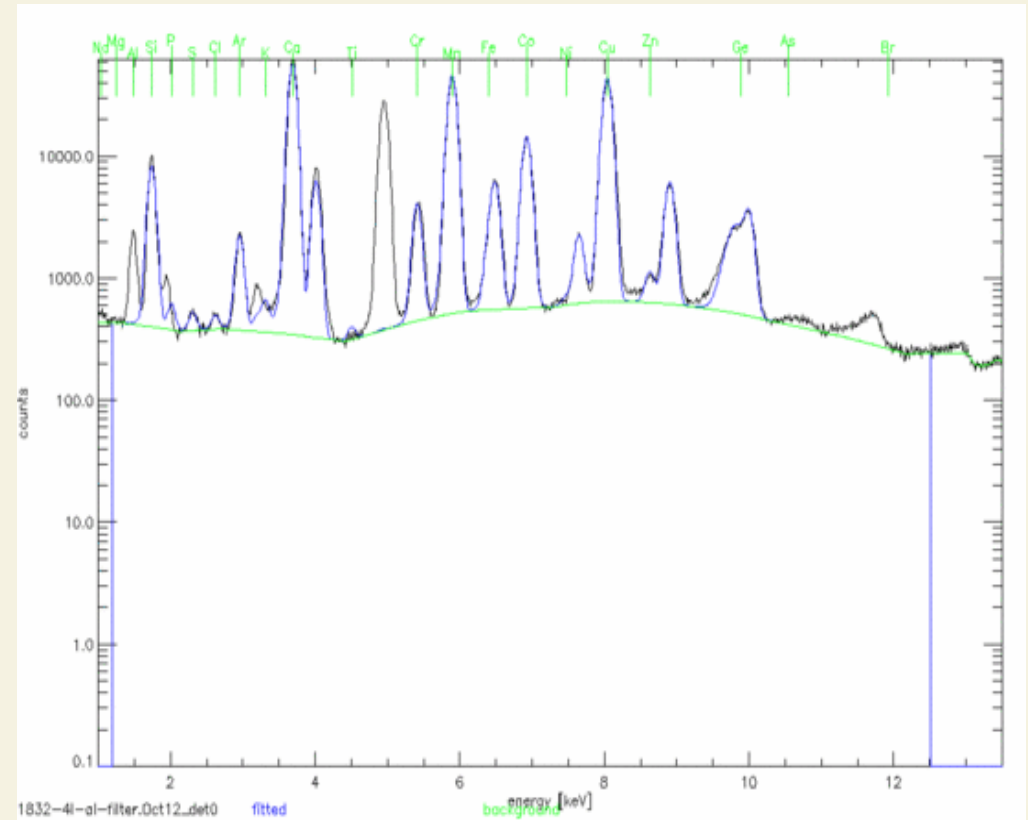


Fluorescence spectra



FLUORESCENCE GEOMETRY

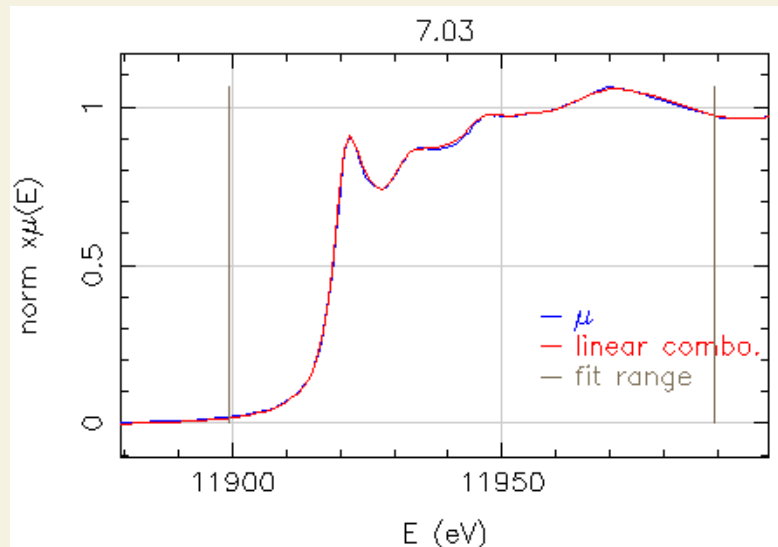
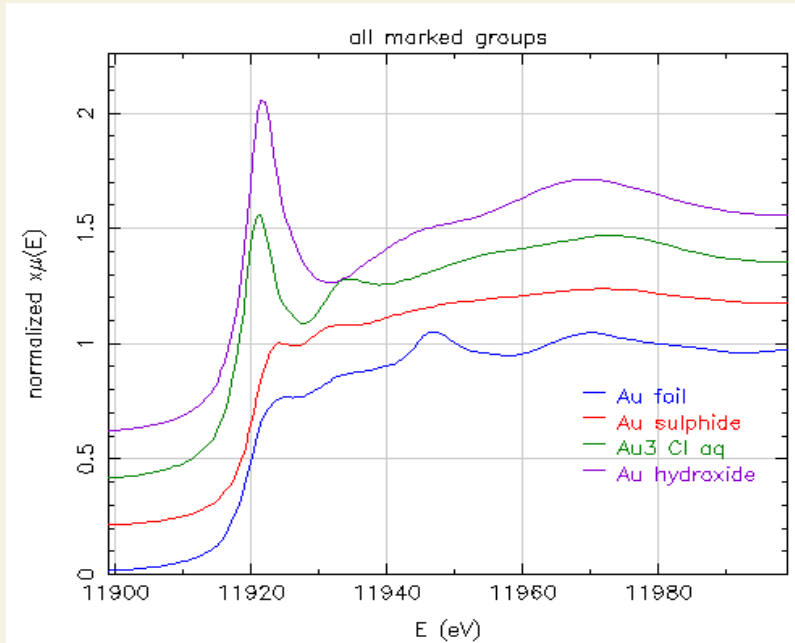
- ~ Incident photon energy = 10 keV
- ~ All elements with absorption edges below 10keV fluoresce at their characteristic energies
- ~ This spectrum is from a standard purchased from NIST
