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

Tony Lanzirotti
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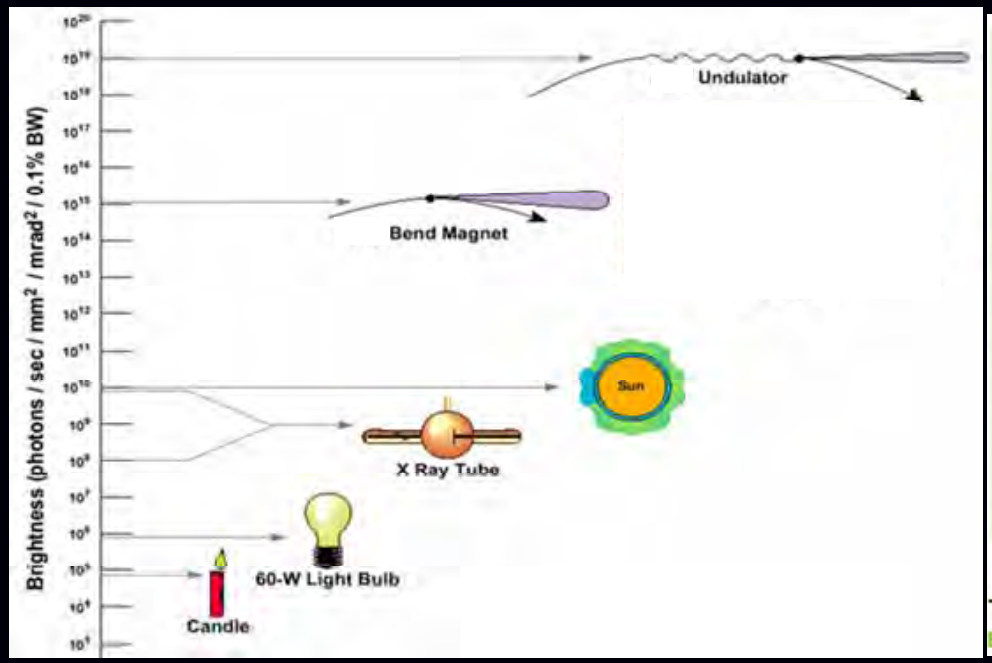
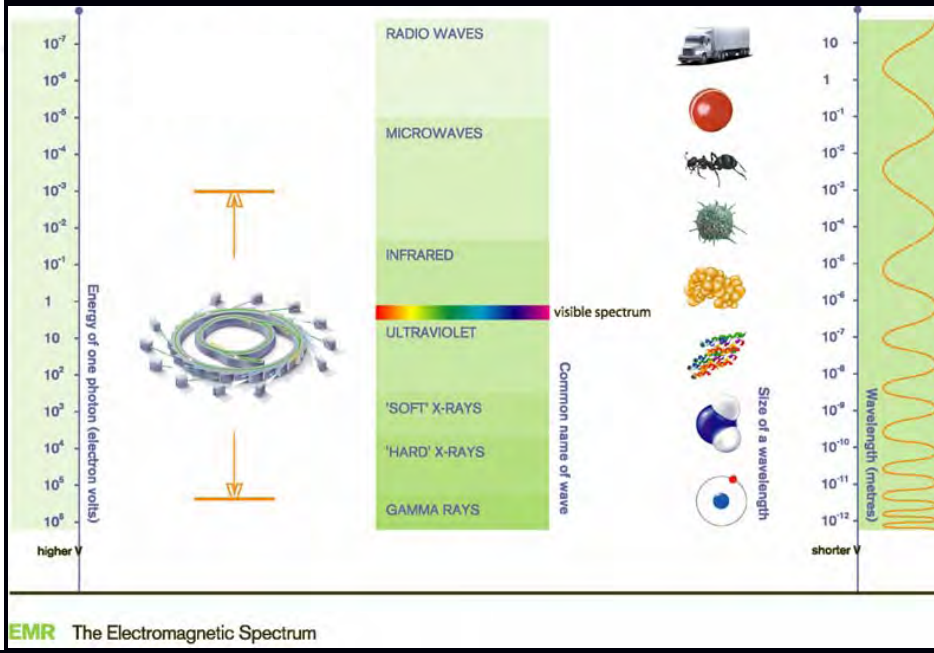
Center for Advanced Radiation Sources

A synchrotron is a facility that produces tiny beams of very bright LIGHT

Synchrotron light is any orders of magnitude brighter than conventional sources, enabling quick experiments on small samples.

***Continuous Spectrum** - from infrared to hard x-rays, optical devices select and scan the light's energy.*





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SET PHASERS TO ANALYZE

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BRIGHT BEAMS NEED BIG SHIPS!

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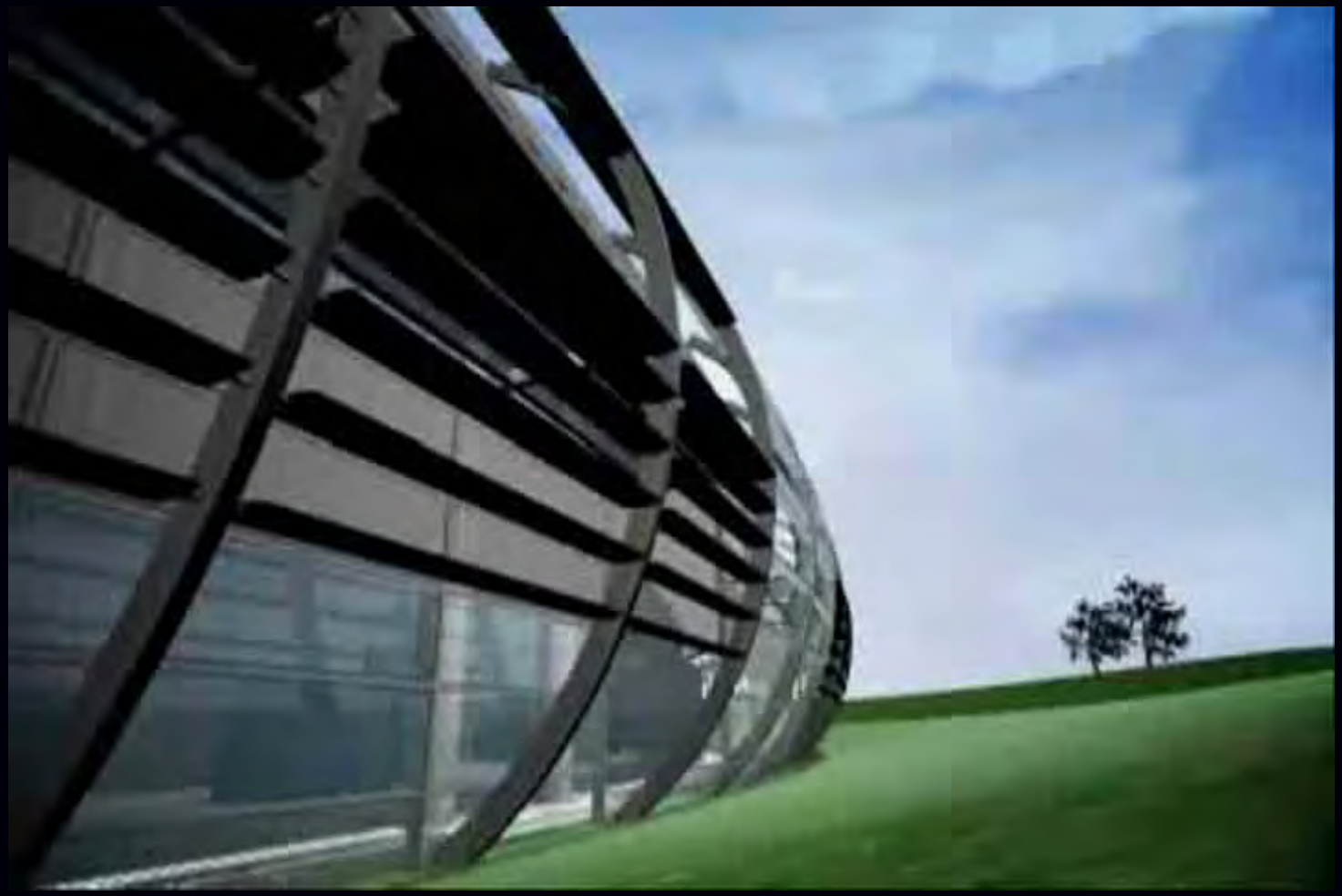
National Synchrotron Light Source

