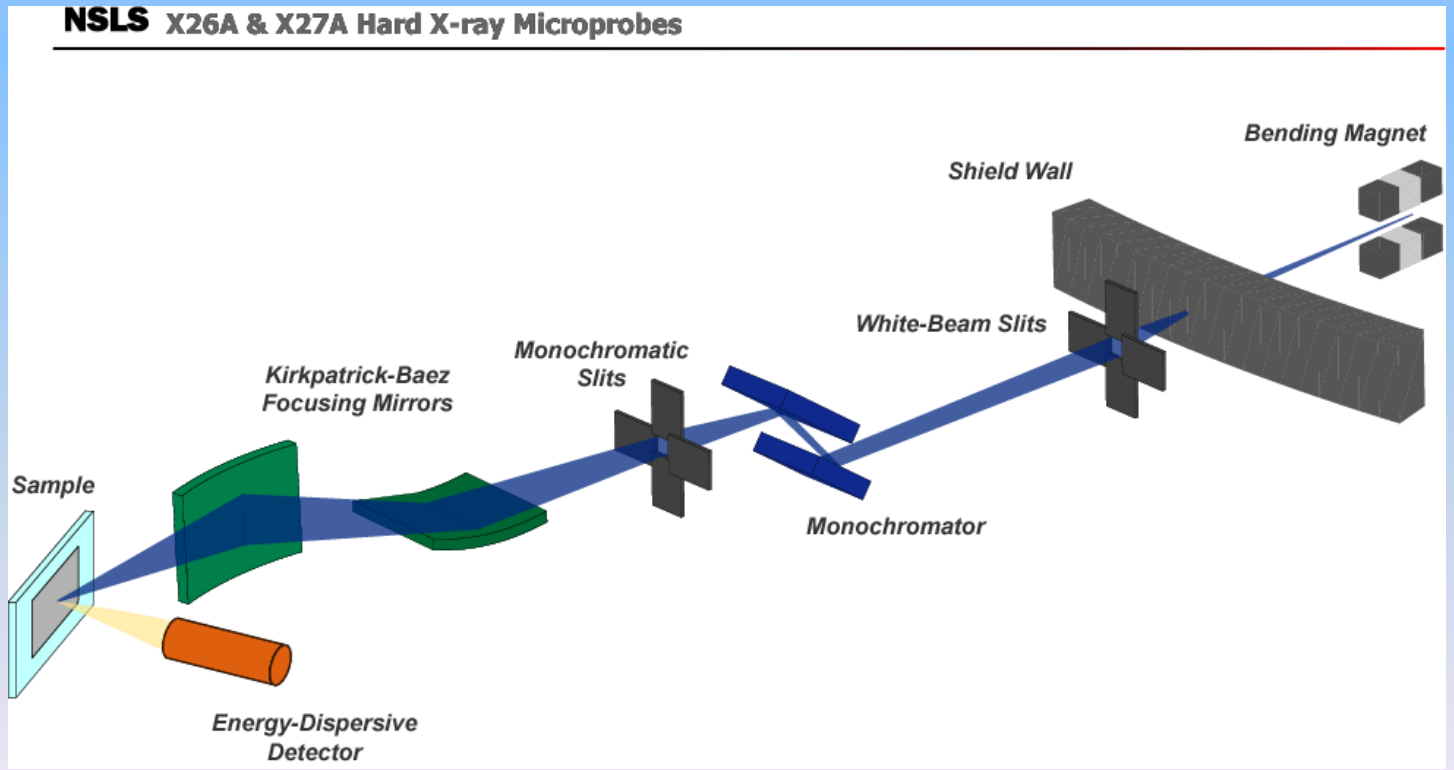
The NSLS's X-ray Microprobes, Imaging the Chemistry of Our Natural World with Pinpoint High Intensity X-ray Beams

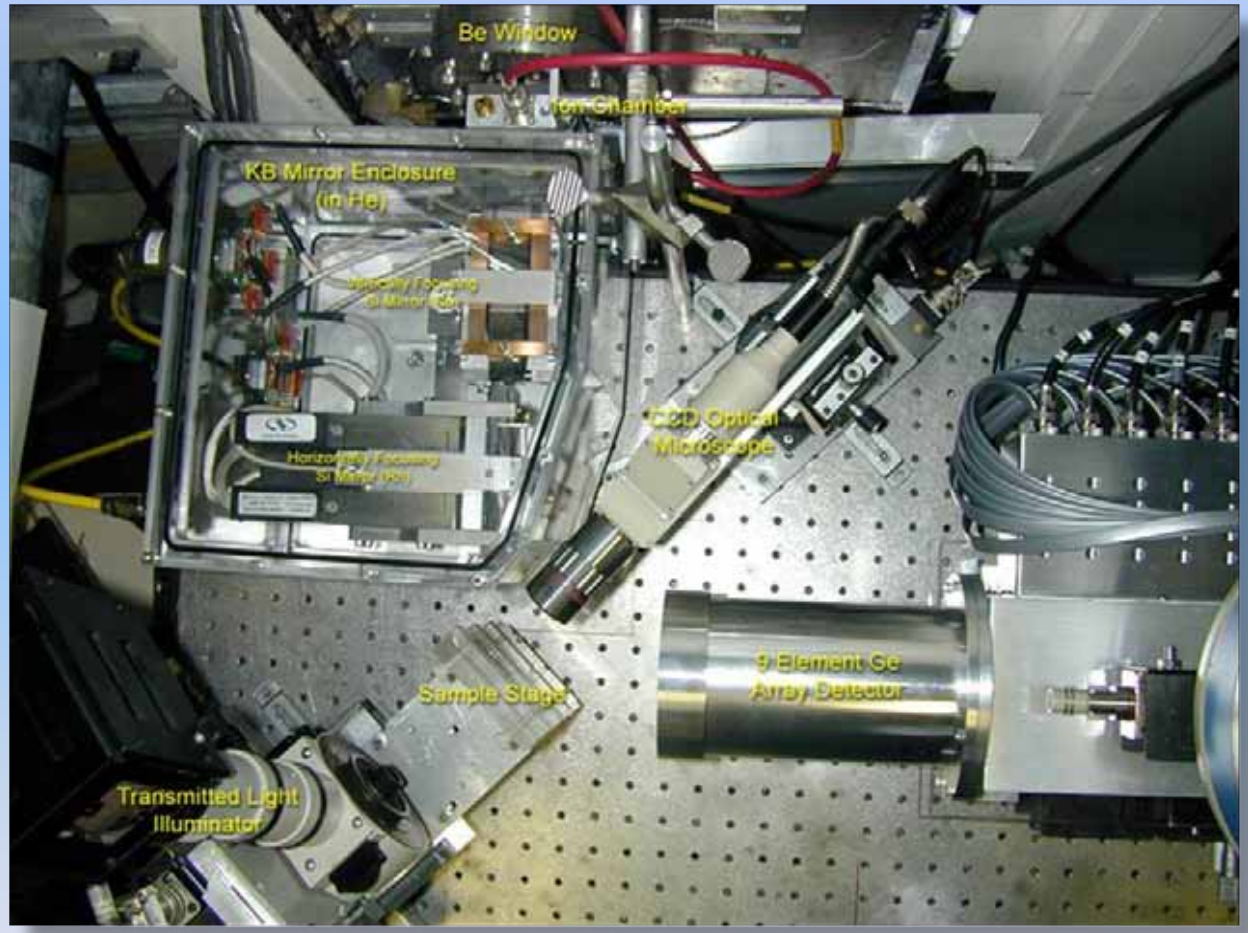
Tony Lanzirotti
University of Chicago
Center for Advanced Radiation Sources

Synchrotron X-ray Microprobes

- *These beamlines focus these bright beams to very small size (<10 µm …f.y.i human hair is ~100 µm diameter) to:*
  - *Examine the distribution of elements at micron scale*
  - *Evaluate the molecular form of these elements*
  - *Determine the mineralogy of a sample at micron scale*



Synchrotron X-ray Microprobes

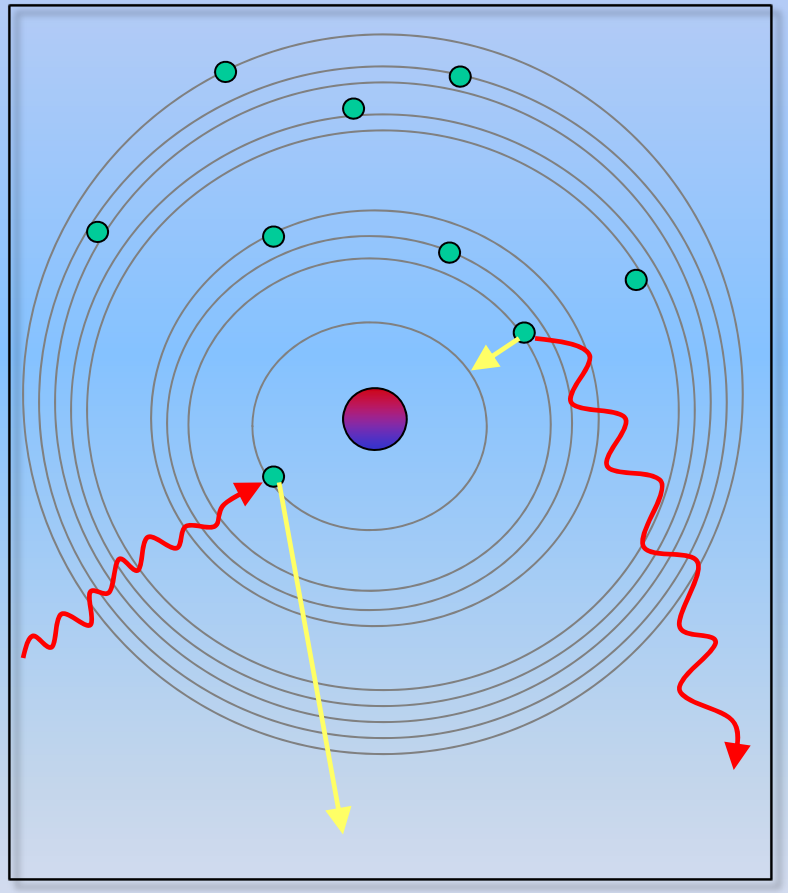


- Elemental analysis done through detecting fluorescent X-rays emitted from a material after excitation.

