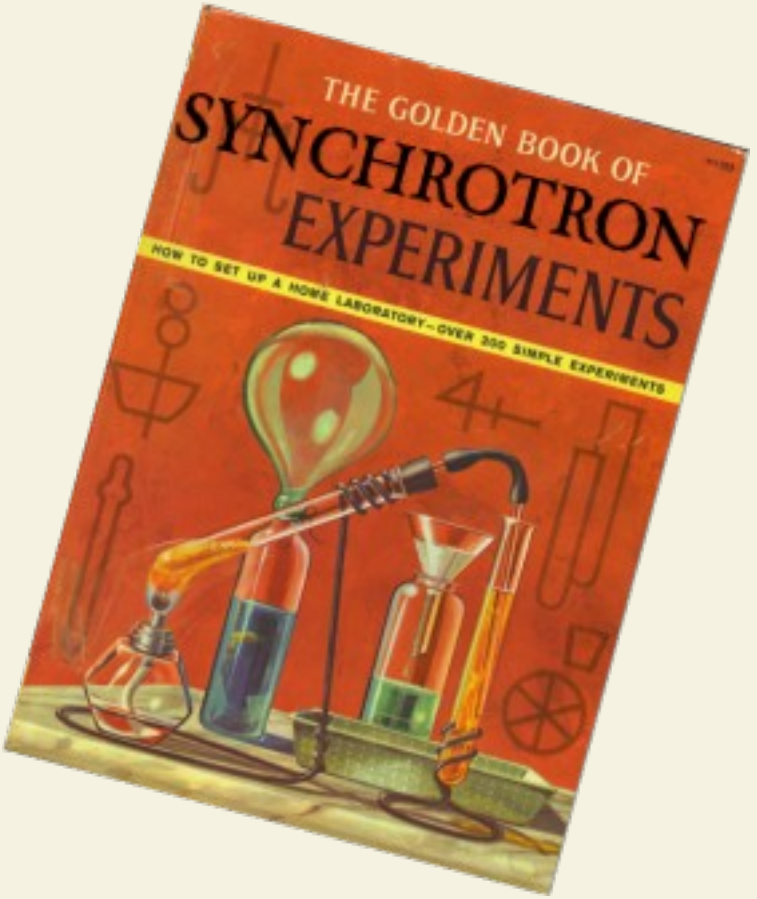
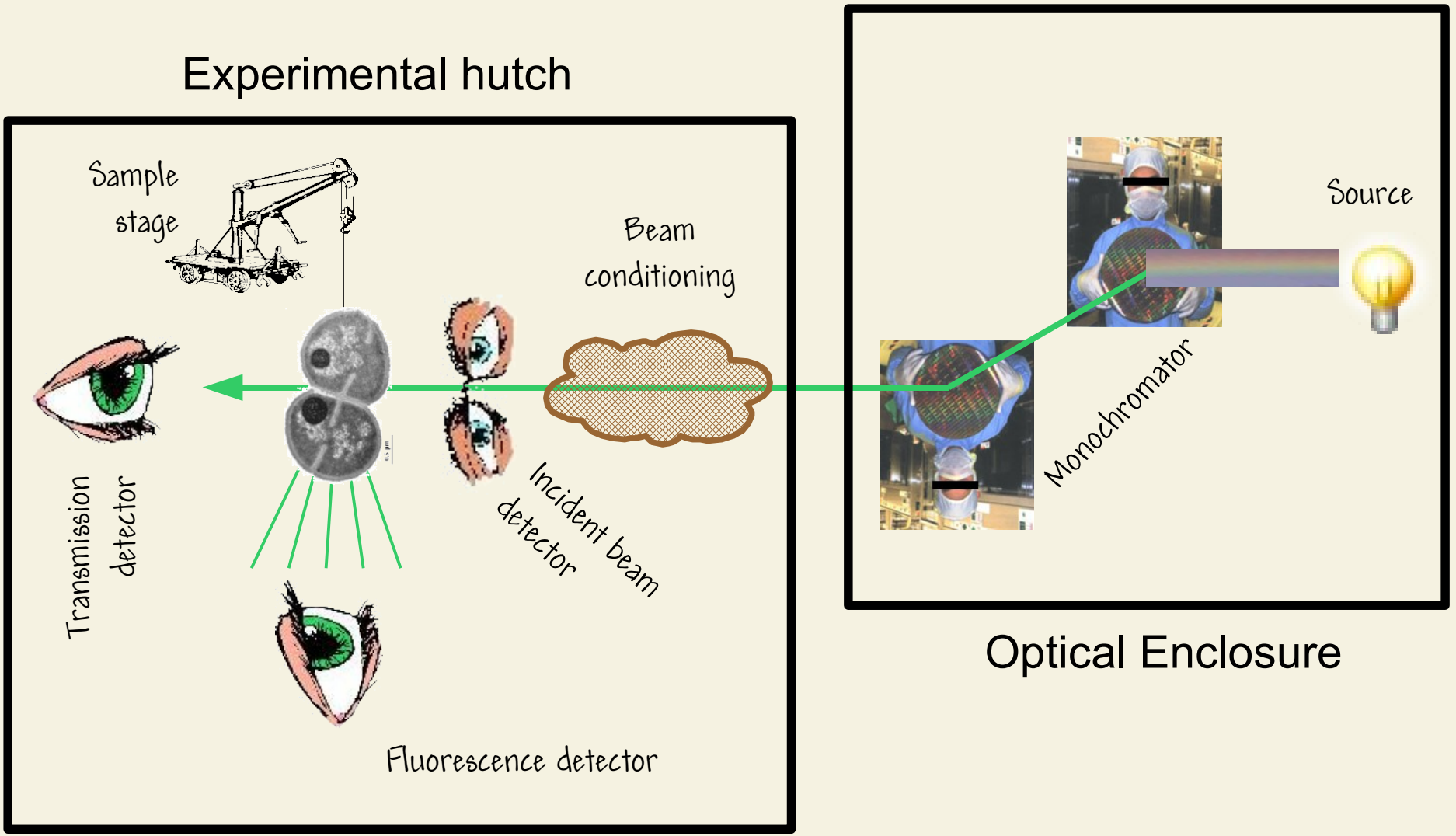
A Synchrotron Spectroscopy Primer