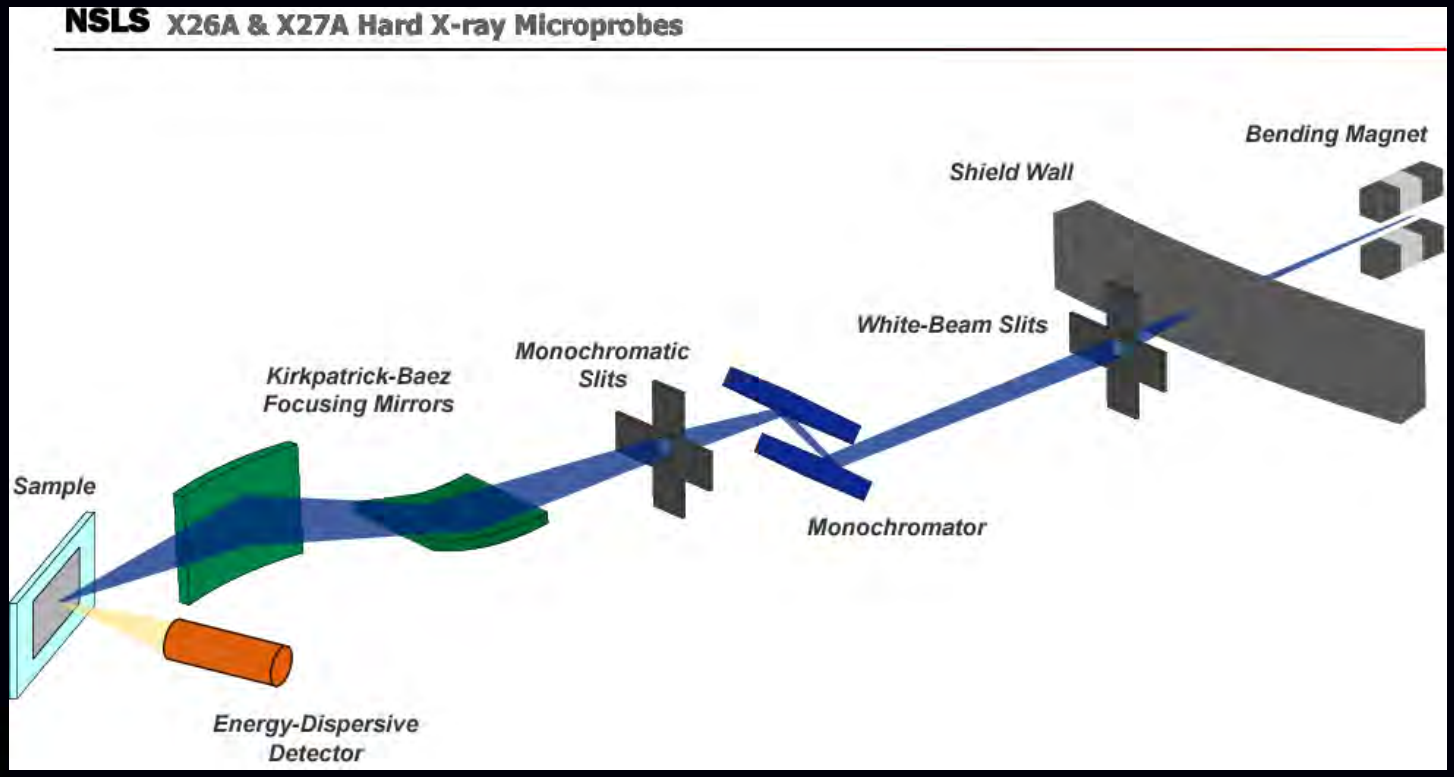
How Does a Synchrotron Work?