- In-situ chemical characterization allows us to analyze elements at the femtogram level (0.000000000000001 or $1x10^{-15}$ grams).

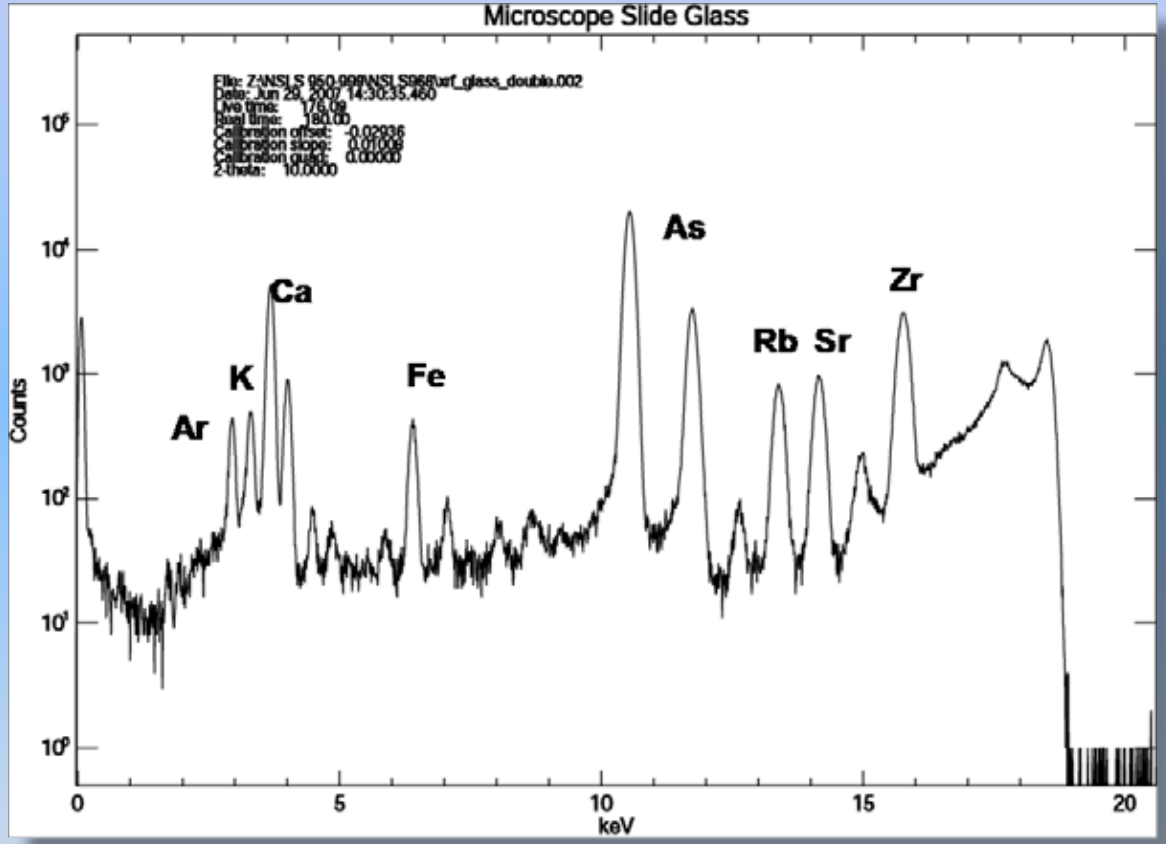
- We can produce “images” of the elemental distribution by scanning the sample through the X-ray beam in small steps.

The X-Ray Fluorescence Process



- A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected it from the atom.
- Higher energy electrons cascade to fill vacancy.
- Giving off characteristic fluorescent X-rays.
- These are detected using very sensitive X-ray detectors.

X-ray Energy Dispersive Spectra

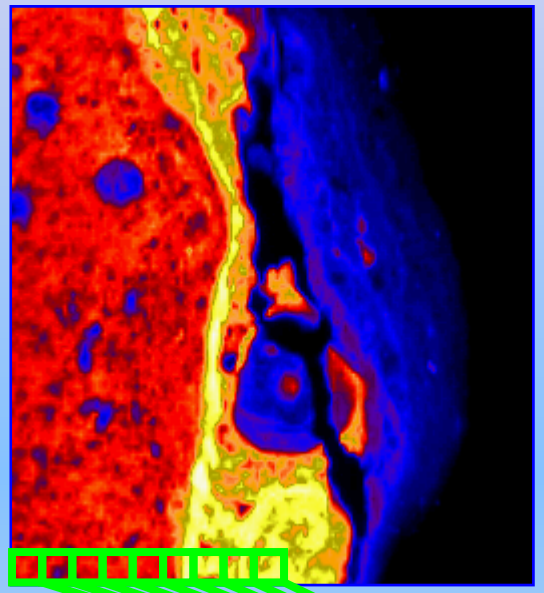


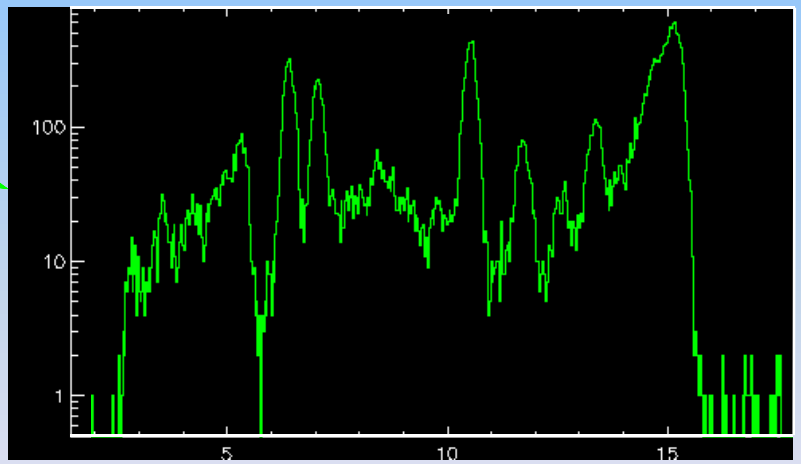
- Energy of the peak is element specific, each element has a characteristic set of excitation and fluorescence energies
- Intensity of the peak is proportional to concentration

Iron: Z=26

Edge	Energy
K	7112
L3	706.8
L2	719.9
L1	844.6

Line	Transition	Energy	Strength
$K\alpha_1$	K-L3	6405.2	0.580
$K\alpha_2$	K-L2	6392.1	0.294
$K\beta_1$	K-M3	7059.3	0.082
$K\beta_3$	K-M2	7059.3	0.043
$K\beta_5$	K-M4,5	7110.0	0.001





- We can then “Scan” the sample through the focused beam to make a map.
- Much of what is done is to “image” the chemistry of a sample

David Patterson, Australian Synchrotron

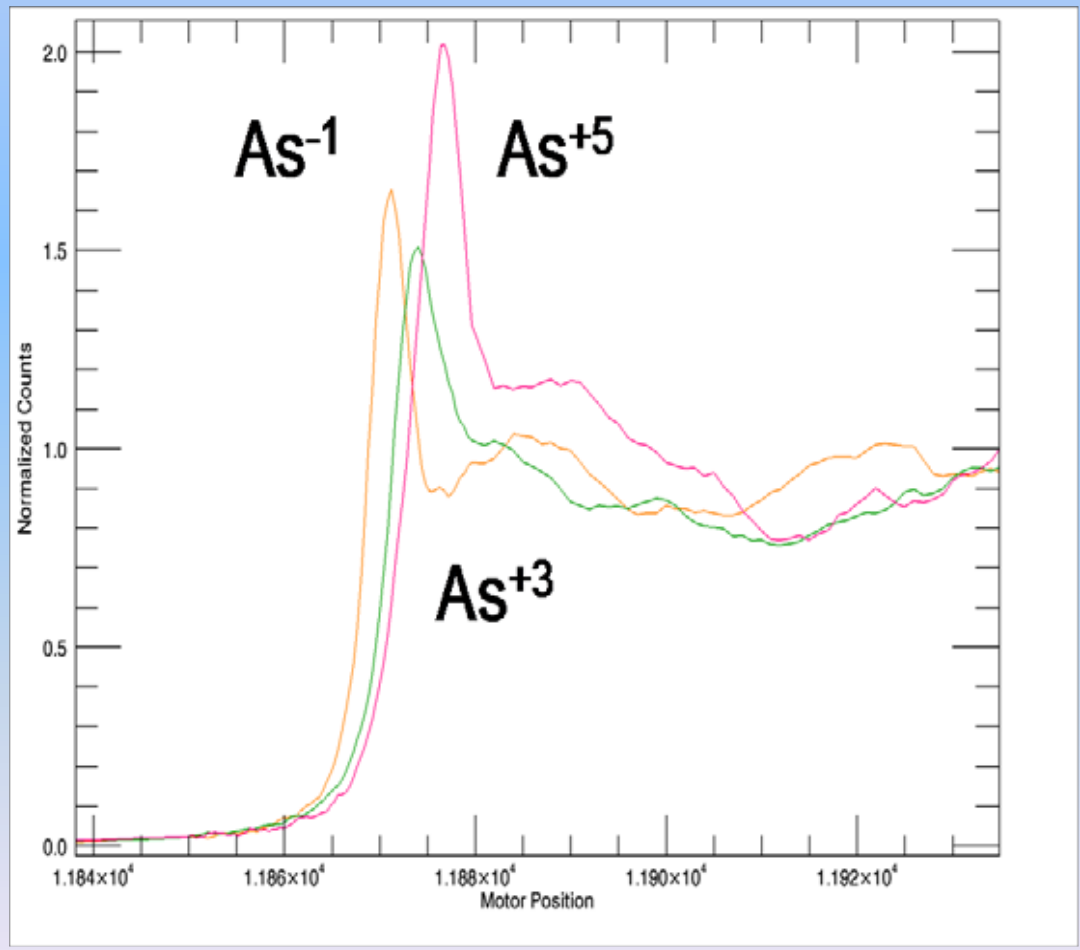
X-ray Absorption Spectroscopy

- We can also measure the absorption of the incident radiation as a function of energy due to its interaction with a sample