- ~ By comparing to this, you can quantify elemental composition in an unknown sample



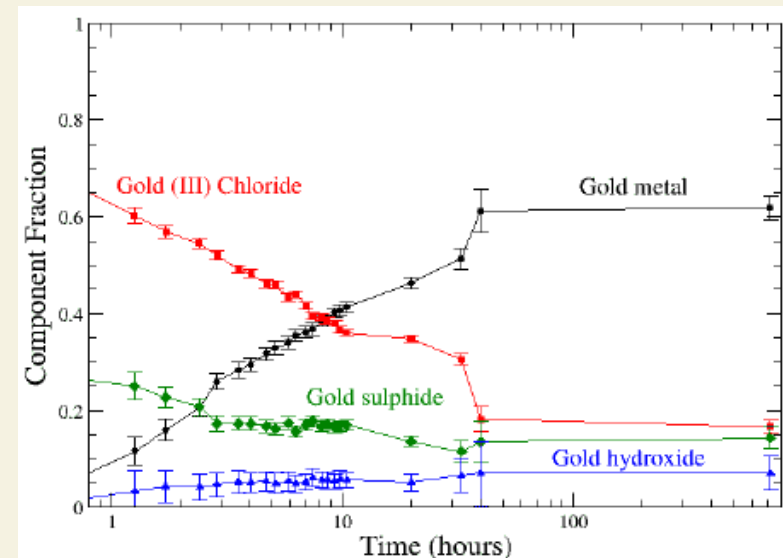
What do we learn from the fluorescence spectrum?

- ~ Spatial distribution of elements
 - ~ K-B mirrors: about 5 micron resolution
 - ~ Fresnel zone plate: about 120 nm resolution
- ~ Concentrations of elements
- ~ Micro-
 - ~ -spectroscopy
 - ~ -diffraction