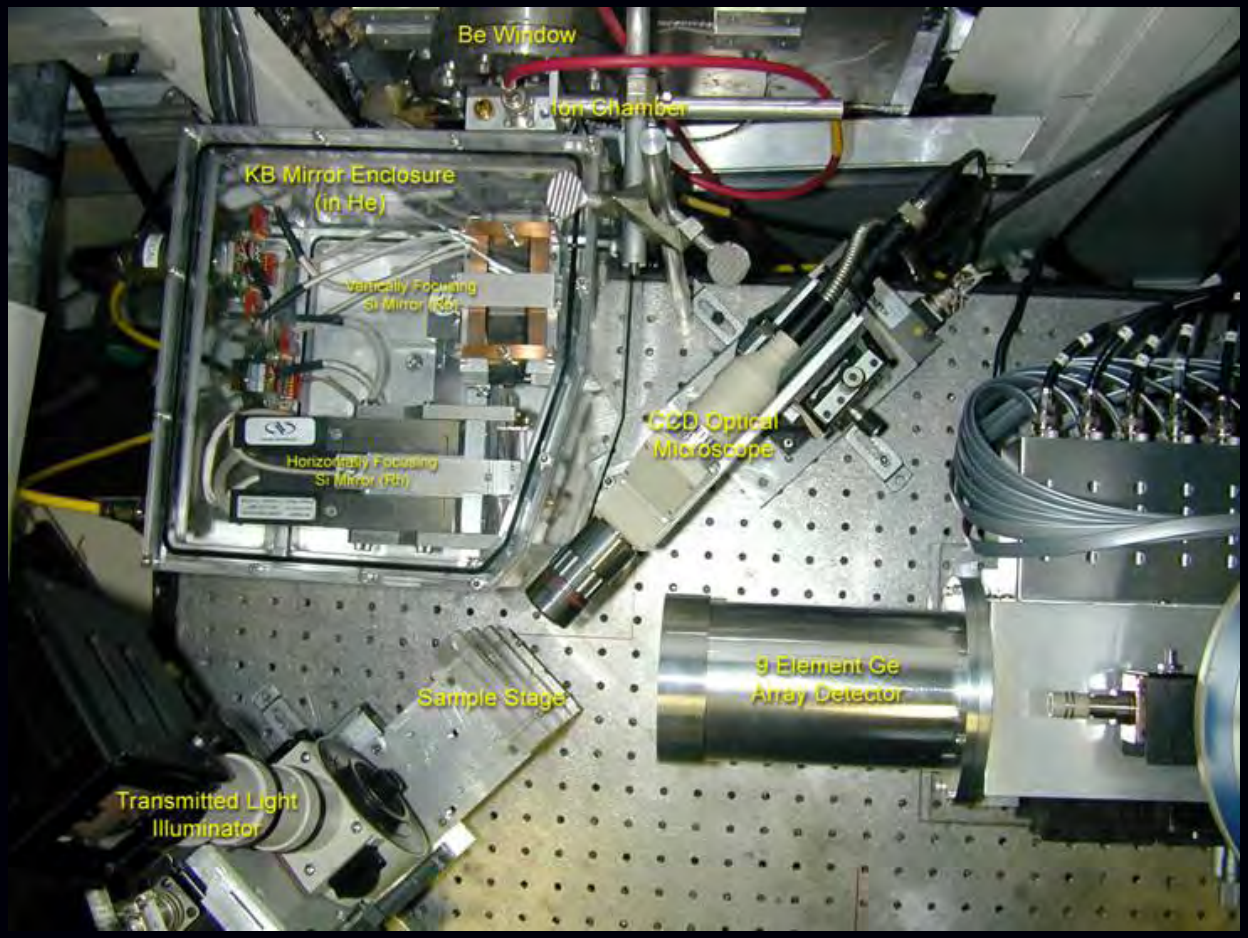
Diamond, UK

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

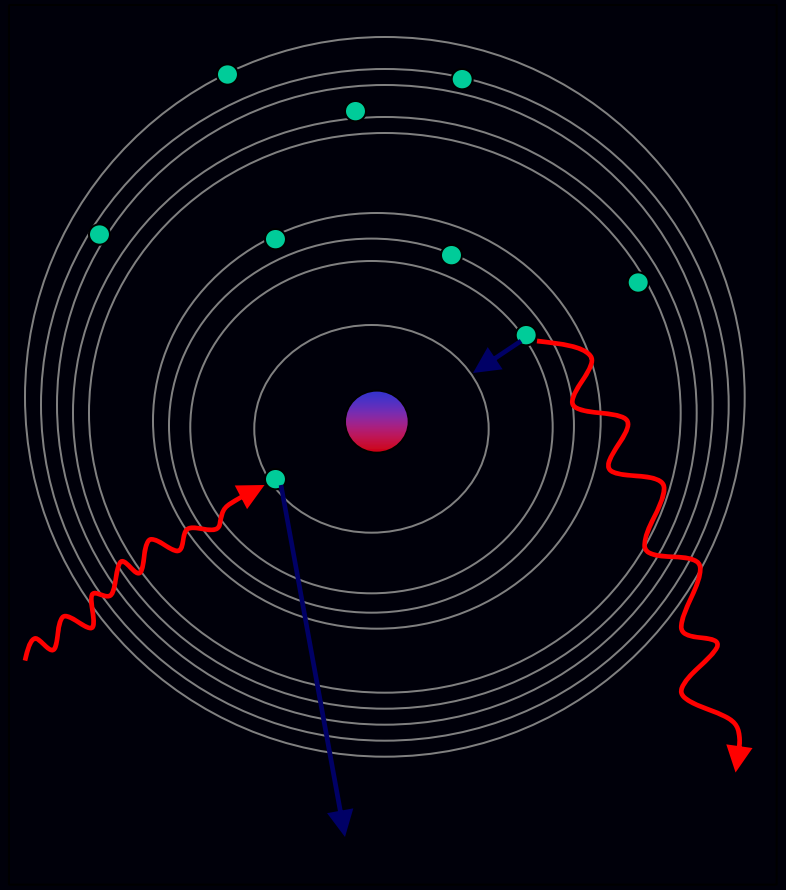


- **Elemental analysis done through detecting fluorescent X-rays emitted from a material after excitation.**

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

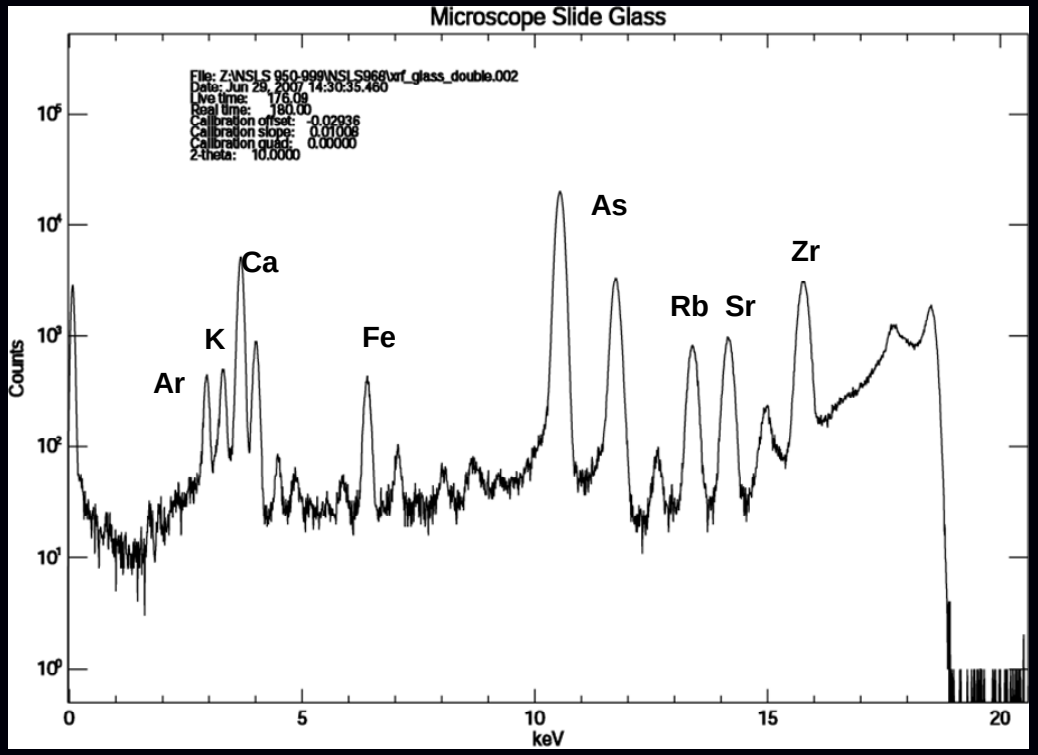
- **We can produce "images" of the elemental distribution by scanning the sample through the X-ray beam in small steps.**