- X-ray absorptions are associated with the excitation of inner shell electrons in atoms

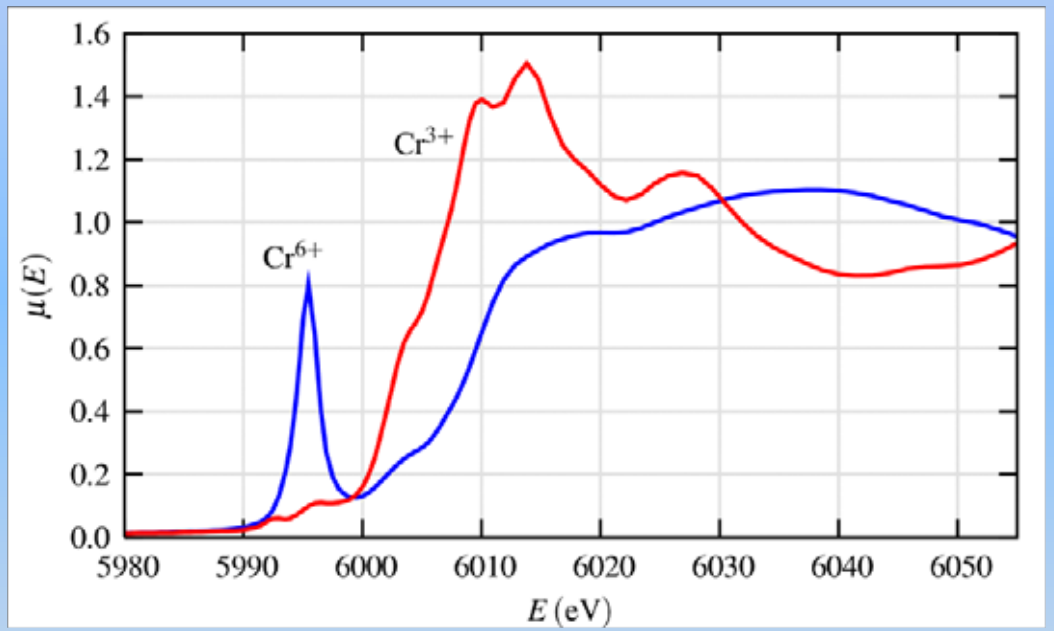
- The shape and intensity of features in an absorption spectra can be used to determine:
  - ❖ the formal valence of an element
  - ❖ the coordination environment (e.g., octahedral, tetrahedral coordination)
  - ❖ and subtle geometrical distortions of the coordination

Arsenic



X-ray Absorption Spectroscopy

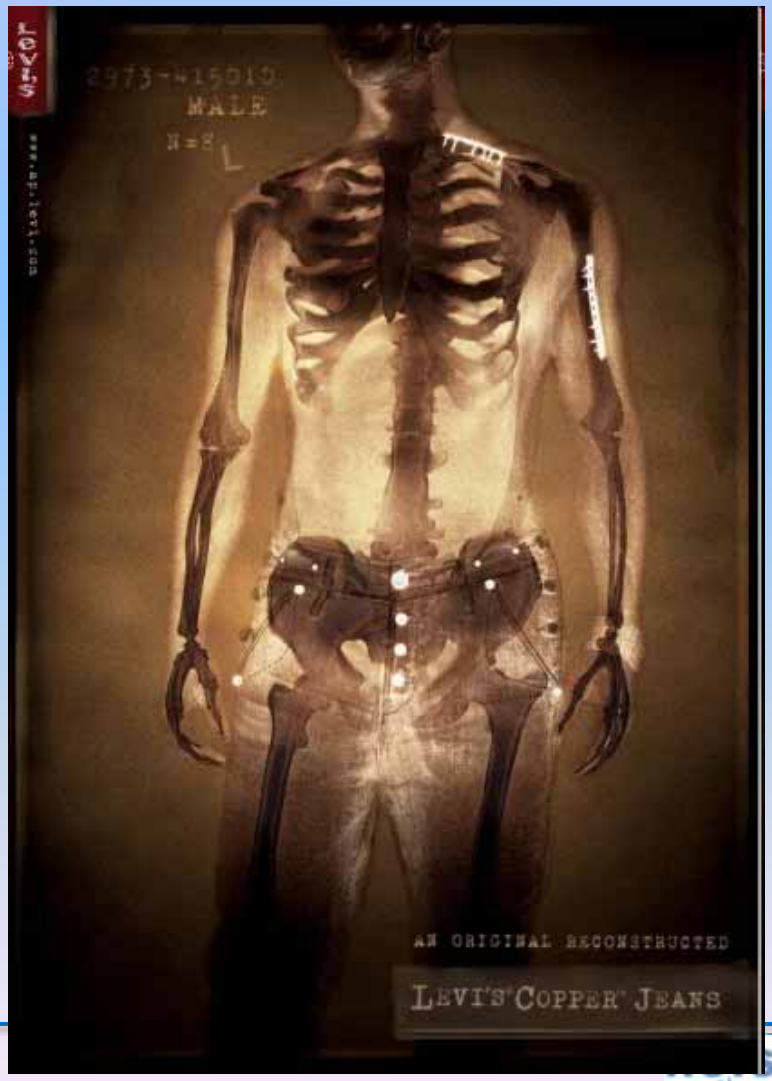
Chromium



Elements that are relatively straight-forward to do spectroscopy (XANES) on: Cr, Ti, Mn, Fe, As, Cu, Ni

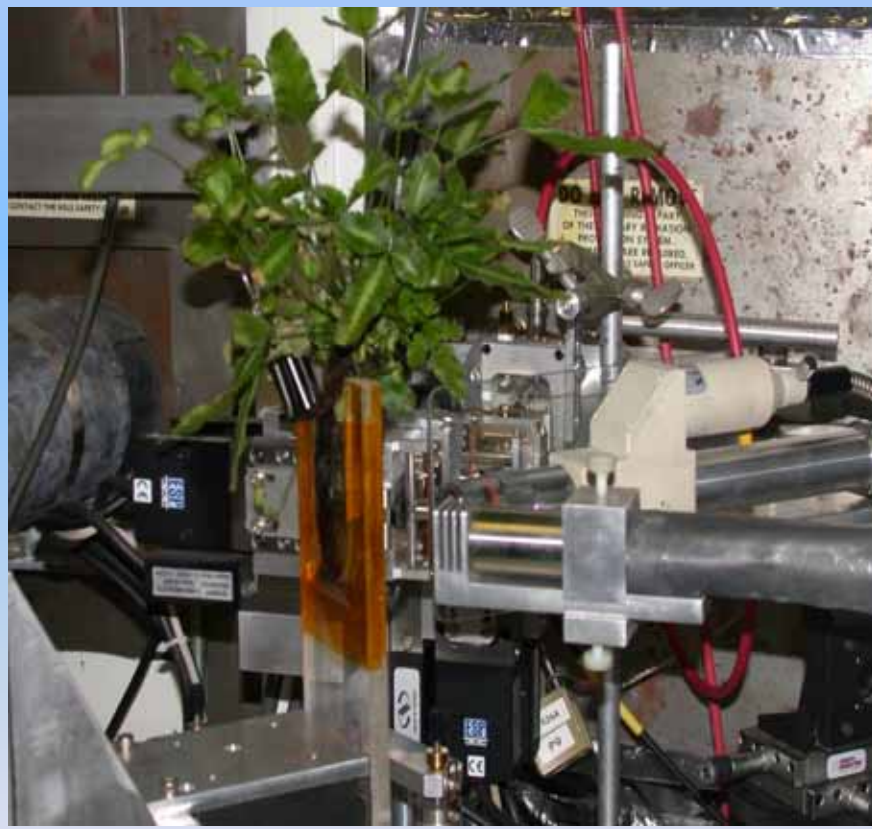
Unique Scientific problems addressed using X-ray Fluorescence Microprobes

- X-rays are penetrative and the power deposited to a sample from the beam is very low



Unique Scientific problems addressed using X-ray Fluorescence Microprobes

- X-rays are penetrative and the power deposited to a sample from the beam is very low
- Samples can be analyzed in a wet or moist state (in-situ)
- Large samples can be analyzed and the analysis generally requires only the most minimal of sample preparation