Learning something from XANES

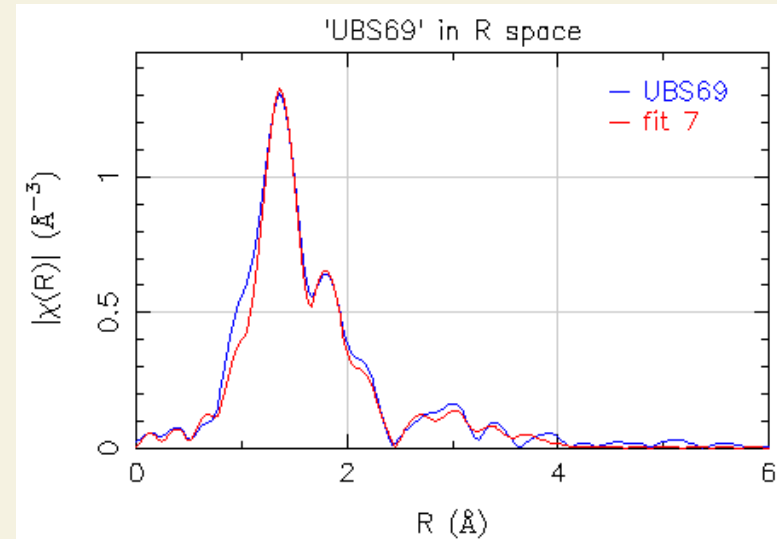
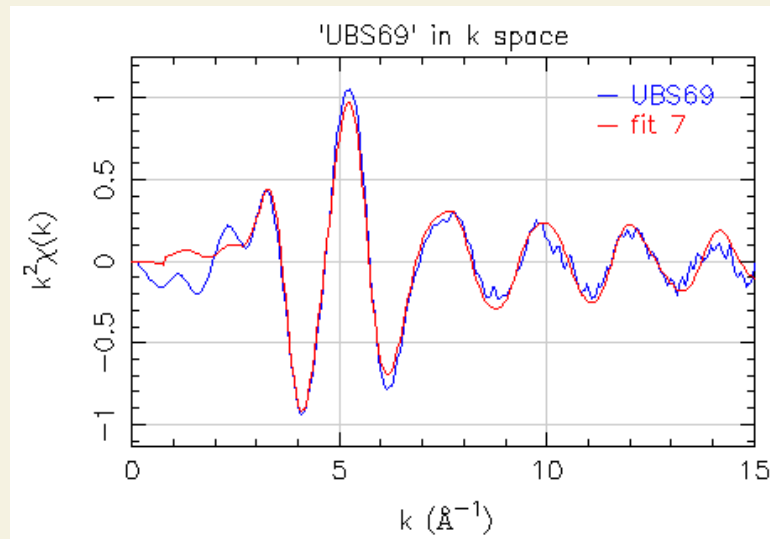
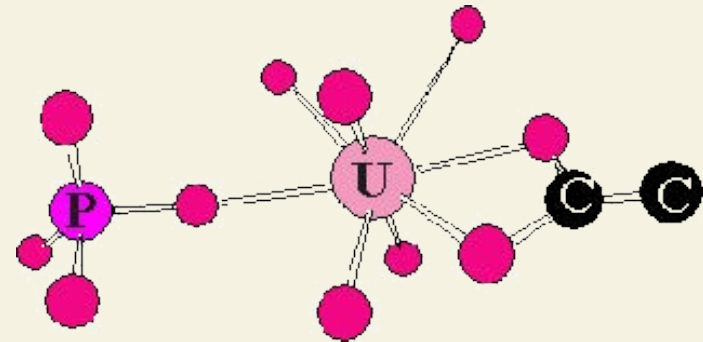


- Gold deposits in South Africa and elsewhere formed by the reduction of Au(III)Cl to Au(0) by cyanobacteria such as *Plectonema boryanum*.
- We expose *P. boryanum* to Au(III)Cl and measure XANES spectra over the course of 720 hours.
- We also measure a variety of standards that are likely to exist in the sample.
- We fit a linear combination of standards to the sample and observe the evolution of the gold species.