The X-Ray Fluorescence Process



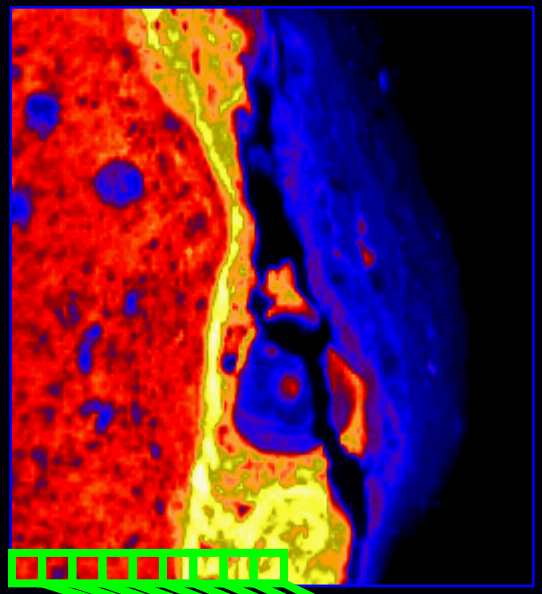
- ***A source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected it from the atom.***
- ***Higher energy electrons cascade to fill vacancy.***
- ***Giving off characteristic fluorescent X-rays.***
- ***These are detected using very sensitive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

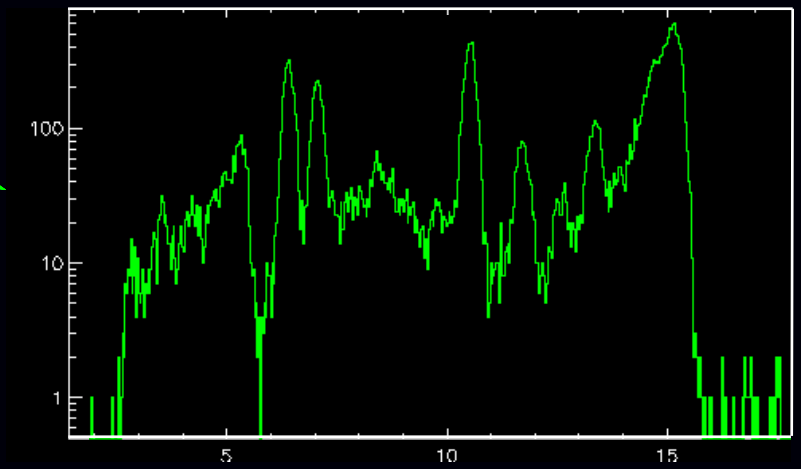
X-ray Energy Dispersive Spectra



- *Energy of the peak is element specific*
- *Intensity of the peak is proportional to concentration*

We can then "Raster" the sample through the beam to make a map





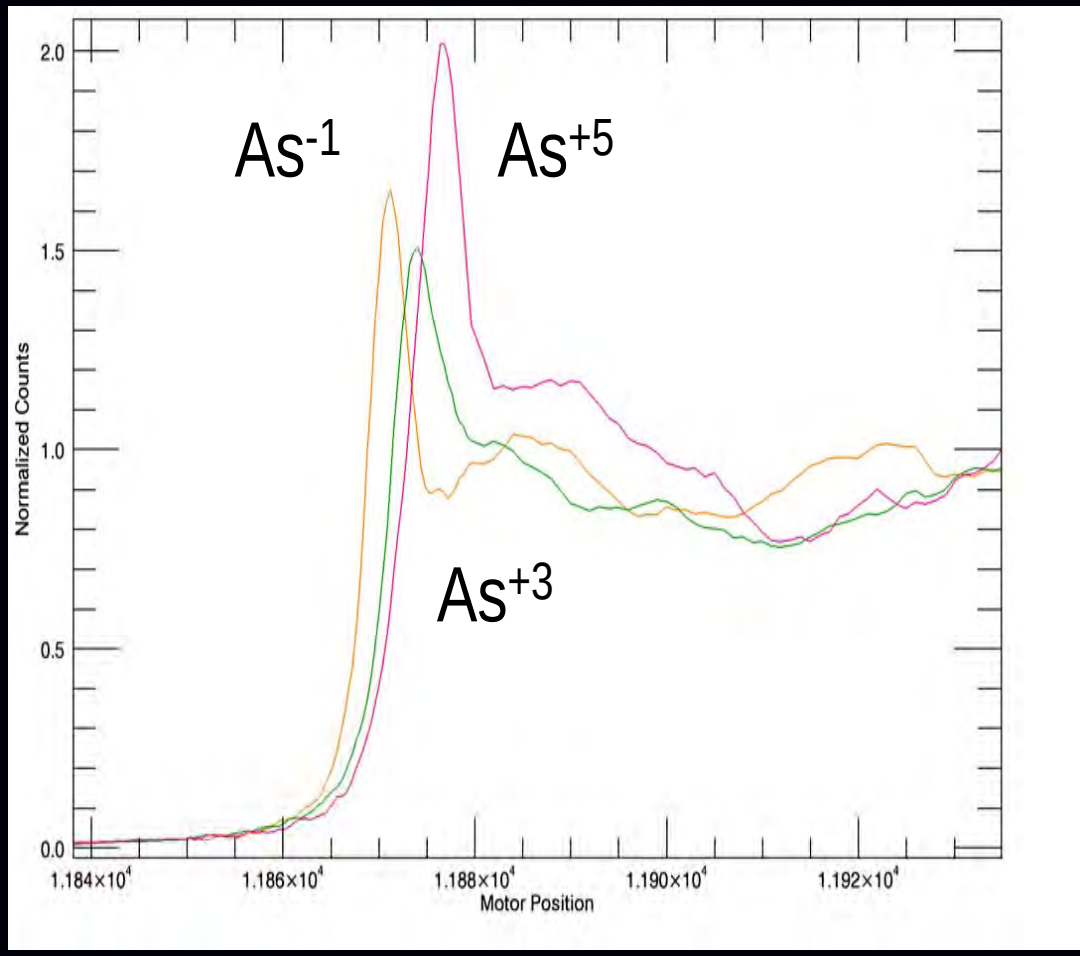
X-ray Absorption Spectroscopy

- *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 deterimene:*
  - ❖ *the formal valence of an element*
  - ❖ *the coordination environment (e.g., octahedral, tetrahedral coordination)*
  - ❖ *and subtle geometrical distortions of the coordination*