Unique Scientific problems addressed using X-ray Fluorescence Microprobes

- X-rays are penetrative and the power deposited to a sample from the beam is very low
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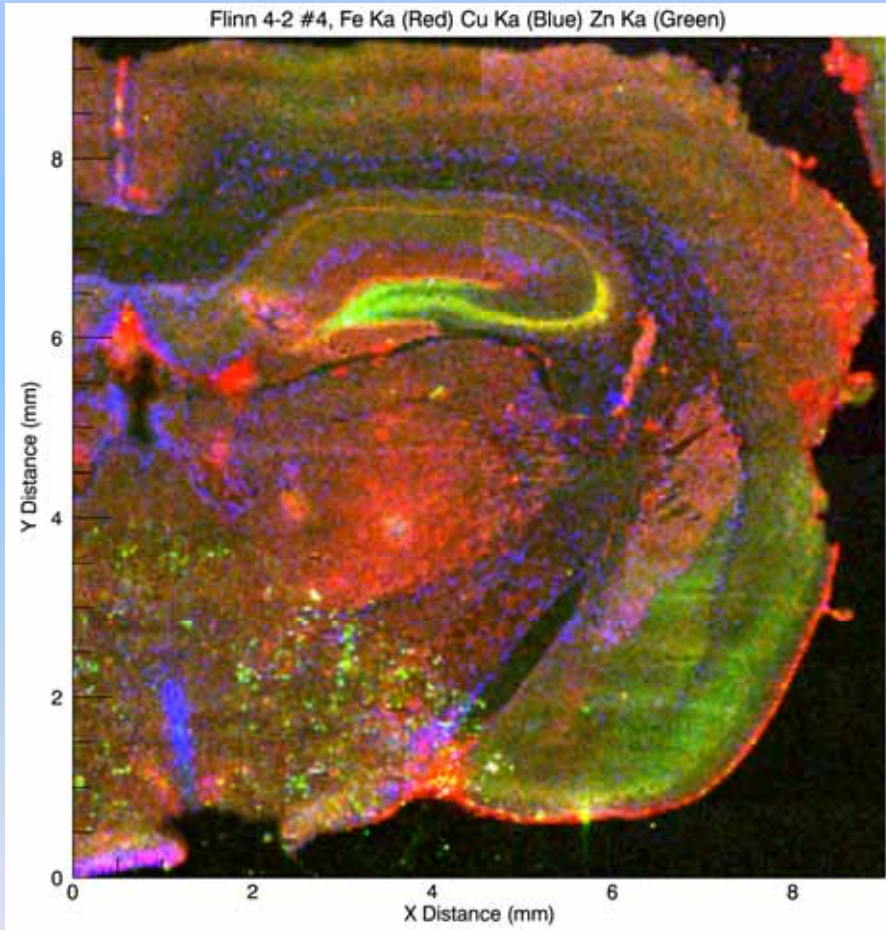
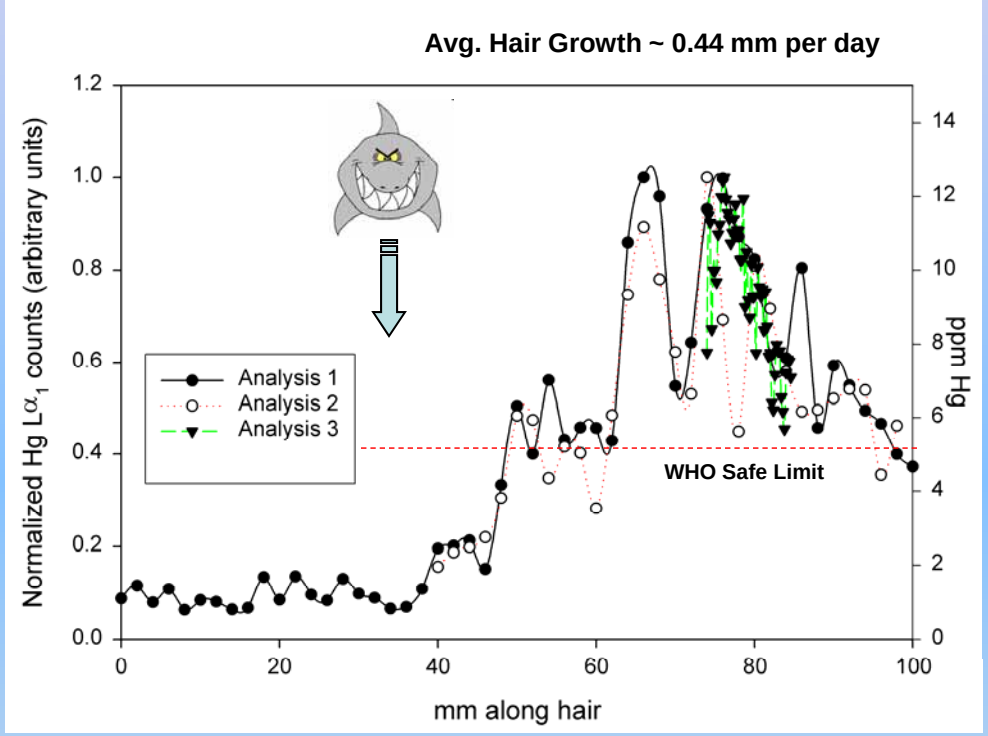
- Large samples can be analyzed and the analysis generally requires only the most minimal of sample preparation
- In its simplest form experiments are done as an “imaging” technique where image “intensity” directly correlates to element concentration
- You get a broad range of elements simultaneously



Some examples of experiments that can be done using X-ray microprobes

Human Health Risks From Methyl Mercury In Fish



- Mercury is a naturally occurring element that is found in air, water and food.
- Most people are exposed to mercury via food. Fish take up mercury as they feed, where it is converted to the more toxic, methylmercury form.
- Pregnant women - or, rather, their unborn babies - are at the greatest risk. Babies developing in the uterus seem to be most vulnerable to the effects of mercury on their nervous systems.
- Synchrotron microprobes allow you to measure heavy metal exposure in hair as a function of time with a resolution of ~15 minutes of hair growth!

Ferdinand II of Aragon

Ferdinand the II (1452 –1516)

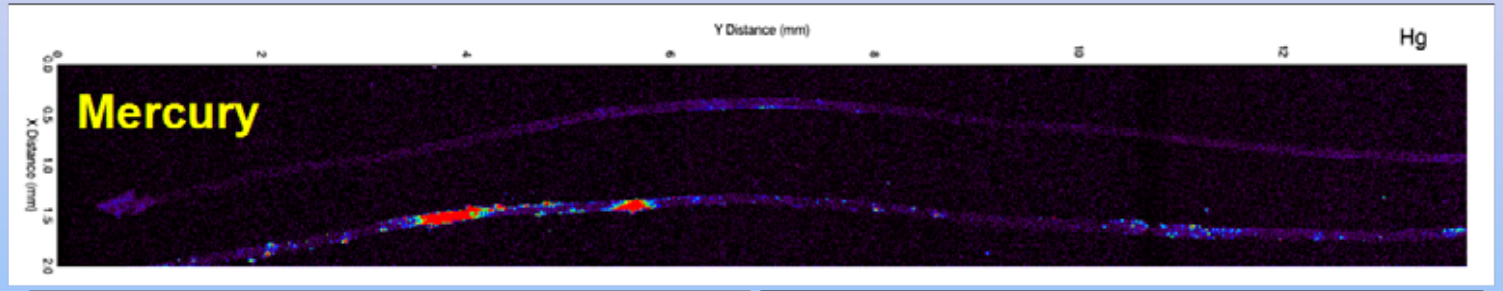
- King of Aragon , Sicily, Naples, Valencia, Sardinia and Navarre
- Husband of Isabella, queen of Castile
- He and Isabella united all of Spain under one rule
- In 1492, Columbus, sailing under the auspices of Ferdinand and Isabella, discovered the New World
- Died in 1516 of an unknown fever associated with bloody diarrhea within a one month period

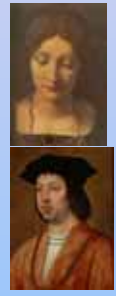
Isabella di Aragon (1470 –1524)

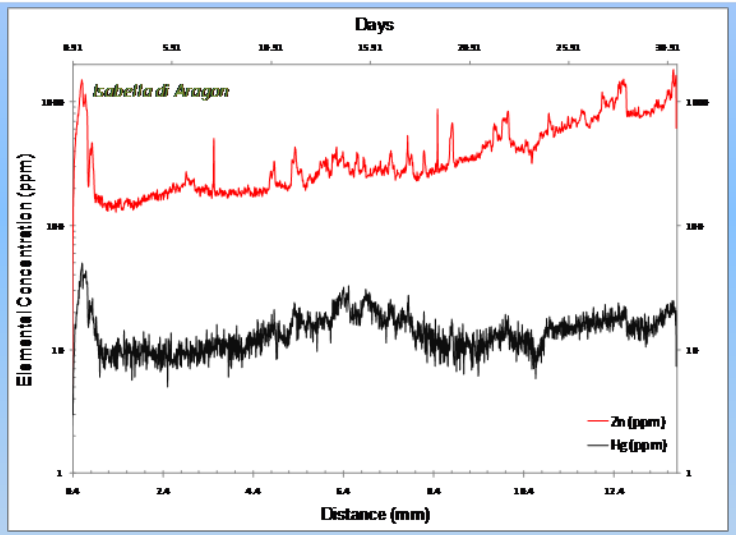
- Princess of Naples, Duchess of Milan
- Sister of Ferdinand II
- Clandestinely married Leonardo da Vinci in 1497
- Suggestions she was the subject of the Mona Lisa
- Isabella died of “plague” in February 1524 although one brief and unique historical account implies that she died of dropsy (edema).

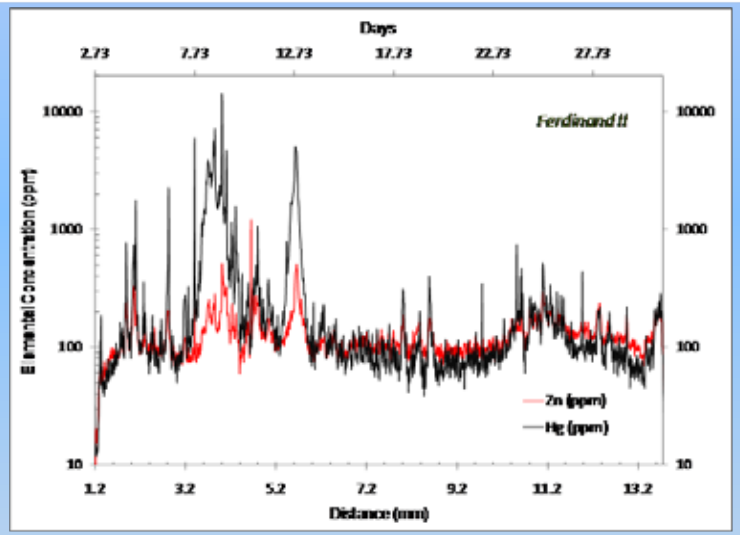
Isabella di Aragon

Lanzirotti, A. Bianucci, R., Quall, R., Ferroglio, E., Nerlich, A., Giuffra, V., Fornaciari, G., and Appenzeller, O. (2011) Leishmaniasis in 15th century Italian nobles and mercury treatment. Proceeding VII World Congress on Mummy Studies.