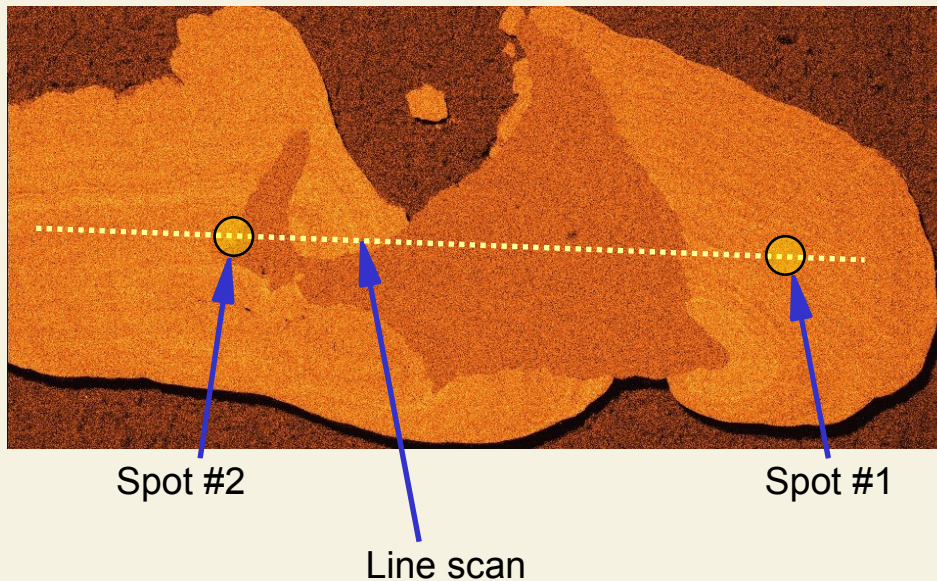


Learning something from EXAFS

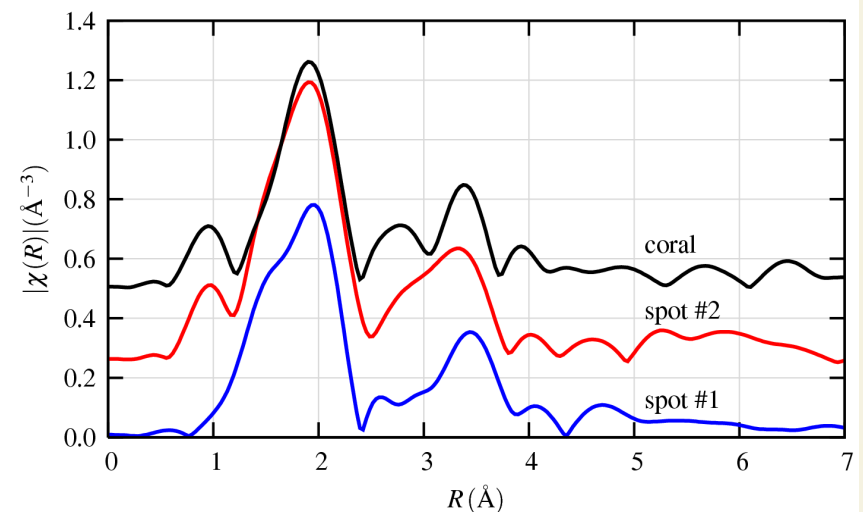
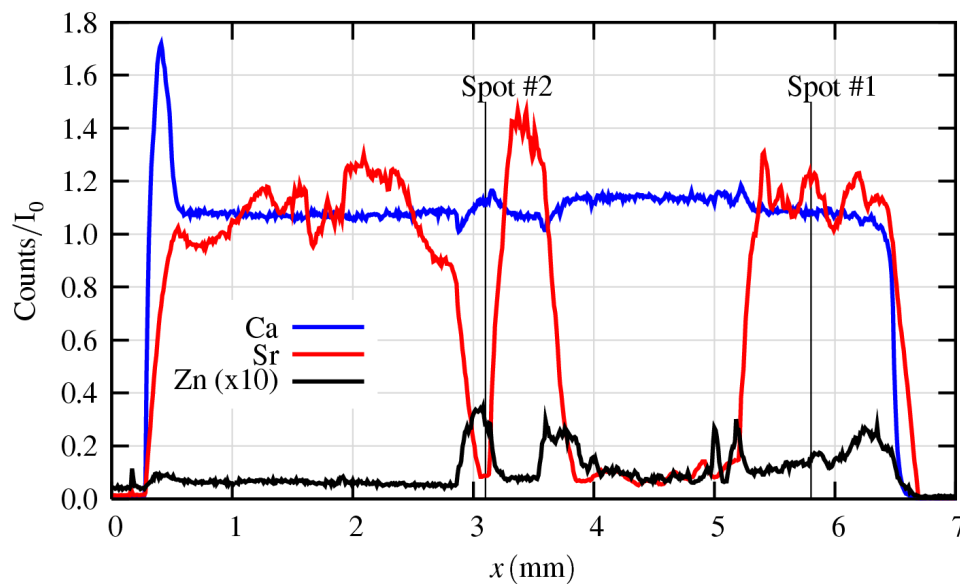
- ~ One component of the fate and transport of contaminants is the metal/bacterial interaction.
- ~ We expose *B. Subtilis* to aqueous uranyl at various pH values and with/without aqueous calcium. Shown are data at pH=6.9 and without added Ca.
- ~ We fit the data with a model that considers hydroxyl, carboxyl, and phosphoryl bonding of U to the bacterial surface. We find that the U is complexed with ~3 phosphoryls and ~1.5 carboxyls.