Arsenic



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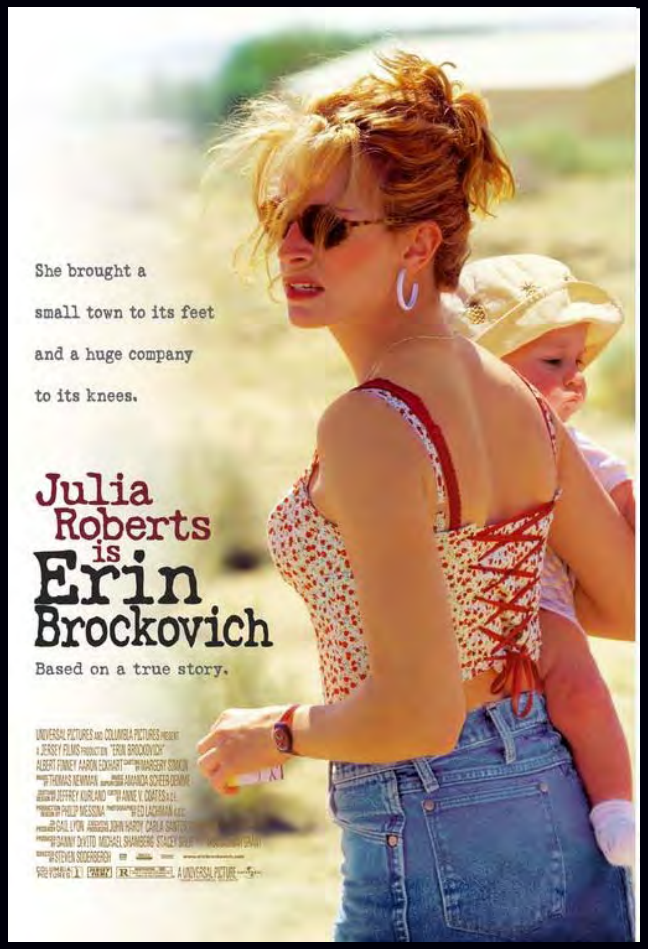
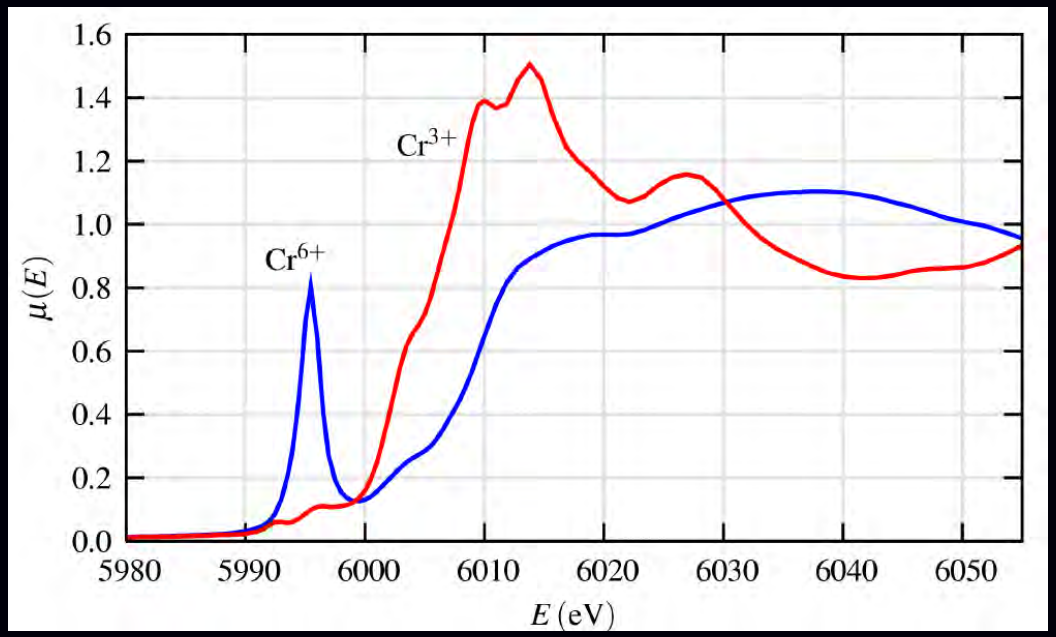


Chromium



So why do this sort of thing with X-rays? (or why is it so easy even I can do it?)

- *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*
- *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*

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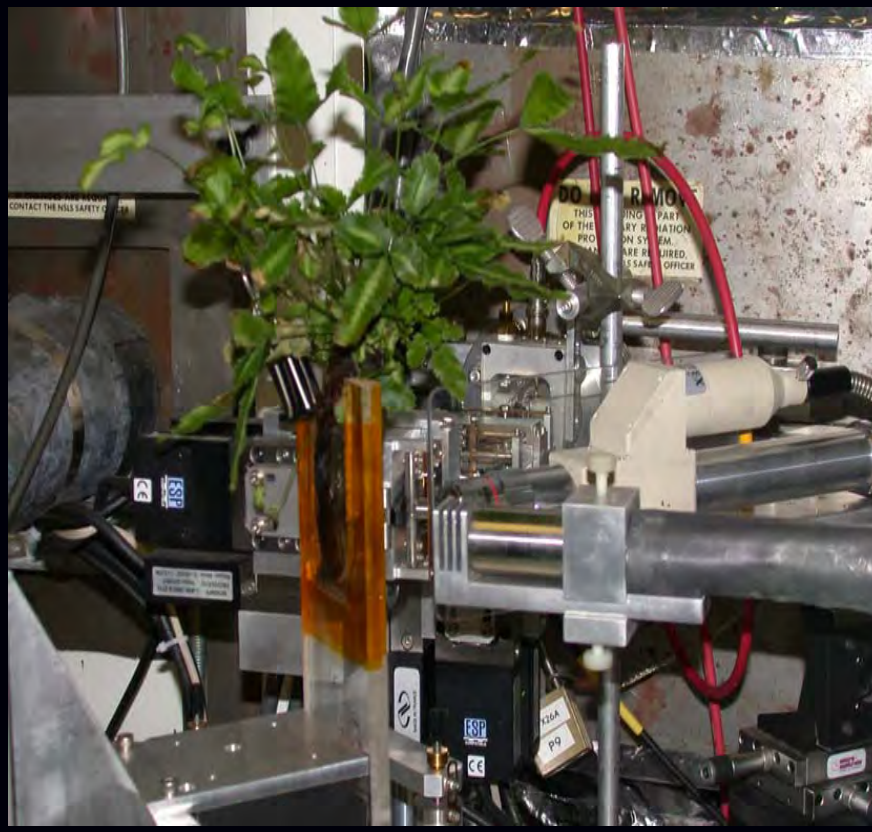