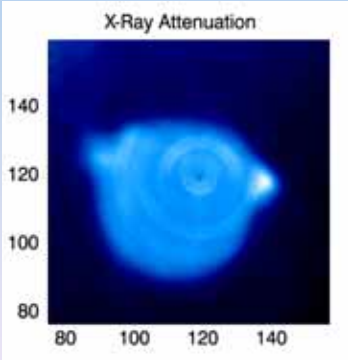


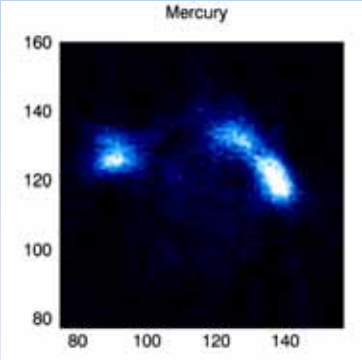






World Health Organization has placed the level at which risk begins at 50 ppm of mercury in hair for most people. The WHO then applied a safety factor of 10, estimating that a level of 5 ppm or less is safe for even the most vulnerable populations.





Brookhaven National Laboratory presents

Science Café

BOOK READING AND DISCUSSION

Forensics at Brookhaven Lab's Light Source: The Truth and the Fiction Behind *Red Herring*

An Evening With Crime Novelist Archer Mayor
Author of the Joe Gunther Mystery Series

Thursday, June 9, 2011
Starting at 7 p.m.

Berkner Hall
Brookhaven National Laboratory

Brookhaven Lab is located on the east side of the William Floyd Parkway (County Route 46), 1-1/2 miles north of Long Island Expressway exit 68

All are invited. Age 16 and older, bring a photo ID.

For more information:
- communityrelations@bnl.gov
- www.bnl.gov
- www.archermayor.com

A Novel Use of a Synchrotron Light Source:
Excerpts From Red Herring
— Archer Mayor, author & 2004 New England Booksellers Association award-winner for fiction

Photon Science as a Powerful Weapon for Forensics:
Next-Generation Mystery Solving at Today's NSLS
— Biochemist Lisa Miller, geochemist Tony Lanzirotti, and physicist Eric Dooryhee, Brookhaven Lab

The NSLS as a Novel Source of Inspiration:
An Interview With Author Archer Mayor

Question & answer discussion to follow

Reception and book-signing in the lobby afterwards, at which free refreshments will be served, and *Red Herring* and other Joe Gunther books will be available for purchase from Borders Stony Brook.

An encore of this presentation will be offered at Borders Stony Brook on Saturday, June 11, 2011 starting at 1 p.m. For more information go to: www.borders.com/online/store/StoreDetailView_79 or call (631) 979-0500

"Mayor's skills are equal to the vigor of his imagination, and we take his word for every twist, every turn, every thunderbolt." — The New Yorker

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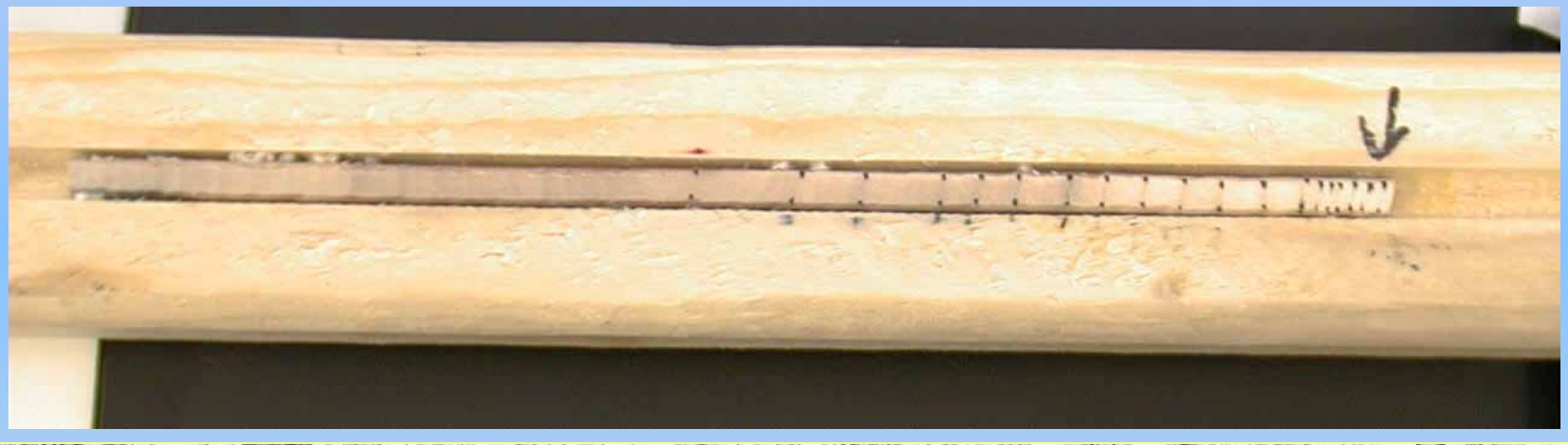
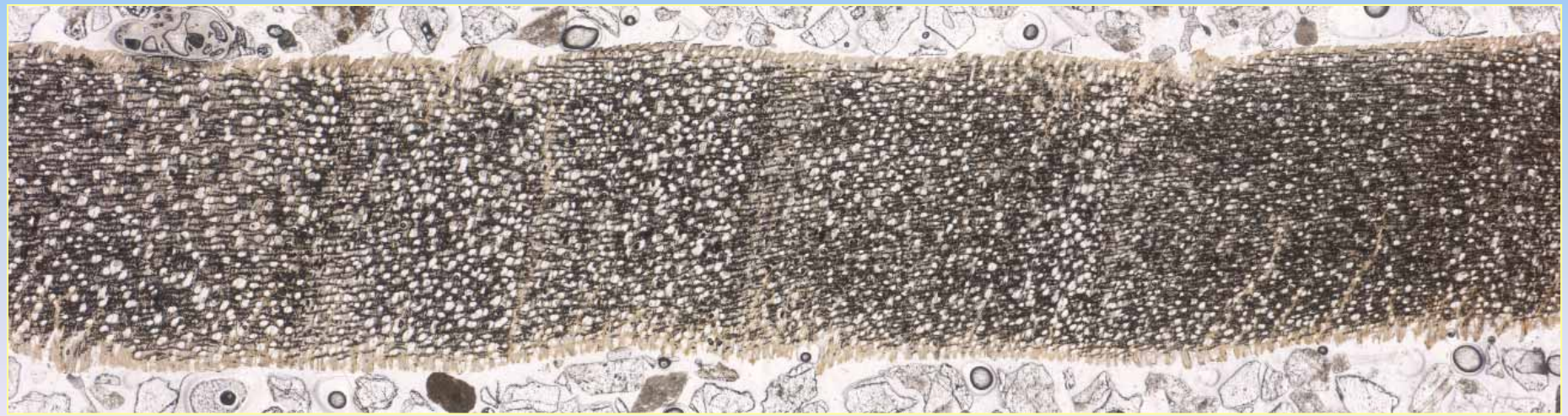
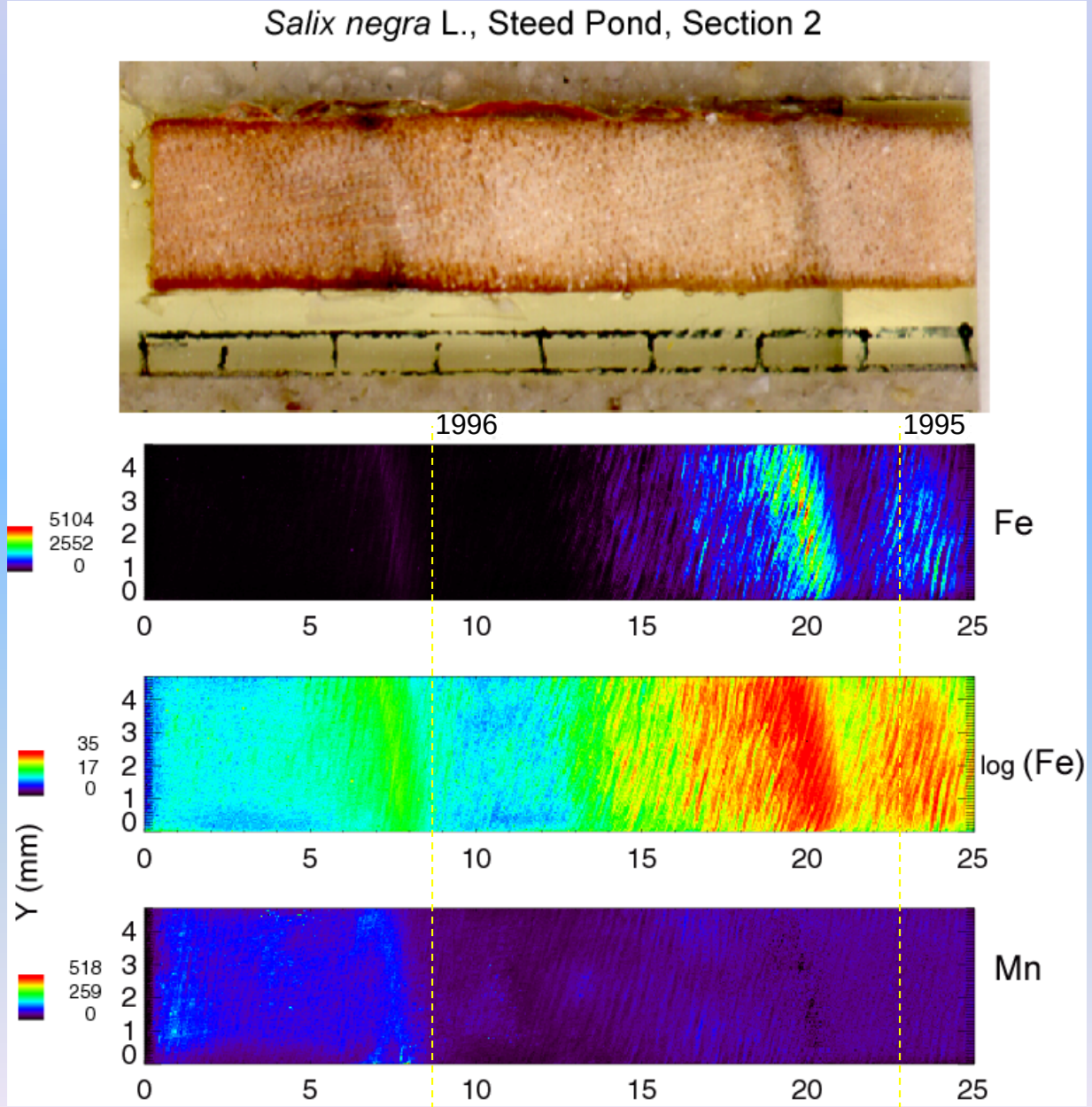
Tree Rings