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

Bruce Ravel : Biosciences Lunchtime Seminar : 16 January 2006

Making and detecting x-rays for spectroscopy

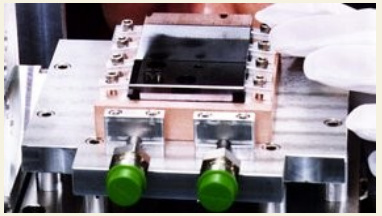


Photos from NABIR, NIST and National Taiwan Normal University

# of course ....

Source =

Monochromator =



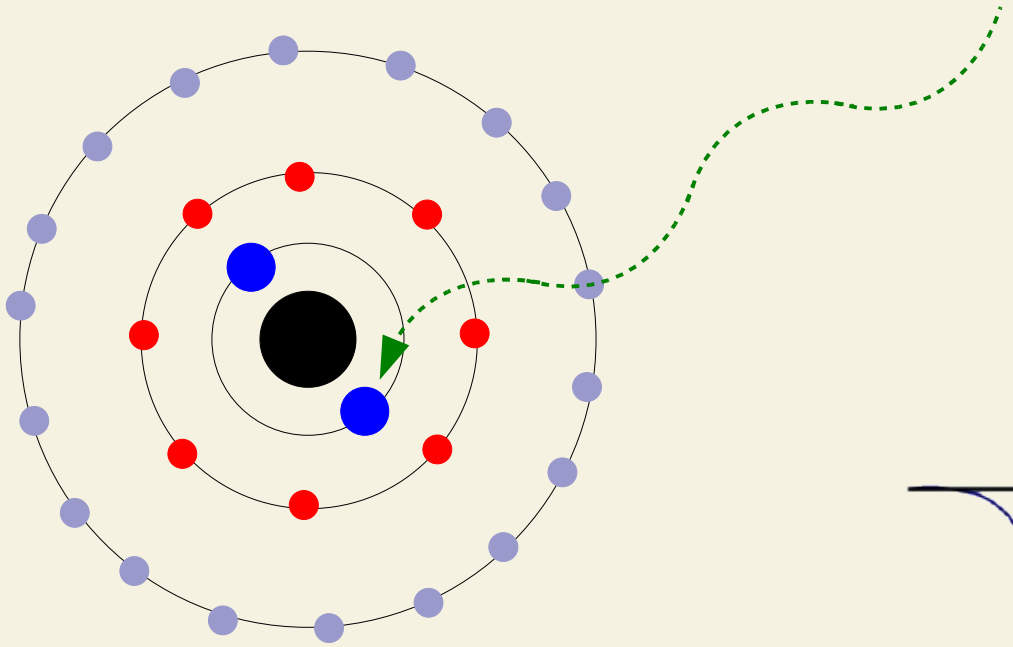
Detector =

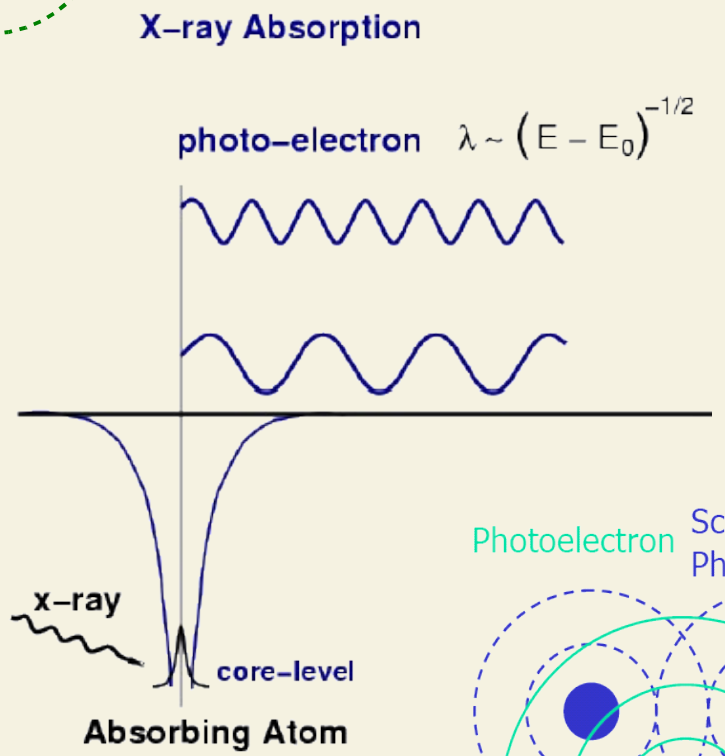
- The sample stage is usually an XY or XYR stage but might also be:
  - Electrochemistry cell
  - Cryostat or furnace
  - High pressure cell
  - Chemical reaction cell
  - etc.....

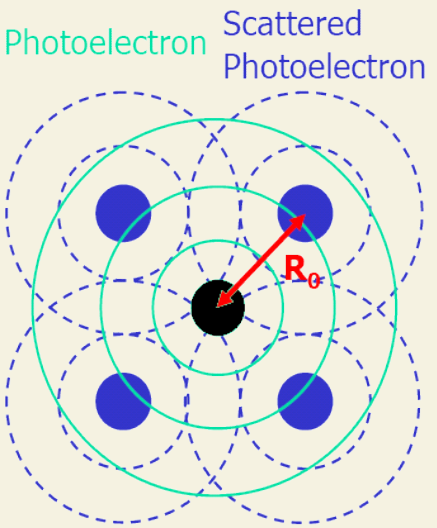
The sample can be almost anything!

Photos of APS and mono courtesy the APS.

When a photon meets an electron







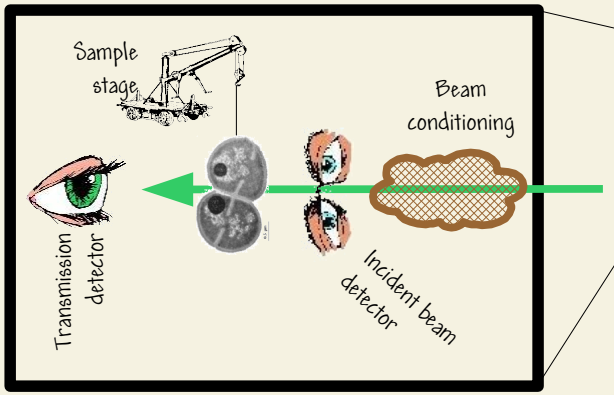
K edge — 1s electrons

L edges — 2s, 2p electrons

M edges — 3s, 3p, 3d electrons

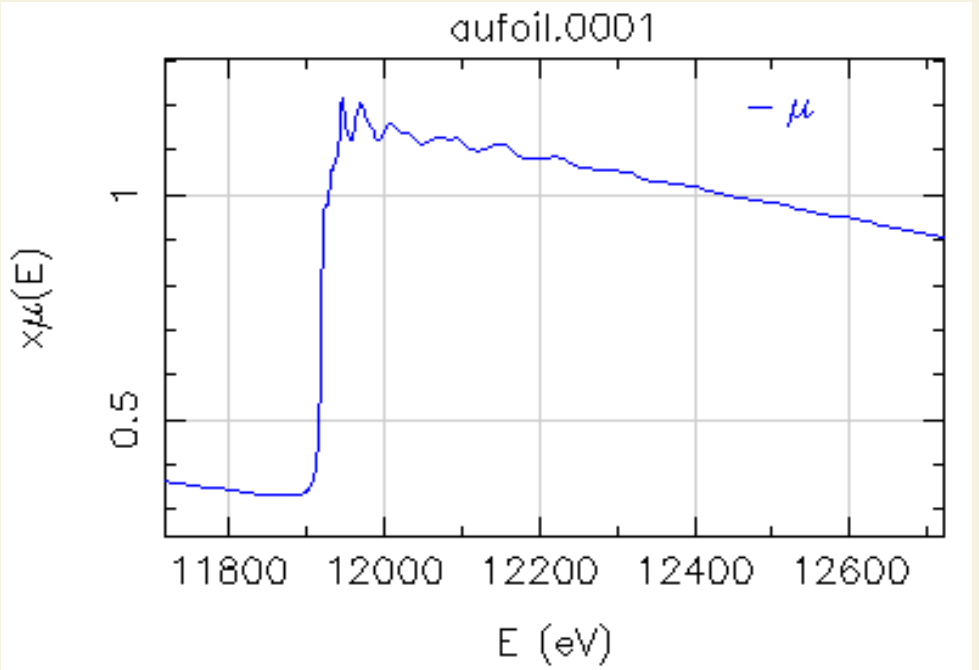
Cartoon of absorber courtesy M. Newville. Cartoon of photoelectron courtesy S. Kelly.