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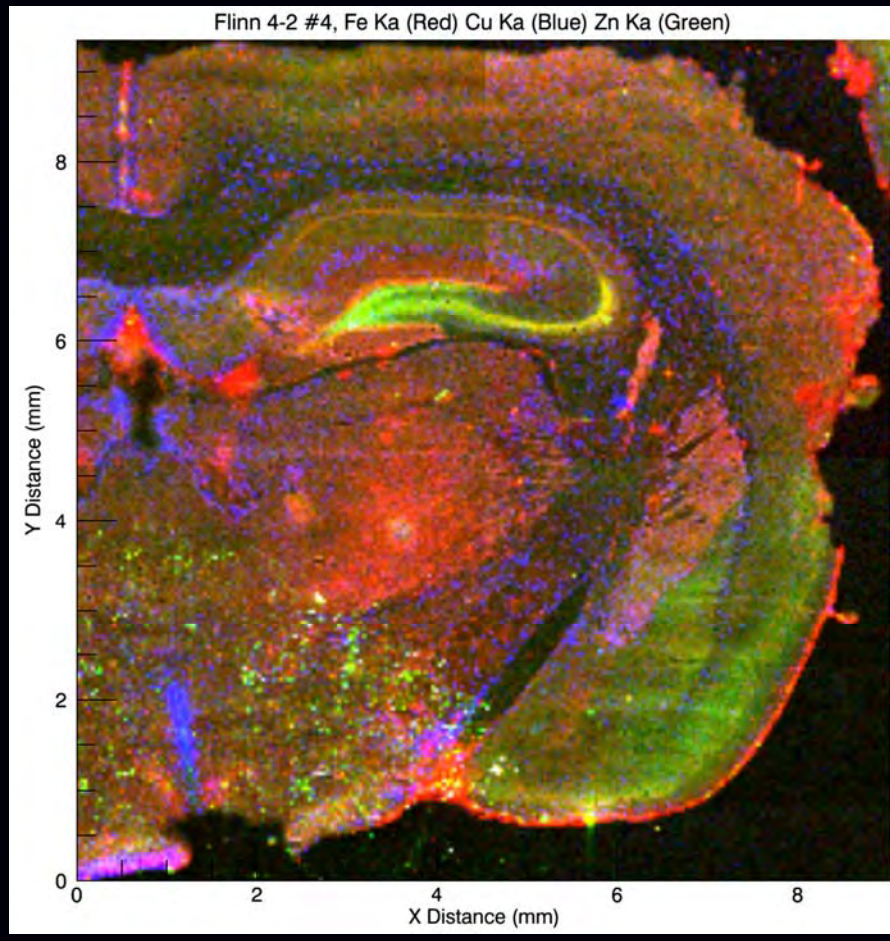
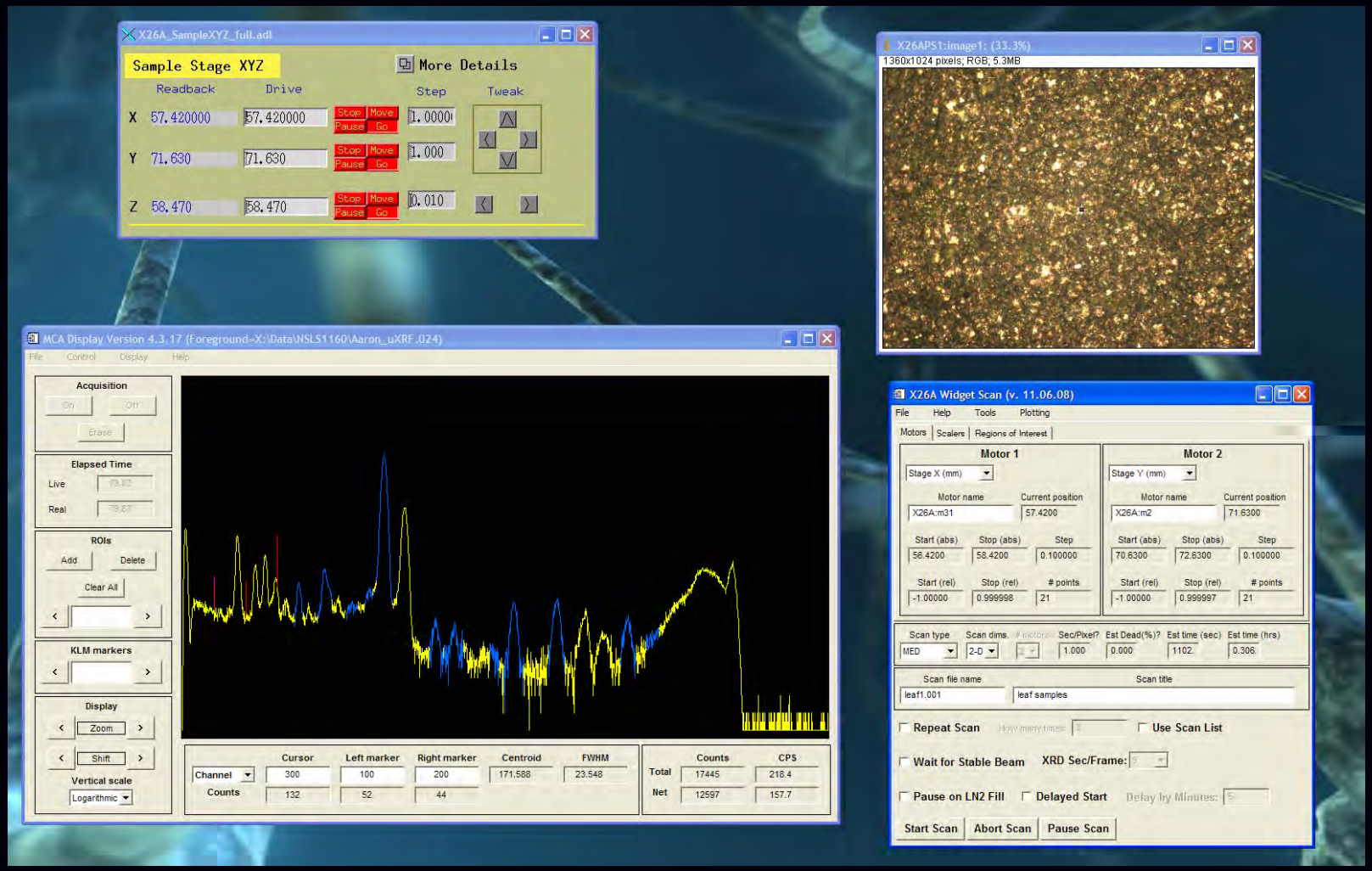


Ease of Use – Even from Afar



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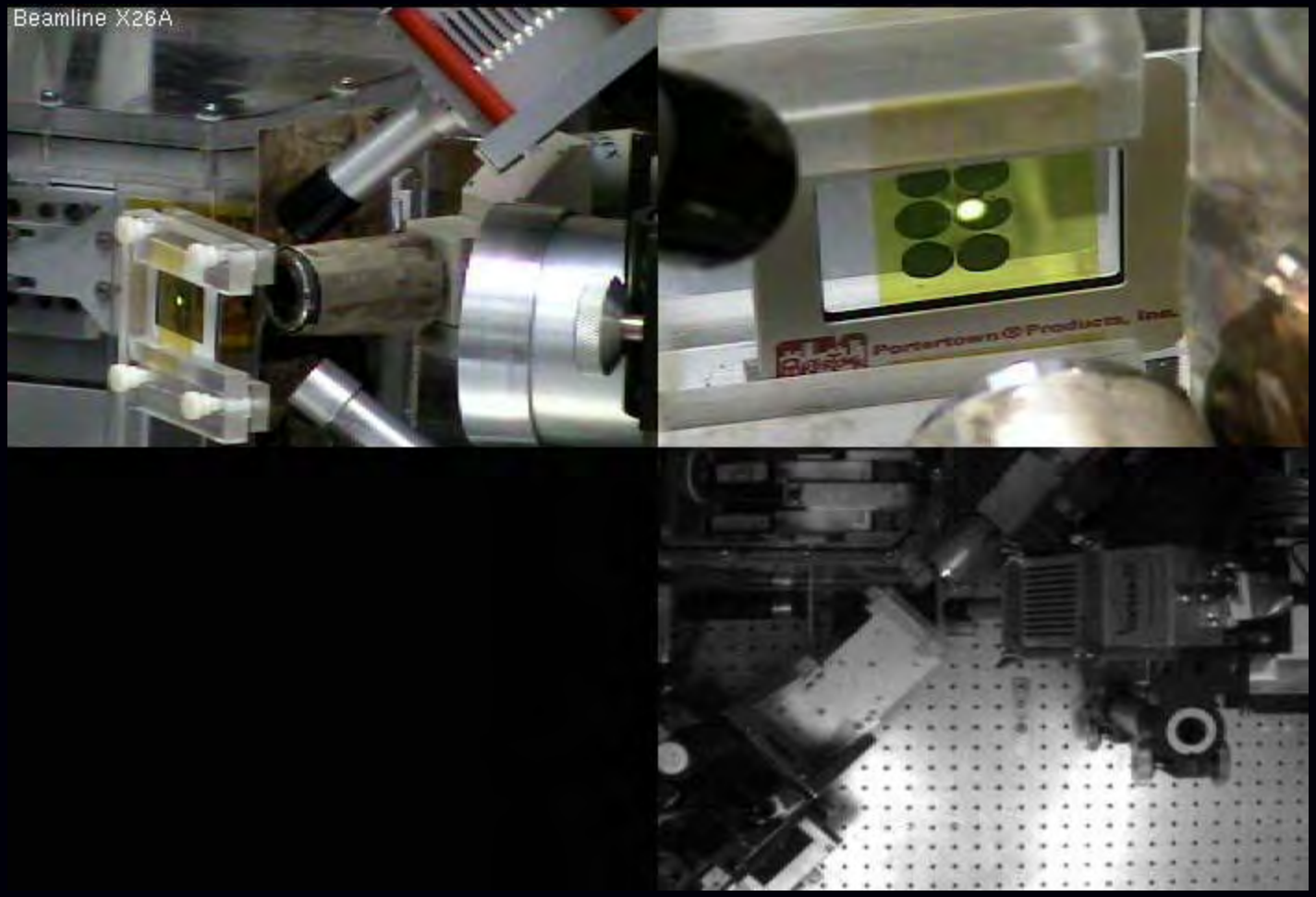