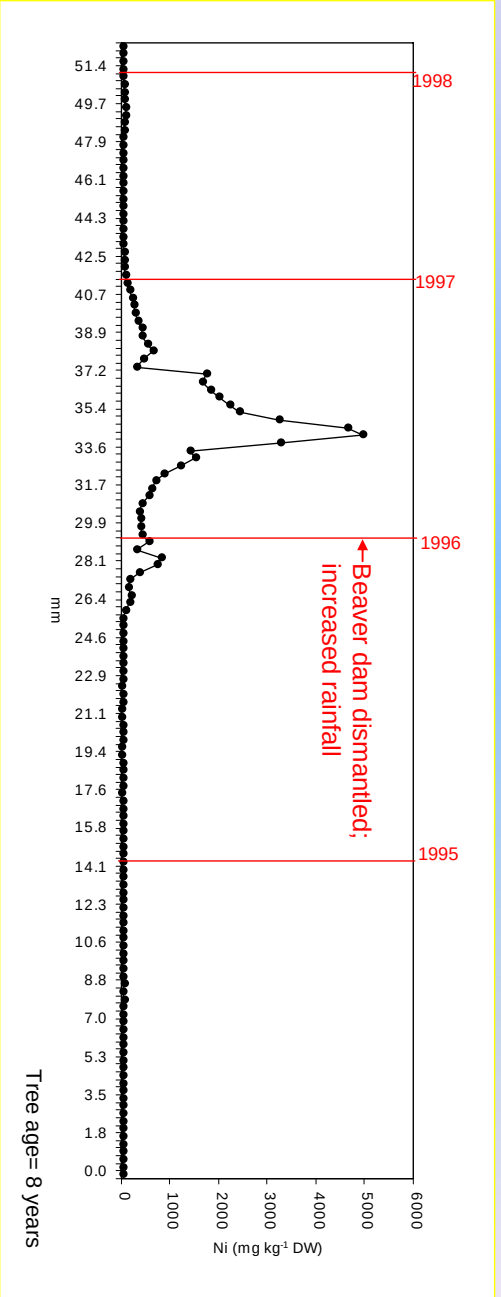
Tree cores of black willows growing at the Savannah River DOE site record contamination from contaminated pond





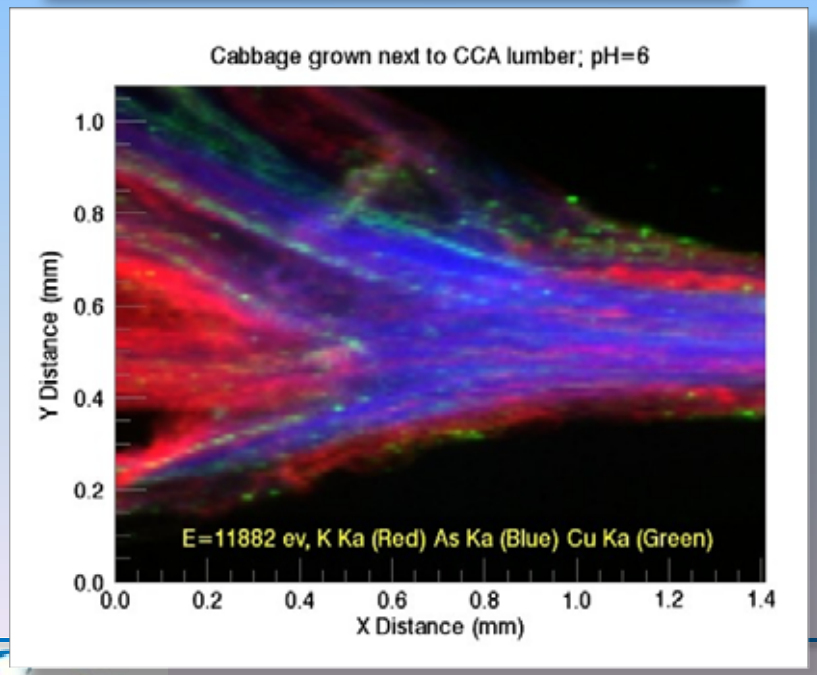
Punshon, T., Bertsch, P., Lanzirotti, A., McLeod, K., and Burger, J. (2003) Geochemical signature of sediment remobilization a contaminated wetland revealed by spatially resolved X-ray microanalysis of annual rings of *salix nigra*. Environ. Sci. and Tech., 37, 1766-1774.

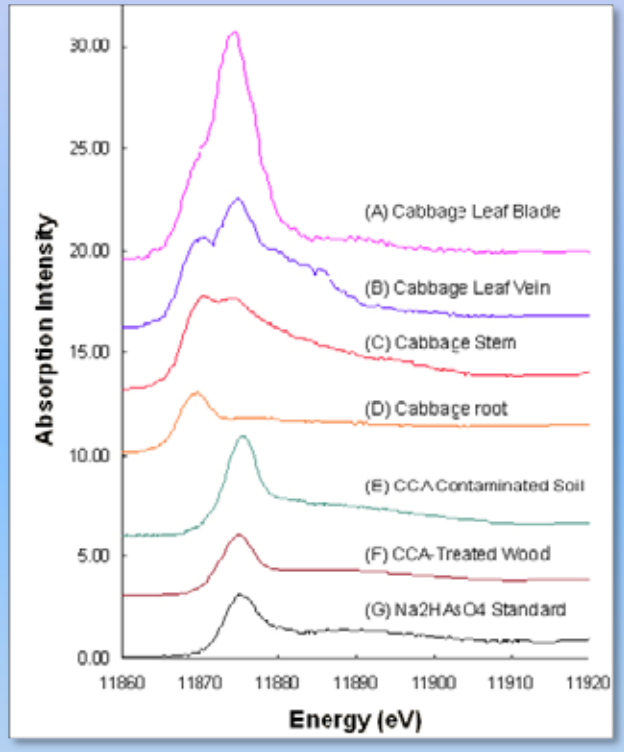

Salix negra L., Steed Pond, Section 2
1996
1995
5104
2552
0
Fe
35
17
0
log (Fe)
518
259
0
Mn
Y (mm)
0
5
10
15
20
25


1998
1997
1996
1995
Beaver dam dismantled; increased rainfall
mm
Ni (mg kg-1 DW)
Tree age= 8 years

Environmental Hazards of Pressure Treated Lumber

Cabbage grown near degrading CCA lumber





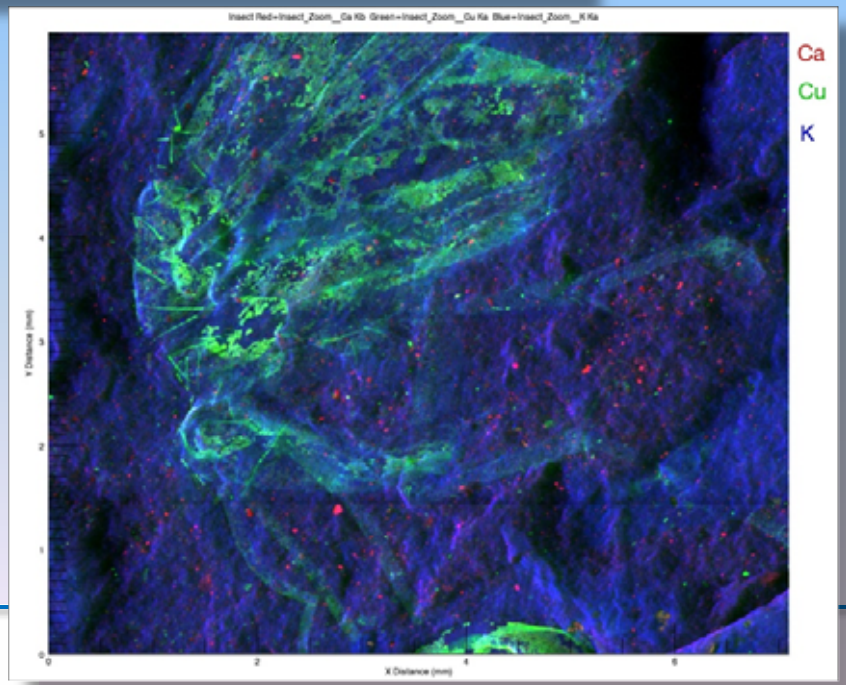
- A 12 foot long 2” x 6” piece of wood injected with an aqueous solution of Copper, Chromate and Arsenic (CCA) under pressure contains enough arsenic, if released, to kill about 250 adults.