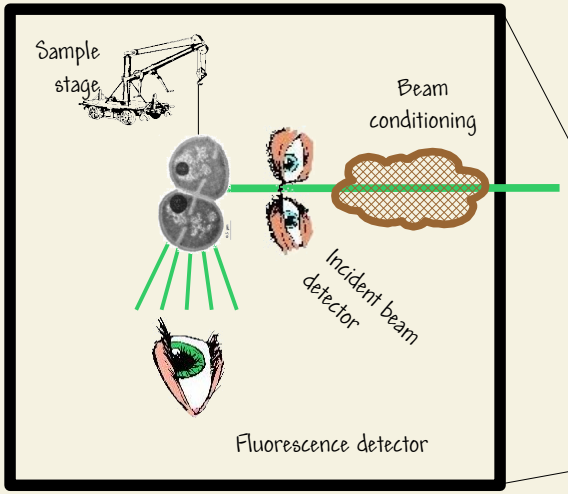
Absorption spectra



TRANSMISSION GEOMETRY

DIRECT MEASURE OF ABSORPTION CROSS-SECTION

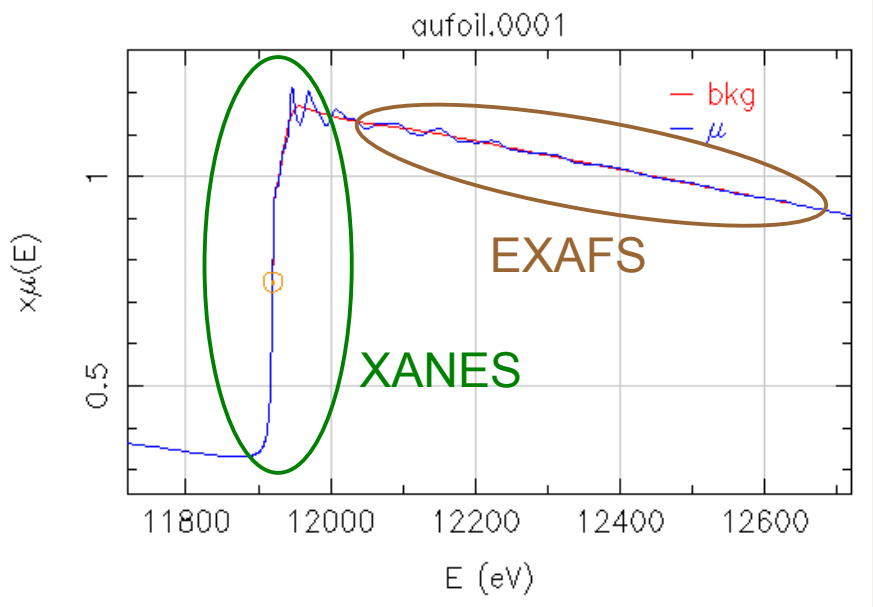




FLUORESCENCE GEOMETRY

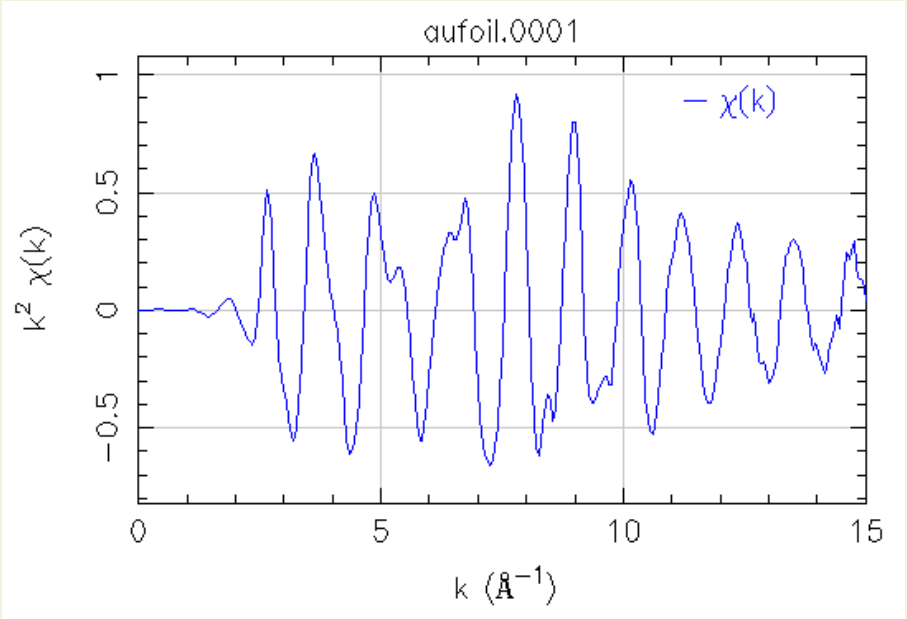
SECONDARY PHOTON PRODUCTION PROPORTIONAL TO ABSORPTION CROSS-SECTION

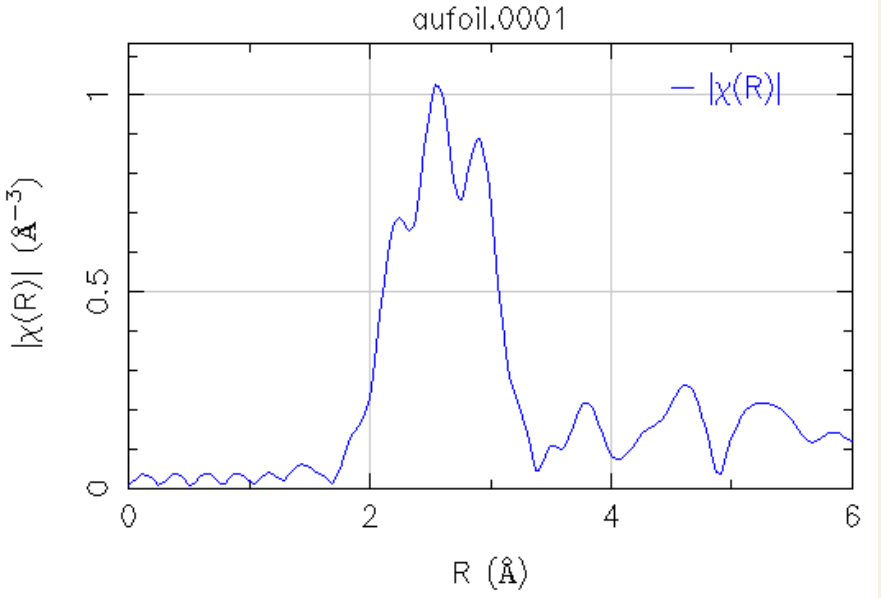
Analyzing the absorption spectrum



EXAFS Data Processing

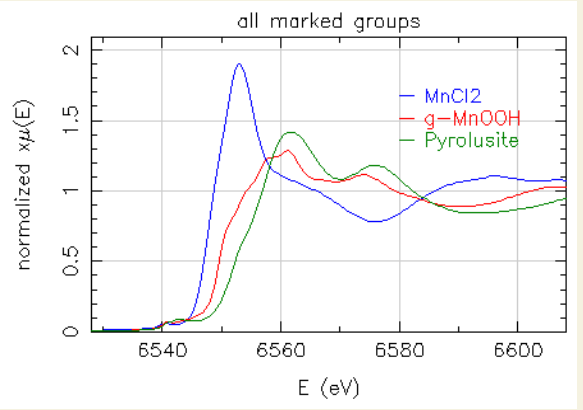
- Fit a spline to approximate the background
- Isolate wiggles, convert to wavenumber
- Fourier transform to obtain a function related to a radial distribution function