Ease of Use – Even from Afar

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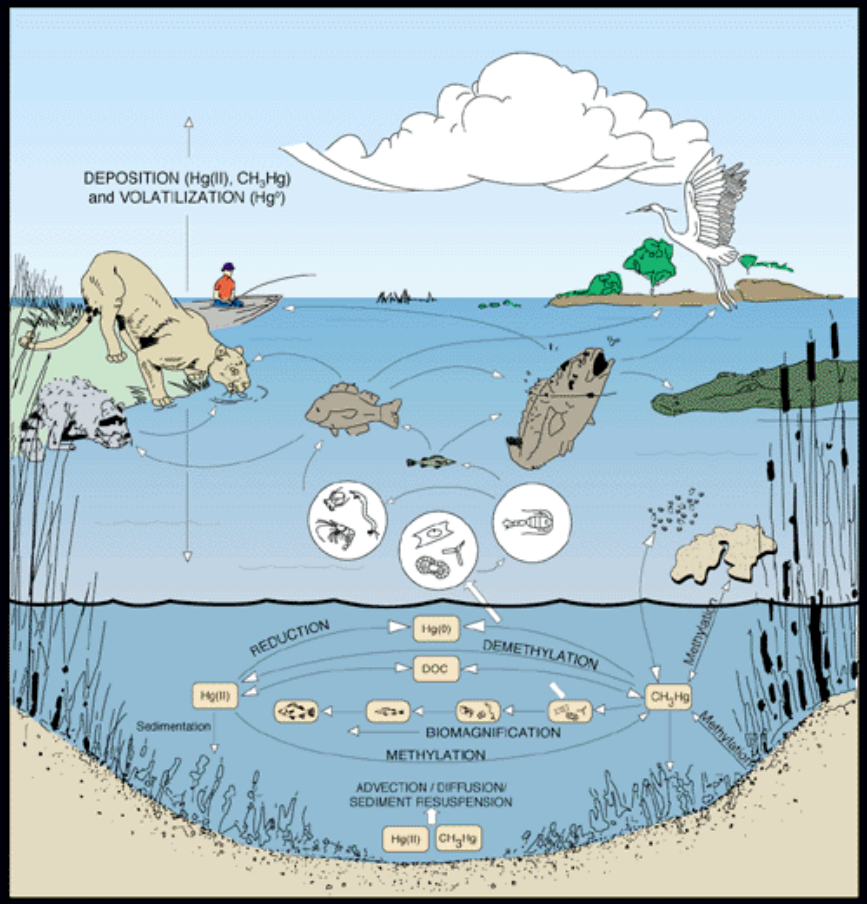
Hair

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. This mercury is in the more toxic, methylmercury form.
- Pregnant women - or, rather, their unborn babies - are at the greatest risk. Babies developing in the uterus (womb) seem to be most vulnerable to the effects of mercury on their nervous systems.

Tony Lanzirotti and Keith Jones (BNL), NSLS
Lanzirotti, A., Jones, K.W., Clarkson, T.W., and Grandjean, P. (2001) Human health risks of methyl mercury. National Synchrotron Light Source Activity Report 2001, 97-99.

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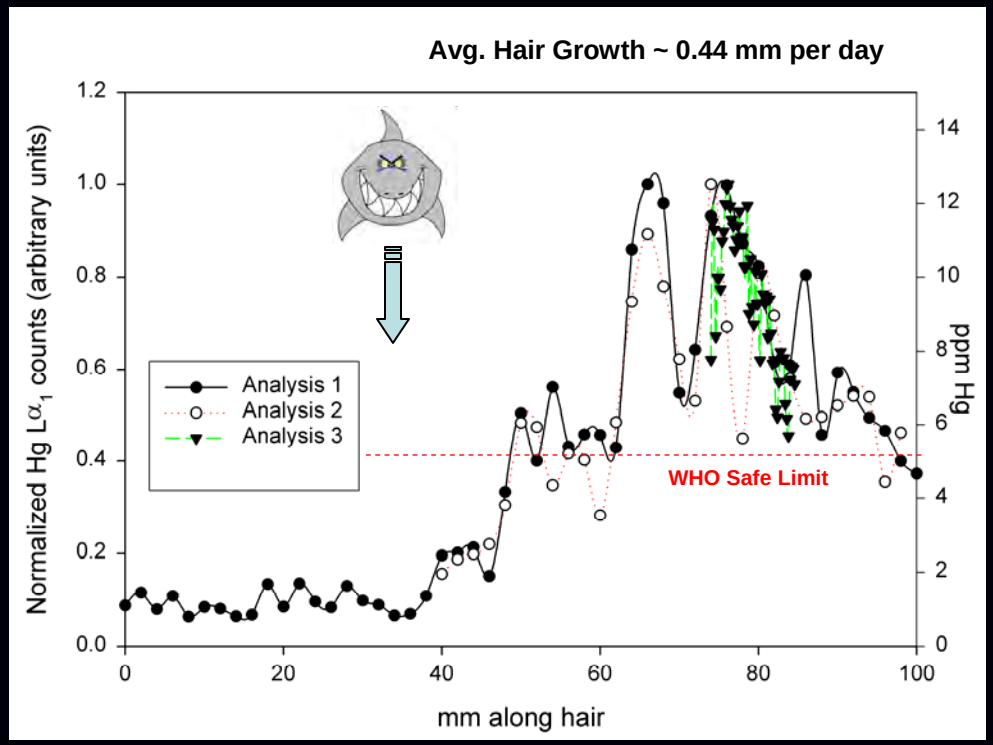