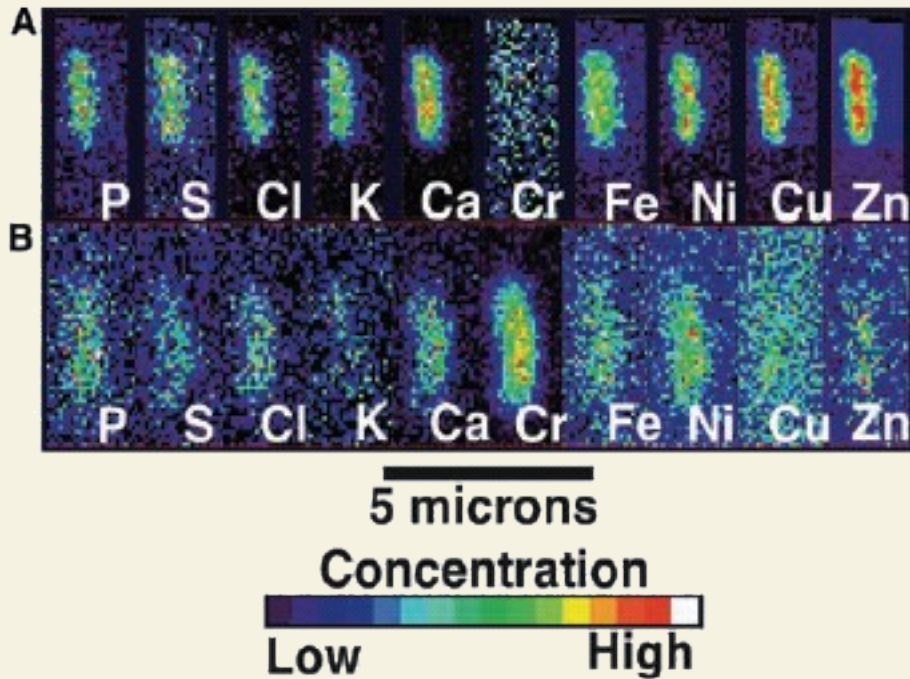
Fluorescence maps 1: Sr distribution in arctic fish ear bones



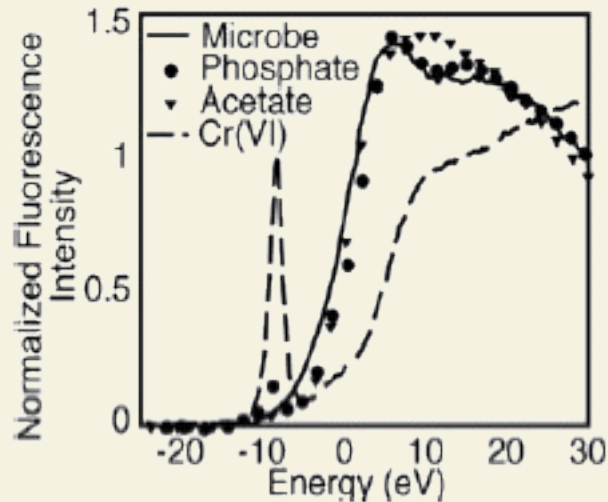
- ~ Ear bone composition gives clues to life cycle, such as time spent in clear of brackish water
- ~ 5 micron spot size using Kirkpatrick-Baez mirrors at 13BM
- ~ Line and areal scans to measure elemental distribution
- ~ Pick interesting spots and measure spectroscopy



Fluorescence maps 2: Elemental distribution in *P. Fluorescens* and lysing by Cr



- ~ Planktonic *P. Fluorescens*, before and after exposure to potassium dichromate
- ~ 120 nanometer spot size using Fresnel zone plate mirrors at 2ID-D
- ~ Areal scans to measure elemental distribution
- ~ Pick interesting spots and measure spectroscopy



And in this corner...