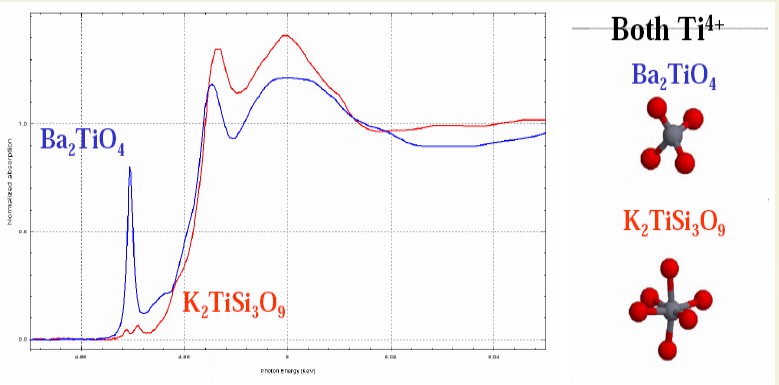


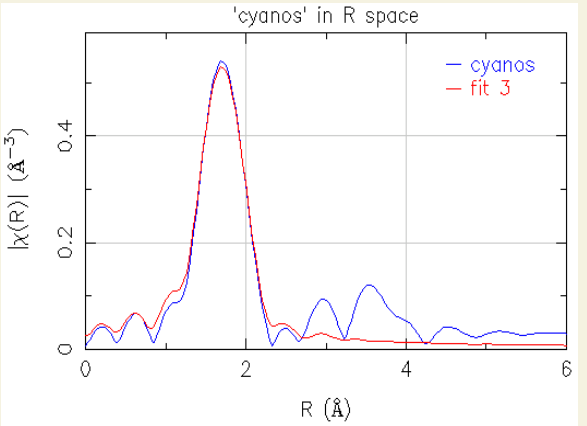


What do we learn from the absorption spectrum?

- 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

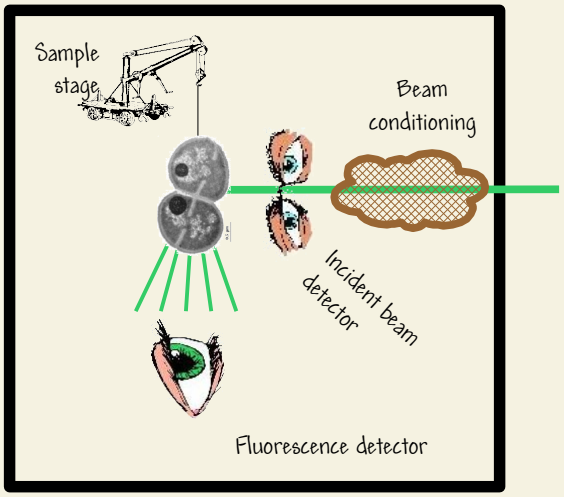




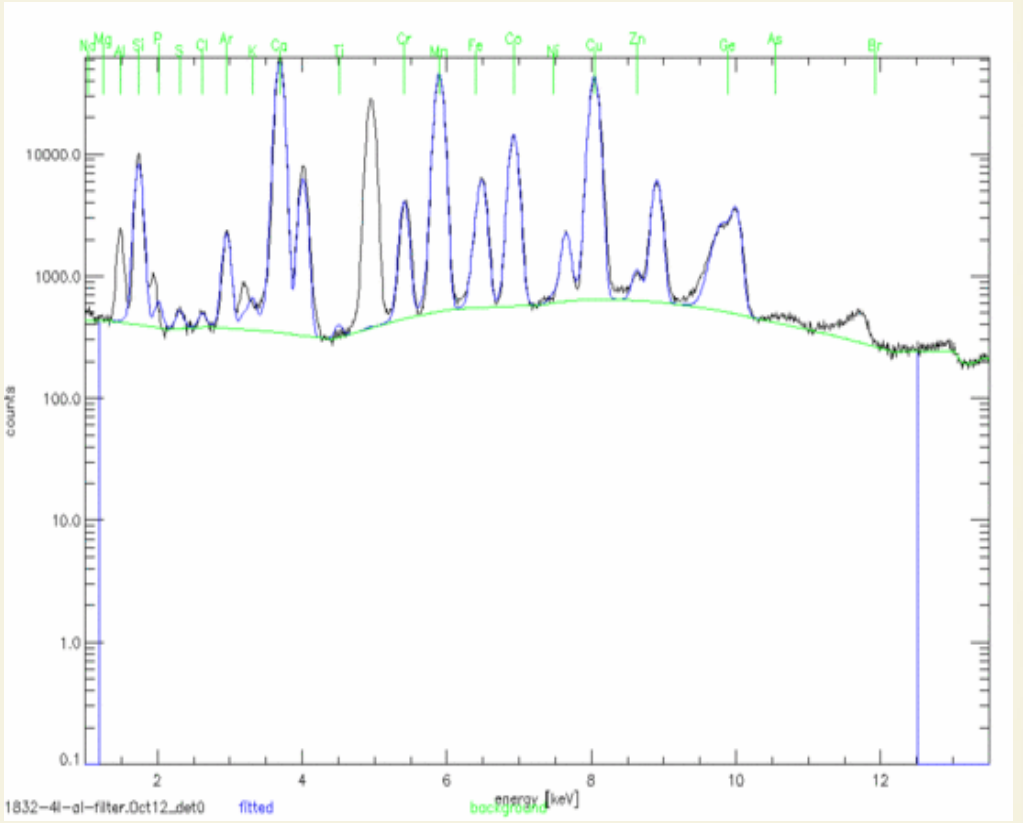


Ti figure courtesy of Simon Bare

Fluorescence spectra



FLUORESCENCE GEOMETRY

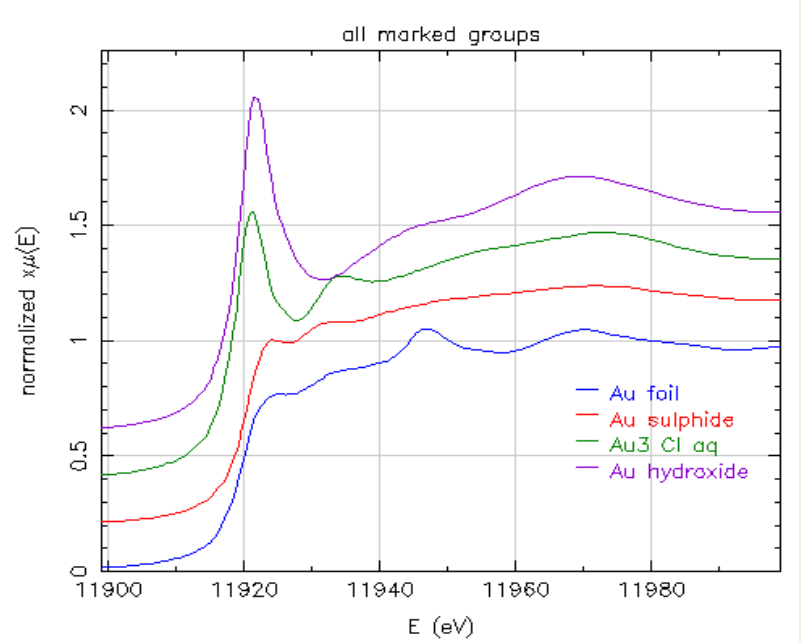


- Incident photon energy = 10 keV
- All elements with absorption edges below 10keV fluoresce at their characteristic energies
- This spectrum is from a standard purchased from NIST
- By comparing to this, you can quantify elemental composition in an unknown sample