Satish Myneni and Matthew Cooper (Princeton) and Tony Lanzirotti, NSLS

Imaging chemical signature of “soft tissue” in fossils

Thermopolis Archaeopteryx, composite P, Si, S, and Fe showing how feather chemistry has been preserved (Uwe Bergman, SSRL)

Fossil of an ancient squid, the tentacles are clearly visible (Uwe Bergman, SSRL)

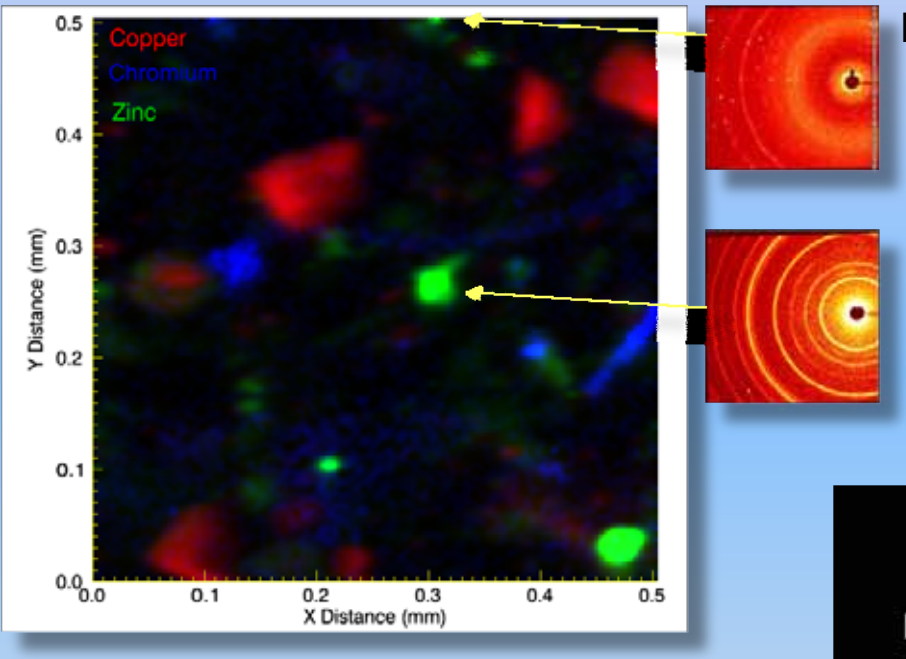


Cretaceous Stonefly fossil, Liaoning, China (Tony Lanzirotti, NSLS)

Chemistry of Household Dust

Americans spend more than 80% of their time indoors
Understanding and managing risk requires understanding metal sources and species

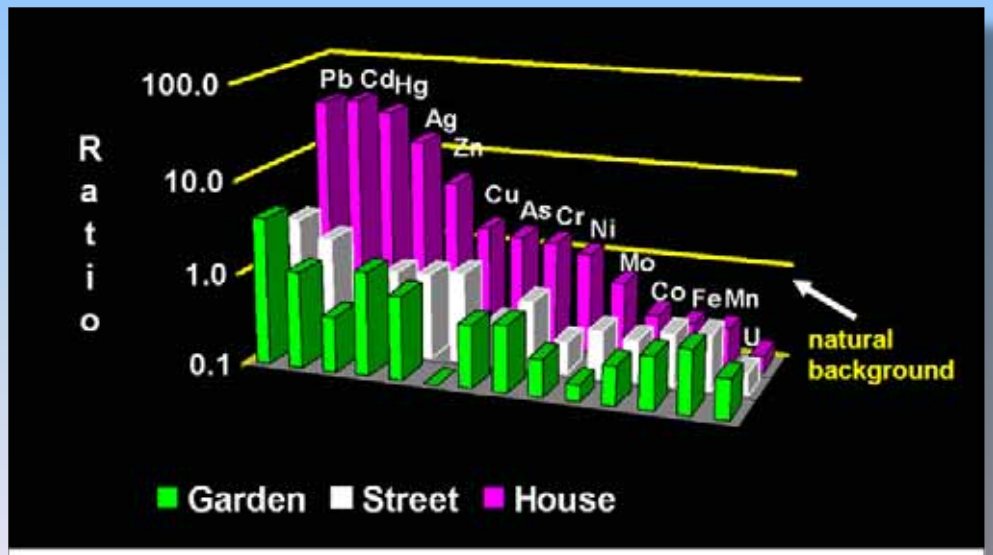
Chemistry of Household Dust



Analysis of Dust from homes in Ottawa, Canada
Identified particles:

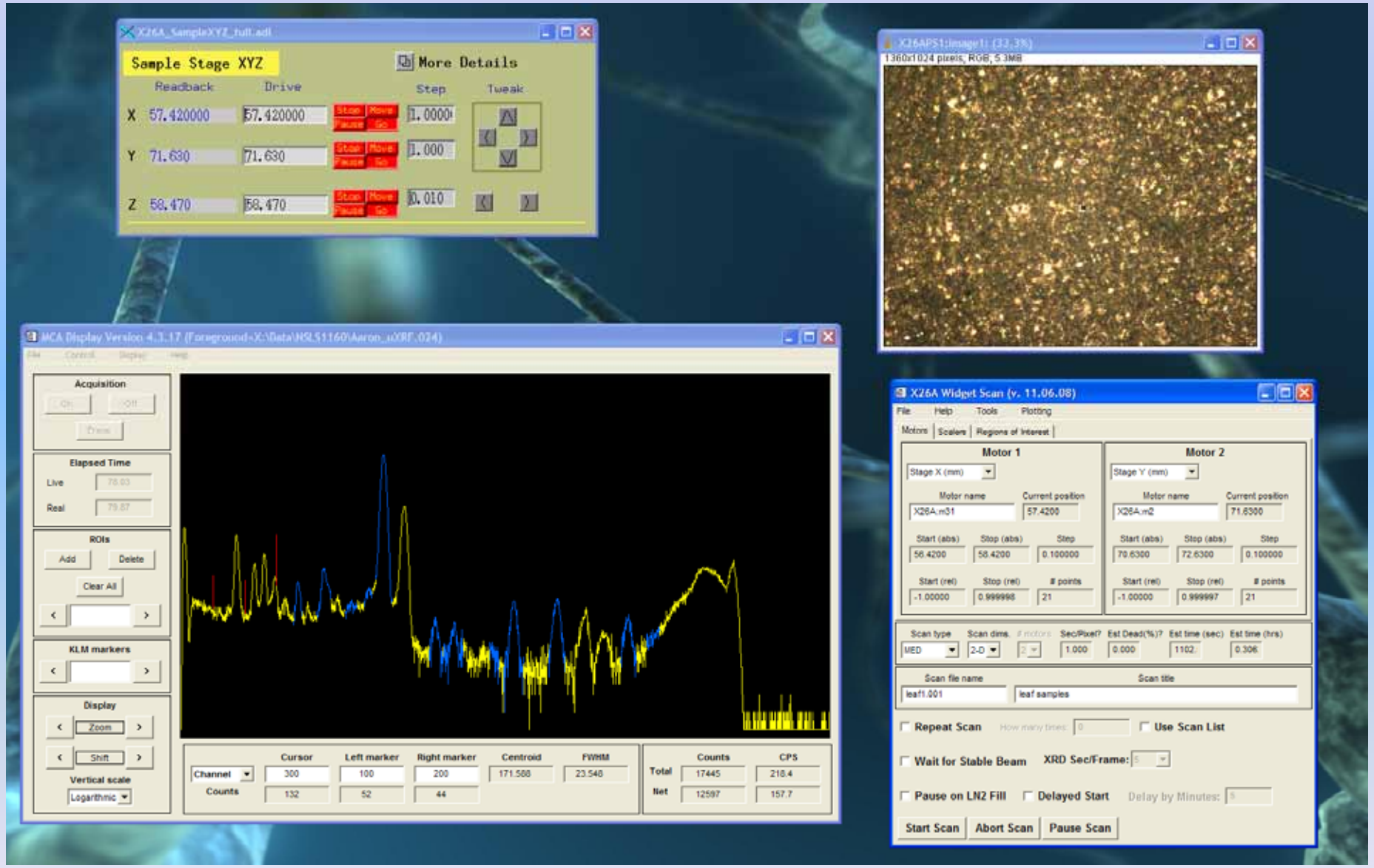
- calcite, vaterite, gypsum (wall boards)
- halite (table salt)
- portlandite (concrete)
- metallic Fe and Cu (electrical, appliances)
- Fe and Cu oxides (oxidized metals)
- wood cellulose, some high in Cu, Cr, As (CCA lumber)
- Pb carbonates and sulfates (paint and solder)

Coupled X-ray fluorescence (chemistry), diffraction (mineralogy), and absorption spectroscopy (speciation) used to characterize variable components in house dust



Rasmussen et al. 2001. *Sci. Tot. Environ.* 267(1-3) 125-140

Heather Jamieson (Queen's U.), Steve Walker (Queen's U.), Tony Lanzirotti, Health Canada, NSLS