LENGTH
SCALE

XAS probes short-range order only, but with element specificity.

XRD measures full pair distributions sensitive to both long (Bragg peaks) and short (diffuse spectrum) range order.

TIME
SCALE

XAS (like XRD) measures an *instantaneous* distribution, averaged over its length scale.
Lifetime $\sim 10^{-15}$ sec

Mössbauer, NMR, and Raman probe excitation with much longer lifetimes

SPATIAL
RESOLUTION

XAS is limited by the measured k -range.
 $\Delta R = \pi/2k_{max}$

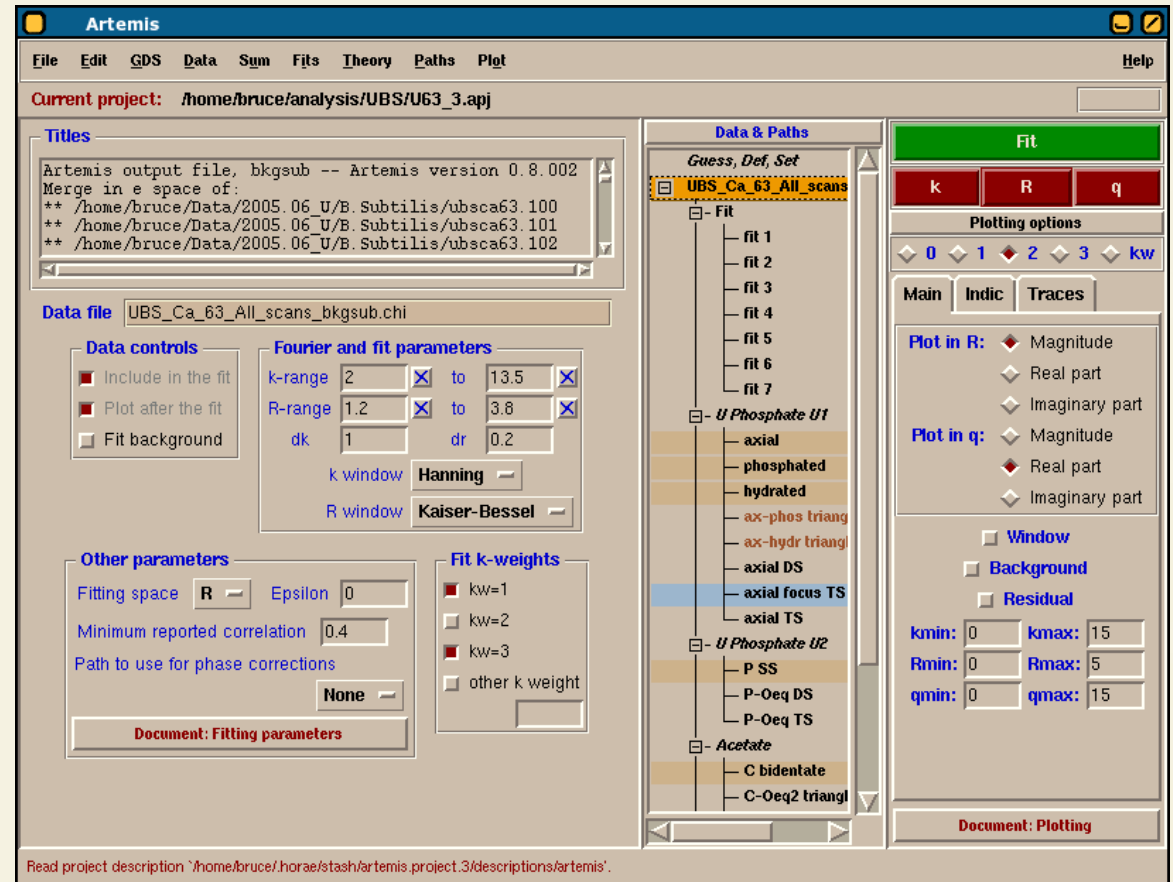
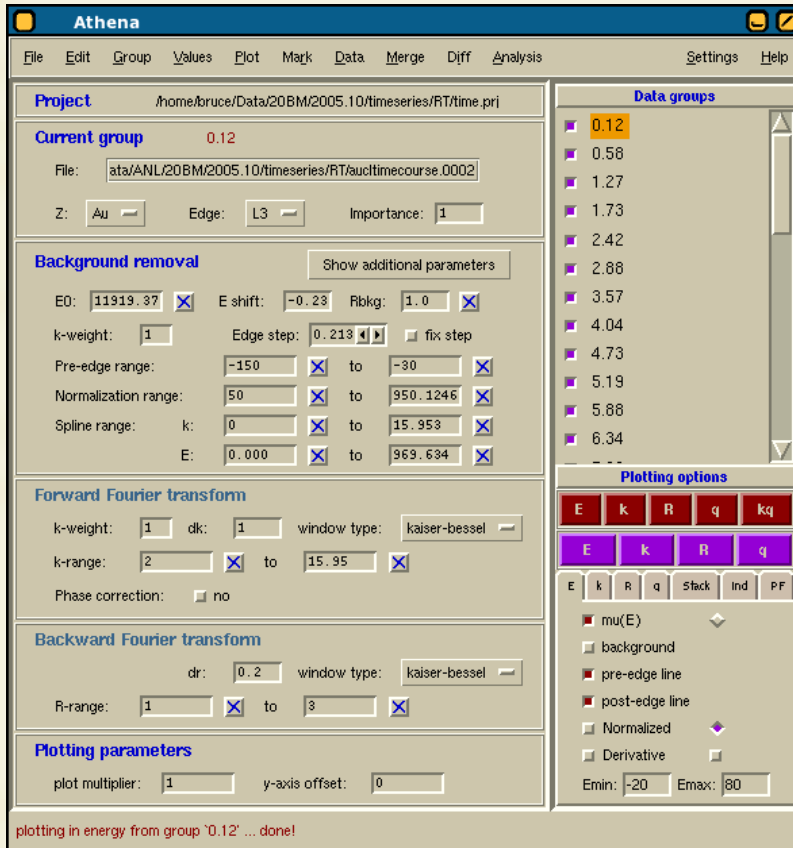
XRD or Raman might be much more sensitive to symmetry breaking, albeit with different length and time scales.