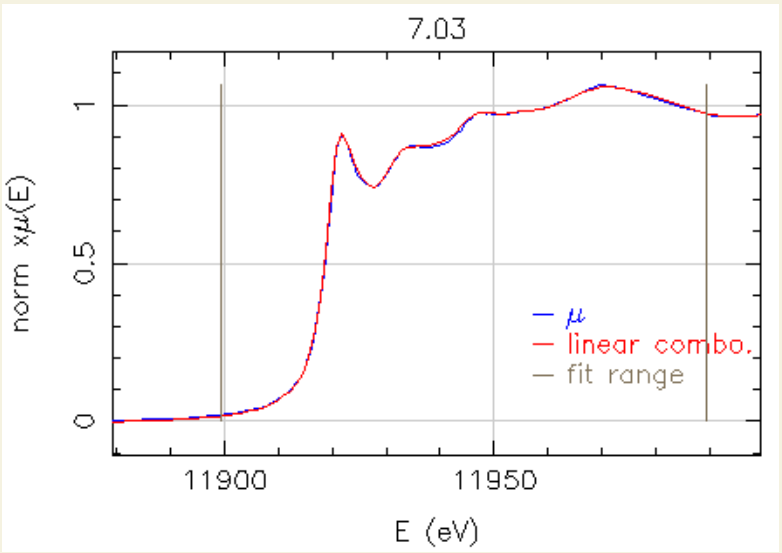
What do we learn from the fluorescence spectrum?

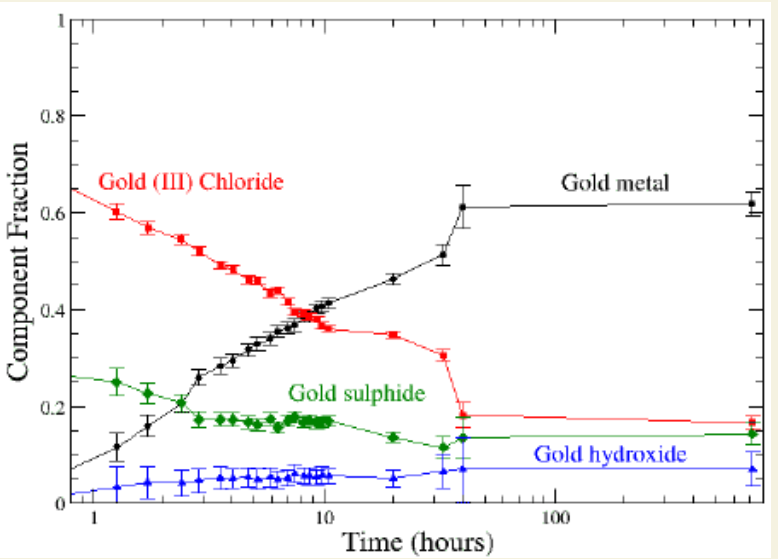
- Spatial distribution of elements
  - K-B mirrors: about 5 micron resolution
  - Fresnel zone plate: about 120 nm resolution
- Concentrations of elements
- Micro-
  - -spectroscopy
  - -diffraction

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.

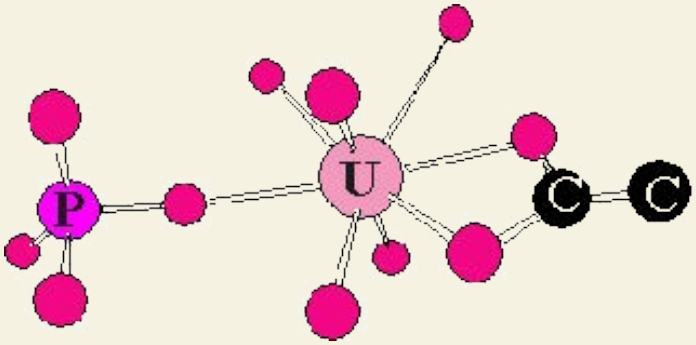


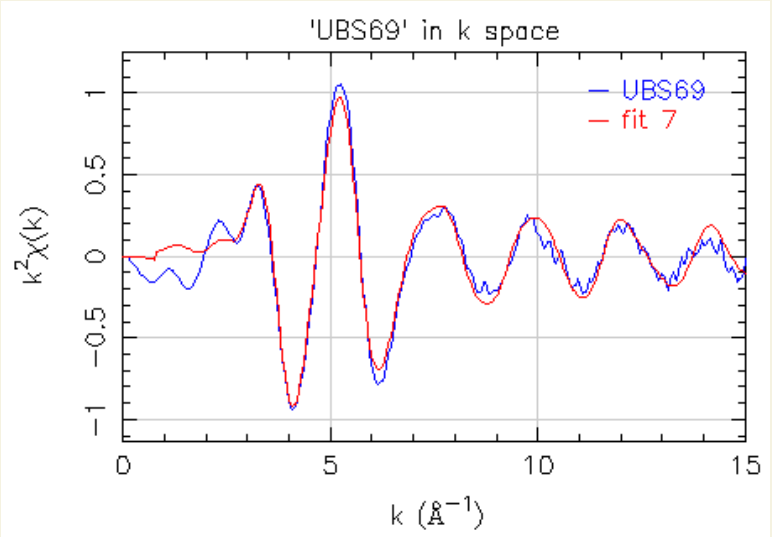


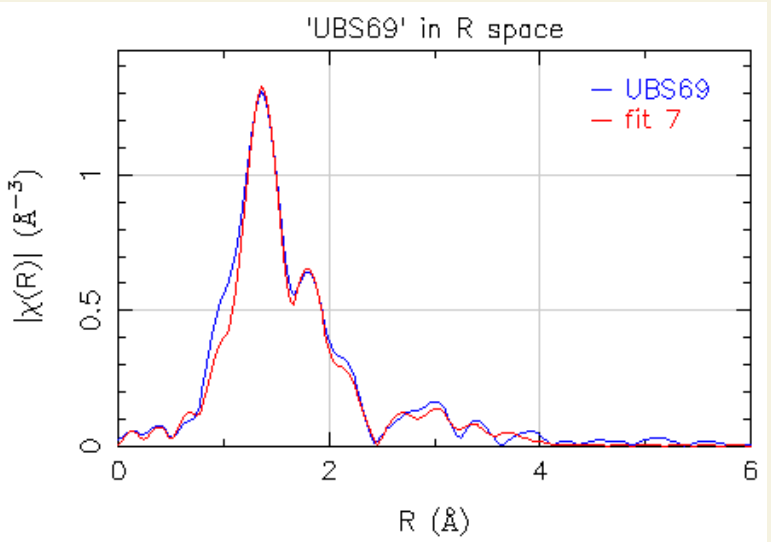
Work done with G. Southam and M. Lengke, University of Western Ontario

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.