X26A_SampleXYZ_full.adl
Sample Stage XYZ
More Details
Readback
Drive
Step
Tweak
X 57.420000 57.420000 1.0000
Y 71.630 71.630 1.000
Z 58.470 58.470 0.010
Stop Move Pause Go
X26APS1:image1: (32.3%)
1360x1024 pixels, RGB, 5.3MB
MCA Display Version 4.3.17 (Foreground=X:\Data\NSLS1160\Aaron_uXRF.024)
Acquisition
On Off
Elapsed Time
Live
Real
ROIs
Add
Delete
Clear All
KLM markers
Display
Zoom
Shift
Vertical scale
Logarithmic
Cursor
Left marker
Right marker
Centroid
FWHM
Channel
Counts
300 100 200 171.588 23.548
132 52 44
Counts
CPS
Total 17445 218.4
Net 12597 157.7
X26A Widget Scan (v. 11.06.08)
File Help Tools Plotting
Motors Scalers Regions of Interest
Motor 1
Stage X (mm)
Motor name
Current position
X26A:m31
57.4200
Start (abs) Stop (abs) Step
56.4200 58.4200 0.100000
Start (rel) Stop (rel) # points
-1.00000 0.999998 21
Motor 2
Stage Y (mm)
X26A:m2
71.6300
70.6300 72.6300 0.100000
-1.00000 0.999997 21
Scan type Scan dims. Sec/Pixel? Est Dead(%)? Est time (sec) Est time (hrs)
MED 2-D 1.000 0.000 1102. 0.306
Scan file name
Scan title
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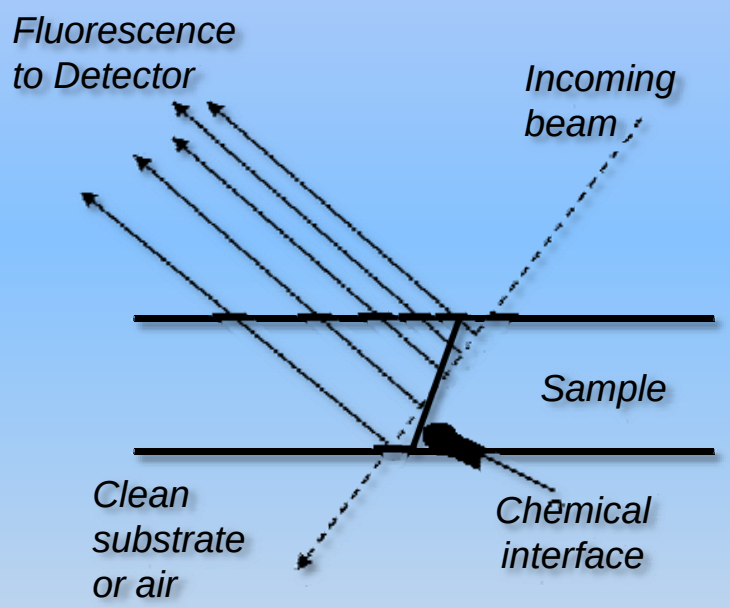
leaf samples
Repeat Scan
Use Scan List
Wait for Stable Beam
XRD Sec/Frame:
Pause on LN2 Fill
Delayed Start
Start Scan
Abort Scan
Pause Scan

Practical considerations in running experiments

Sample Preparation



For SXRF samples in any form can be analyzed

Third dimension (depth) is important

- Sampling depth is relatively large (compared to EMPA, for example) and element dependent
- Optimum thickness for highest sensitivity
- Need to know thickness for absorption corrections
- Buried objects (e.g., inclusions) can be analyzed
- Clean substrates need to be used

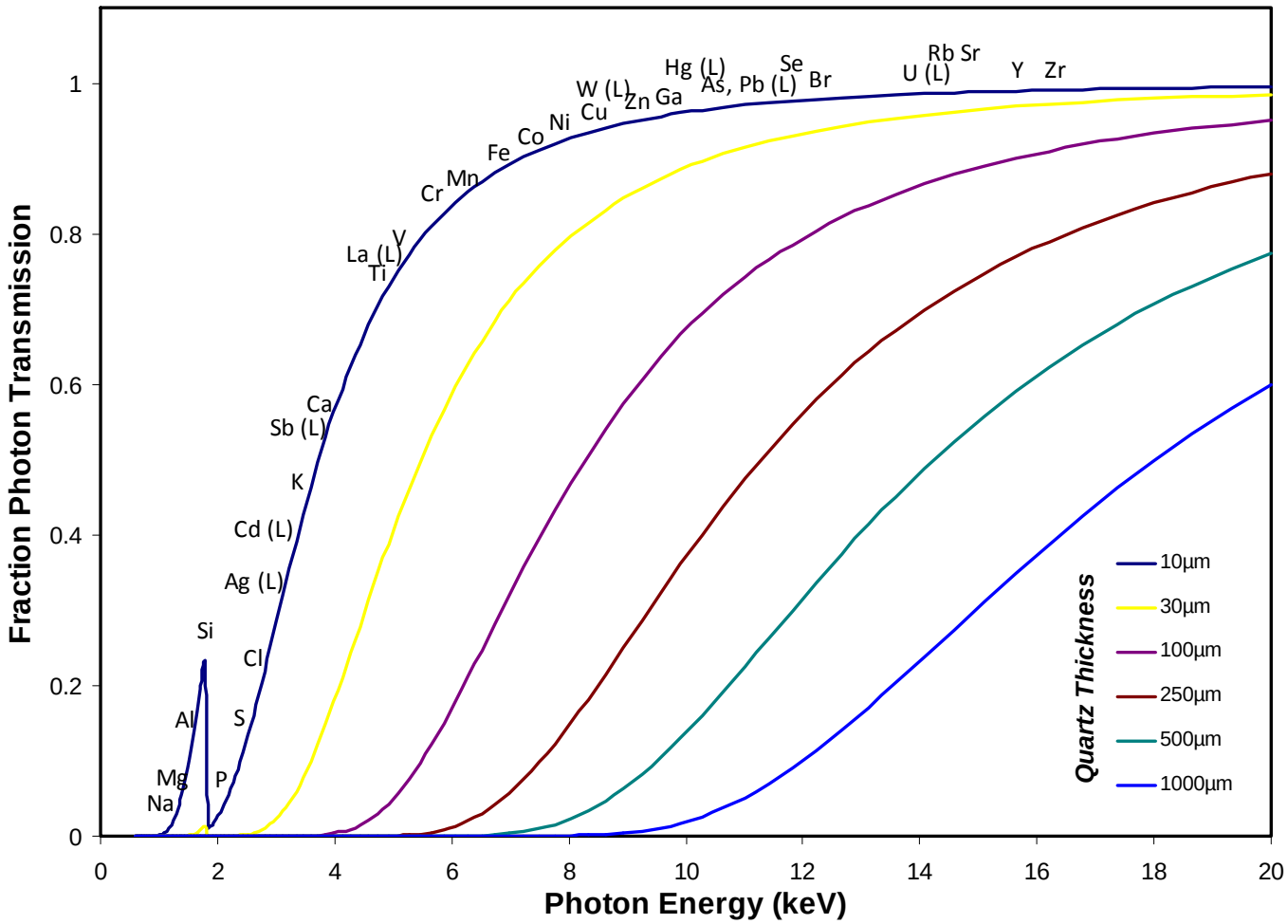
Typical sample mounts

- Thin sections on pure silica slides
- Dispersed particles on plastic film or silica
- Individual particles on fibers or film
- Contained liquids

Sample Preparation

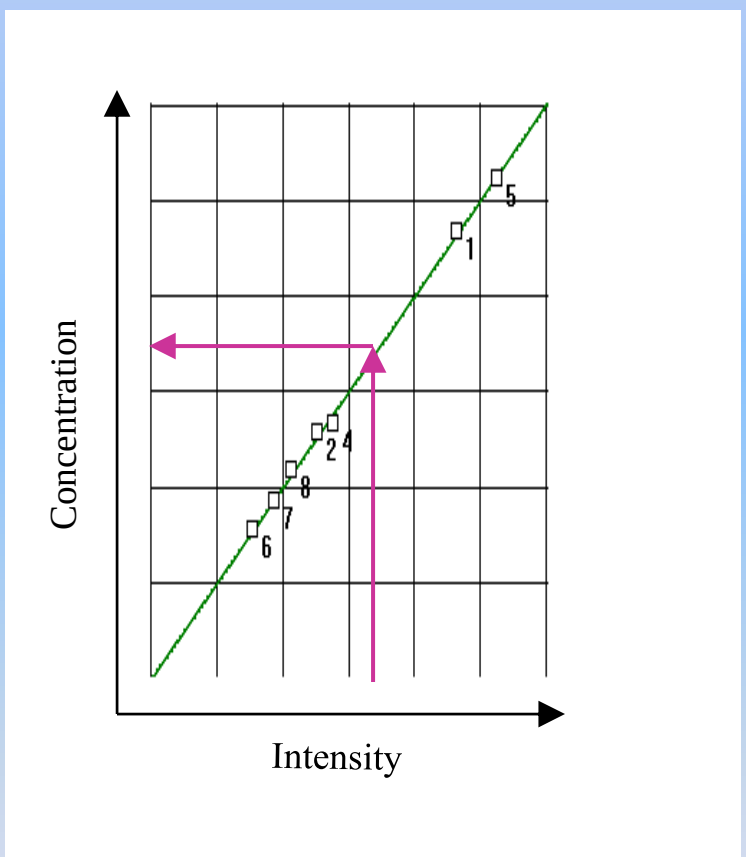
- Large samples feasible, but best to stick to 35mm format or microscope slides
- Thick samples OK, but beware analysis of buried materials
- Avoid substrates that are trace element impure
- Be aware of higher scatter and background from dense substrates such as glass
- Standard microscope slides are very dirty.
- Scotch tape actually very clean, as are mylar and polypropylene films.

Detection Sensitivity



- XRF detection at NSLS typically between 2-20 keV
- XAS analysis generally between 5-20 keV

Quantification



XRF is a reference method, standards are required for quantitative results.

Standards are analysed, intensities obtained, and a calibration plot is generated (intensities vs. concentration).

XRF instruments compare the spectral intensities of unknown samples to those of known standards.

While this is the most accurate approach, for microbeam XRF this is also usually the most impractical.

- Matrix matched standards
- Standards that are spatially homogeneous at the µm scale
- Effects of thickness
- All these can be dealt with, but complex