STRUCTURAL
DISORDER

XAS sees disorder in interatomic distance.

XRD, Mössbauer, & Raman see disorder about crystal position.

Dealing with spectroscopy data

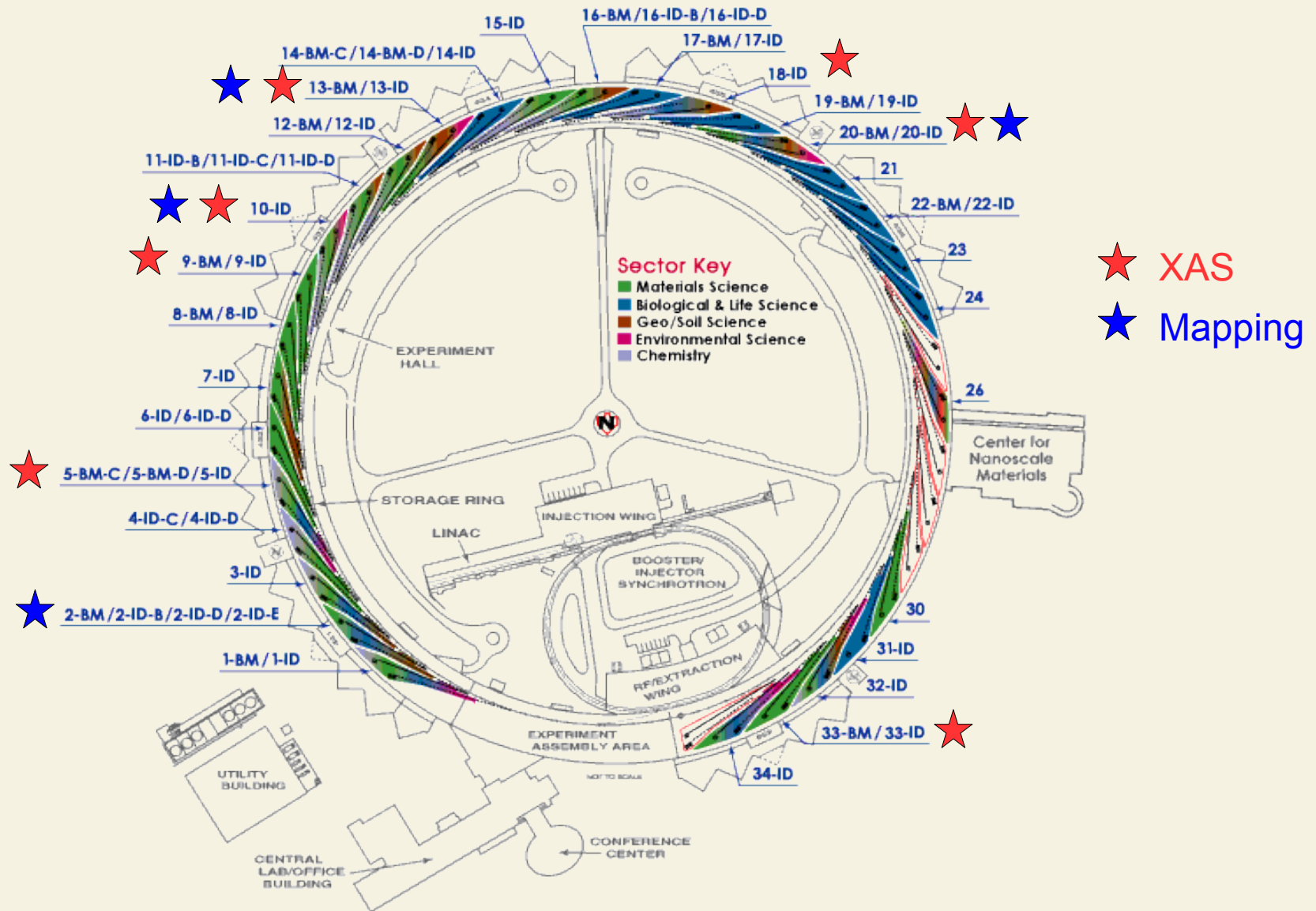


ATHENA: XAS DATA PROCESSING

ARTEMIS: EXAFS DATA ANALYSIS

<http://cars9.uchicago.edu/~ravel/software>

Spectroscopy beamlines at the APS



Applying for beamtime.

The screenshot shows a Mozilla Firefox browser window displaying the Scientific Access website. The browser's address bar shows the URL http://aps.anl.gov/Users/Scientific_Access/index.html. The website header features the Advanced Photon Source logo and the Argonne National Laboratory logo. A navigation menu includes links for About, News, Science, User Information, Education, and Facility. A search bar is located on the right side of the header.

The main content area is titled "Scientific Access" and contains the following text:

Collaborative Teams
About APS Science

Scientific Access

The APS is an open user facility that makes beam time available to the international scientific community through a peer-reviewed proposal process.

Two access modes are available: General Users and Partner Users. General Users are those who require less than 10% of the beam time on a beamline in a given cycle. Partner Users are those whose work involves a greater scope and greater commitment by both the user and the APS. Specific requirements govern both modes of access.

[Become a User](#)
Step-by-step guide to joining the APS user community.

[General Users](#)
Policy and process for participating in the APS as a General User, including proposal system, instructions, and deadlines.

[Partner Users](#)
Policy and process for participating in the APS as a Partner User, as well as summary of current Partner User projects. A Collaborative Access Team (CAT) is one type of Partner User.

[Facility Information](#)
Directories of resources and capabilities, operating schedule, real-time status information, properties of the source.

The footer contains logos for The University of Chicago, U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences. It also includes links for [Privacy & Security Notice](#), [Contact Us](#), [Phonebook](#), and [Site Map](#).

The browser's status bar at the bottom shows the system tray with icons for Adblock, weather (Now: Partly Cloudy and 49°F, Tonight: 40°F, Fri: 41°F, Sat: 36°F), and other utility icons.

Contact information

- ~ Ken, Ed, Shelly, and I all have offices in E-wing of building 203.
- ~ Phone / email: 2-5033 / bravel@anl.gov
- ~ Web: <http://cars9.uchicago.edu/~ravel> or Google for bruce+exafs
- ~ At the APS, I am often found at MRCAT, Sector 10 or Building 433, Room B007