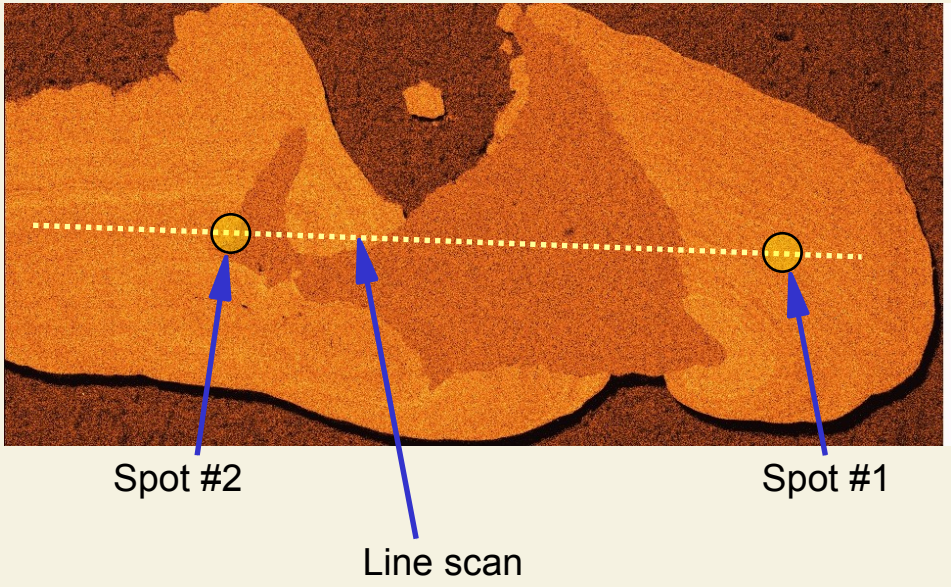




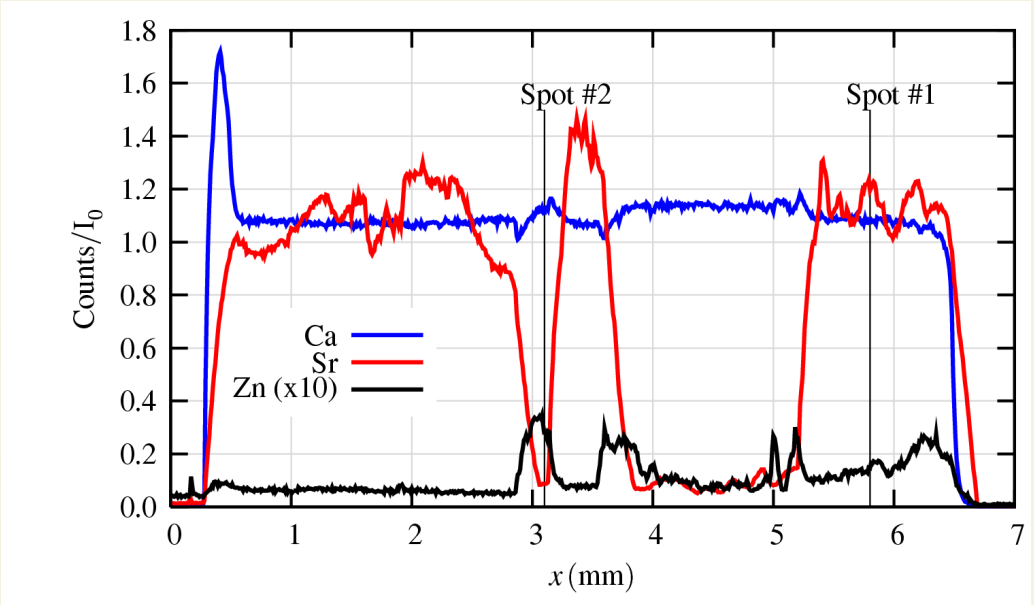


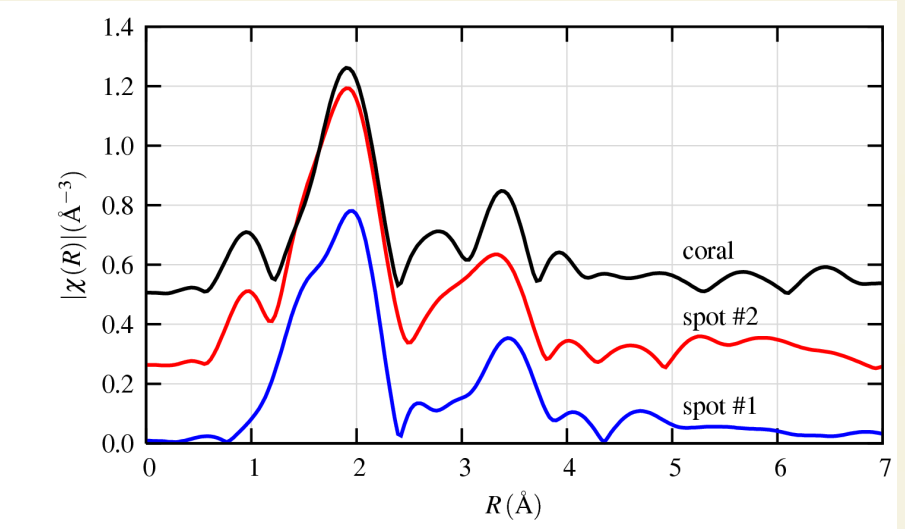
Work done with J. Fein, Notre Dame. Uranyl image courtesy S. Kelly.

Fluorescence maps 1: Sr distribution in arctic fish ear bones



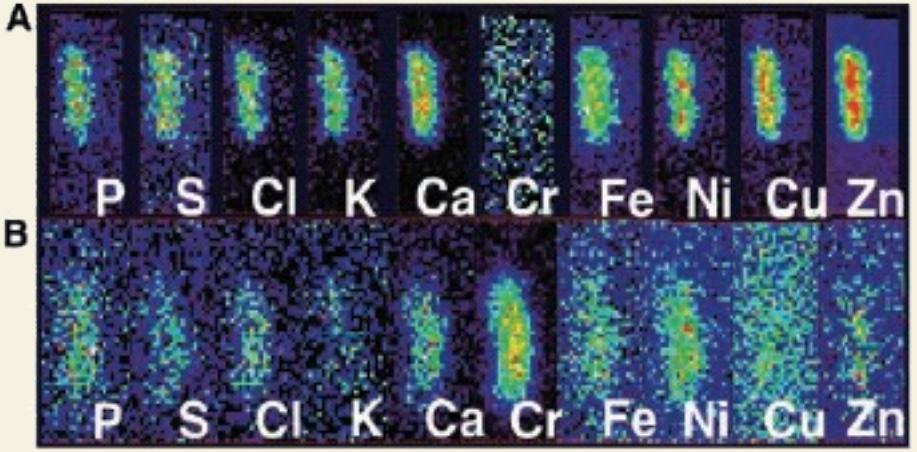
- Ear bone composition gives clues to life cycle, such as time spent in clear of brackish water
- 5 micron spot size using Kirkpatrick-Baez mirrors at 13BM
- Line and areal scans to measure elemental distribution
- Pick interesting spots and measure spectroscopy

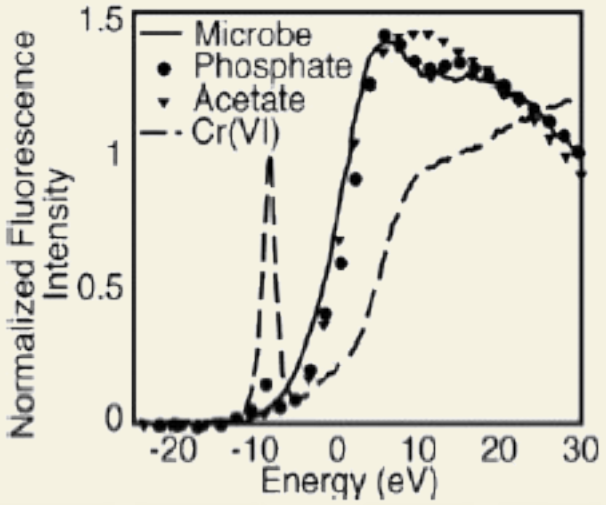




All images courtesy Matt Newville, research by Ken Severin, Tom Trainor, Univ of Alaska, Fairbanks, Randy Brown, US Fish and Wildlife Service

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

K. M. Kemner, S. D. Kelly, B. Lai,1 J. Maser, E. J. O'Loughlin, D. Sholto-Douglas, Z. Cai, M. A. Schneegurt, C. F. Kulpa Jr., K. H. Nealson *Science* **306** (2004) 686-7

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 ~ 10^{-15} sec

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

SPATIAL RESOLUTION

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

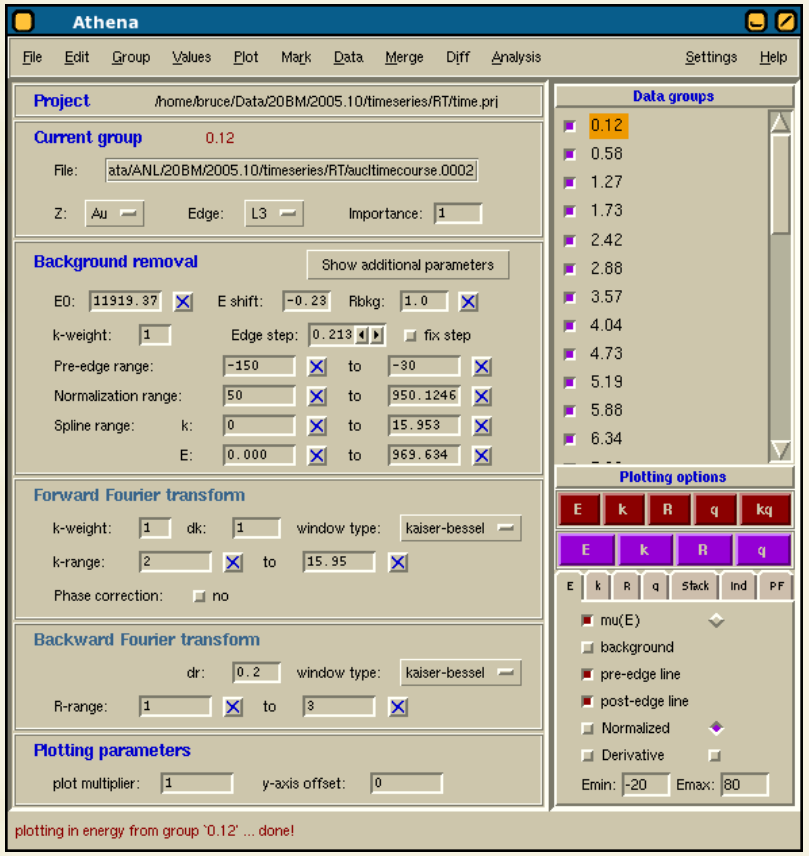
XRD or Raman might be much more sensitive to symmetry breaking, albeit with different length and time scales.

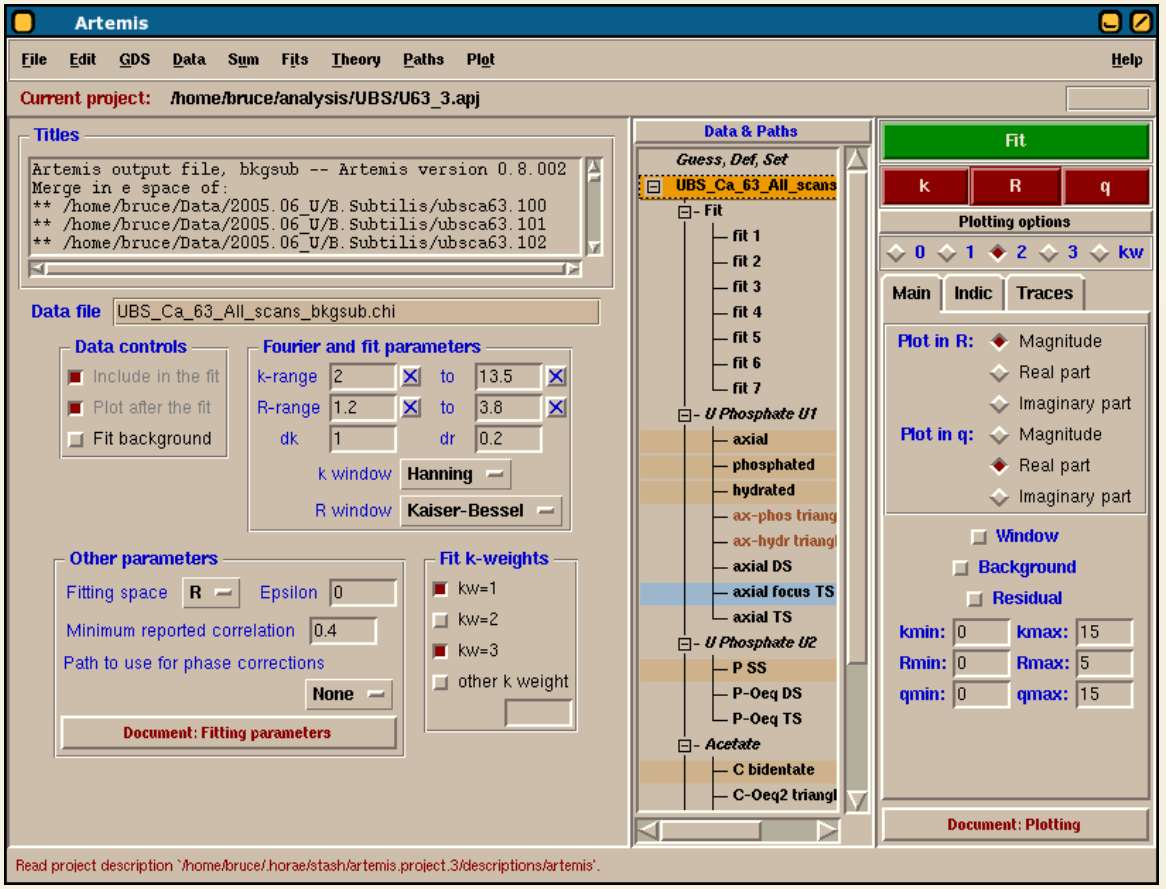
STRUCTURAL DISORDER

XAS sees disorder in interatomic distance.

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

Dealing with spectroscopy data



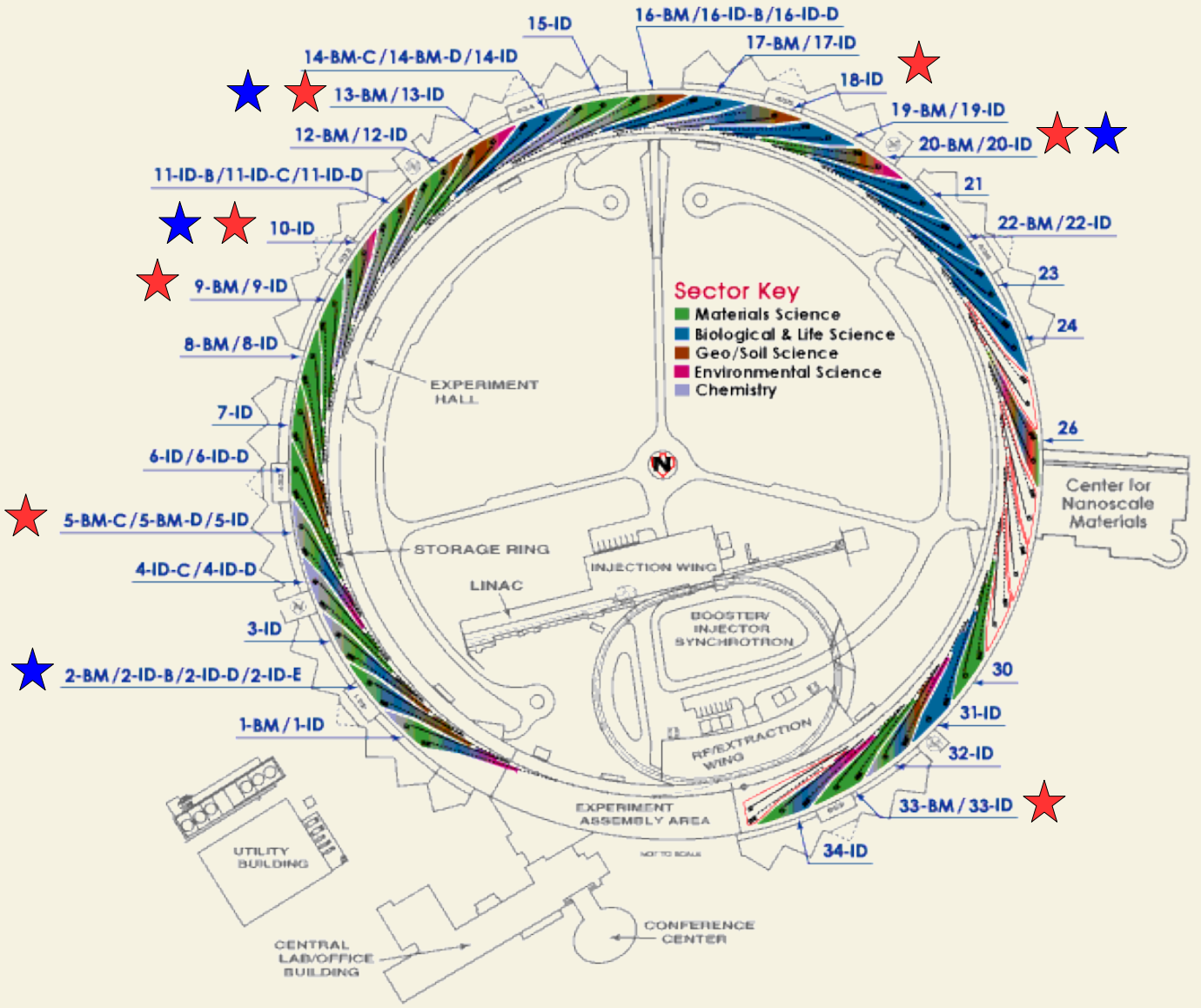


ATHENA: XAS DATA PROCESSING

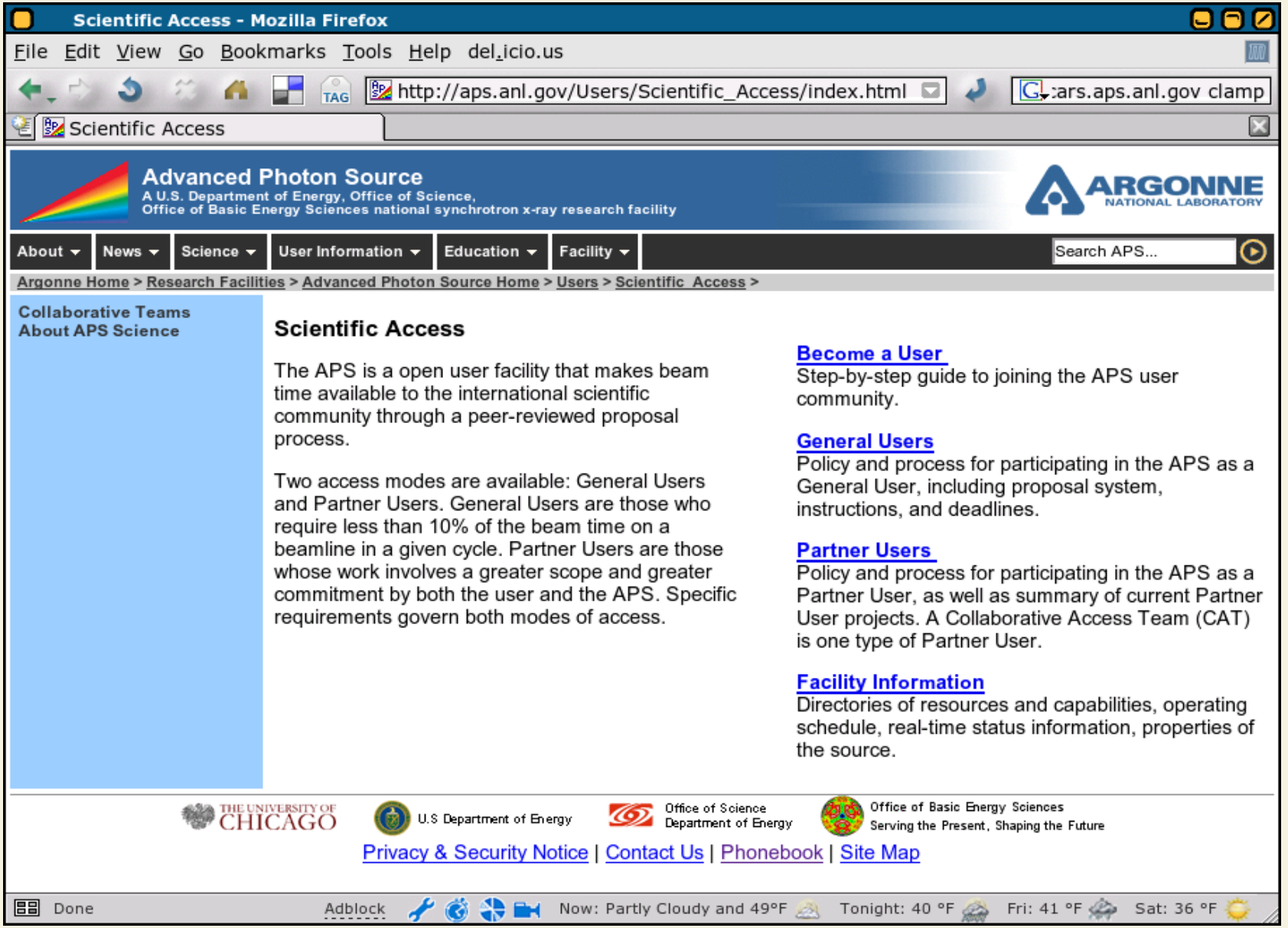
ARTEMIS: EXAFS DATA ANALYSIS

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

Spectroscopy beamlines at the APS



Applying for beamtime.



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