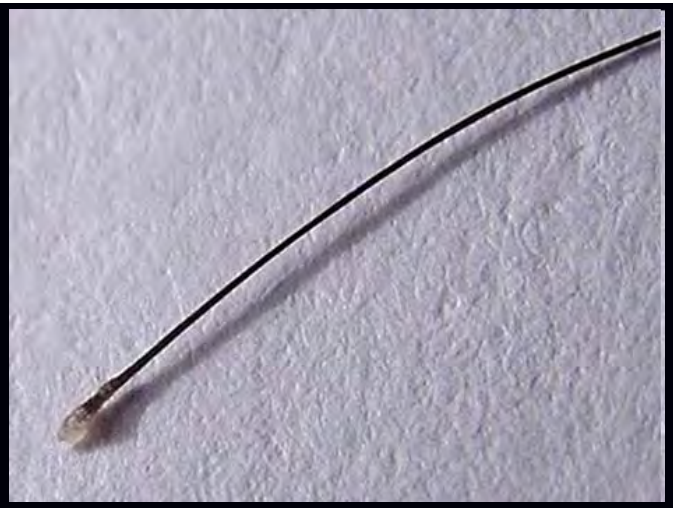

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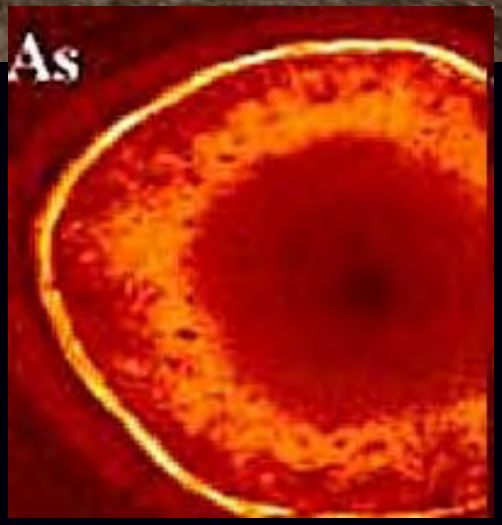
Phar Lap



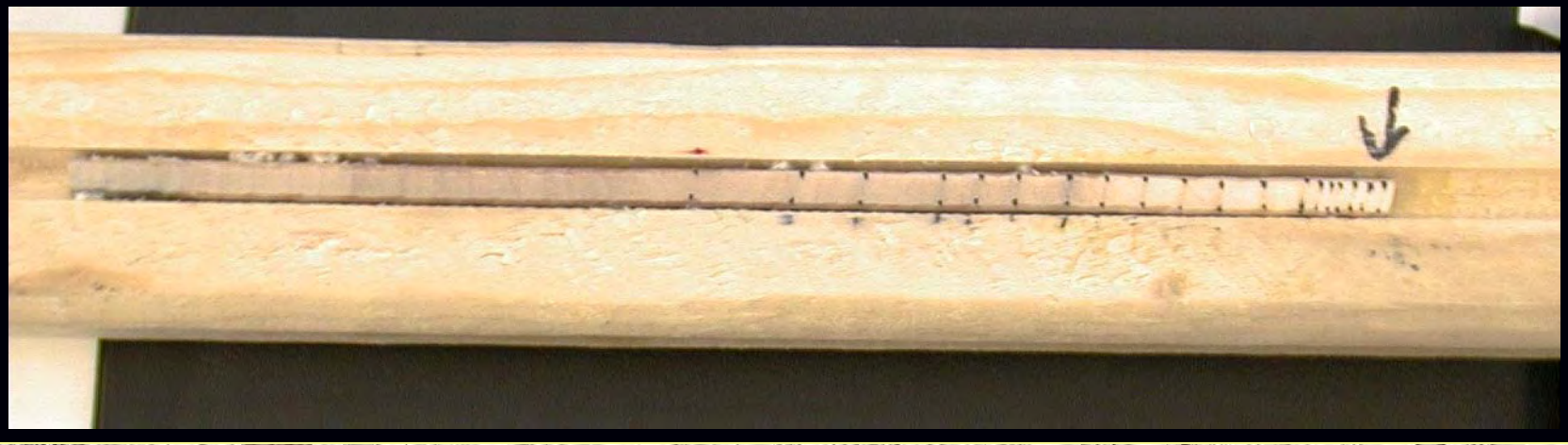
- *Phar Lap was a New Zealand-bred gelding that won 37 of his 51 starts, dominating Australian racing.*
- *He went to the United States in 1932, won his first race on US soil but died at the Menlo Park race track in California on April 5, 1932 under mysterious circumstances.*
- *While conspiracy theories flourished following Big Red's death, including suggestions gangsters had killed him off, poisoning had always been suspected.*
- *Synchrotron results appear to show that Phar Lap may well have ingested a single large dose of arsenic between one and two days before he died.*

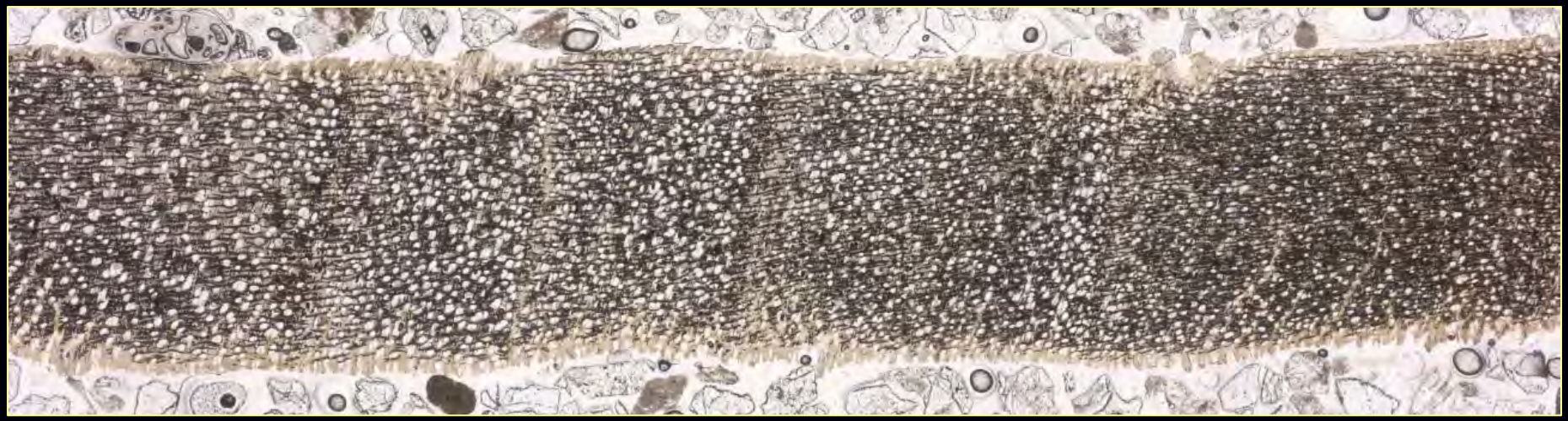
Ivan Kempson (Univ. of S. Australia), APS
(Kempson, I. M., and D. A. Henry (2010)., Determination of Arsenic Poisoning and Metabolism in Hair by Synchrotron Radiation: The Case of Phar Lap, Angewandte Chemie International Edition, 9999(9999), NA.

Plants

Tree Rings

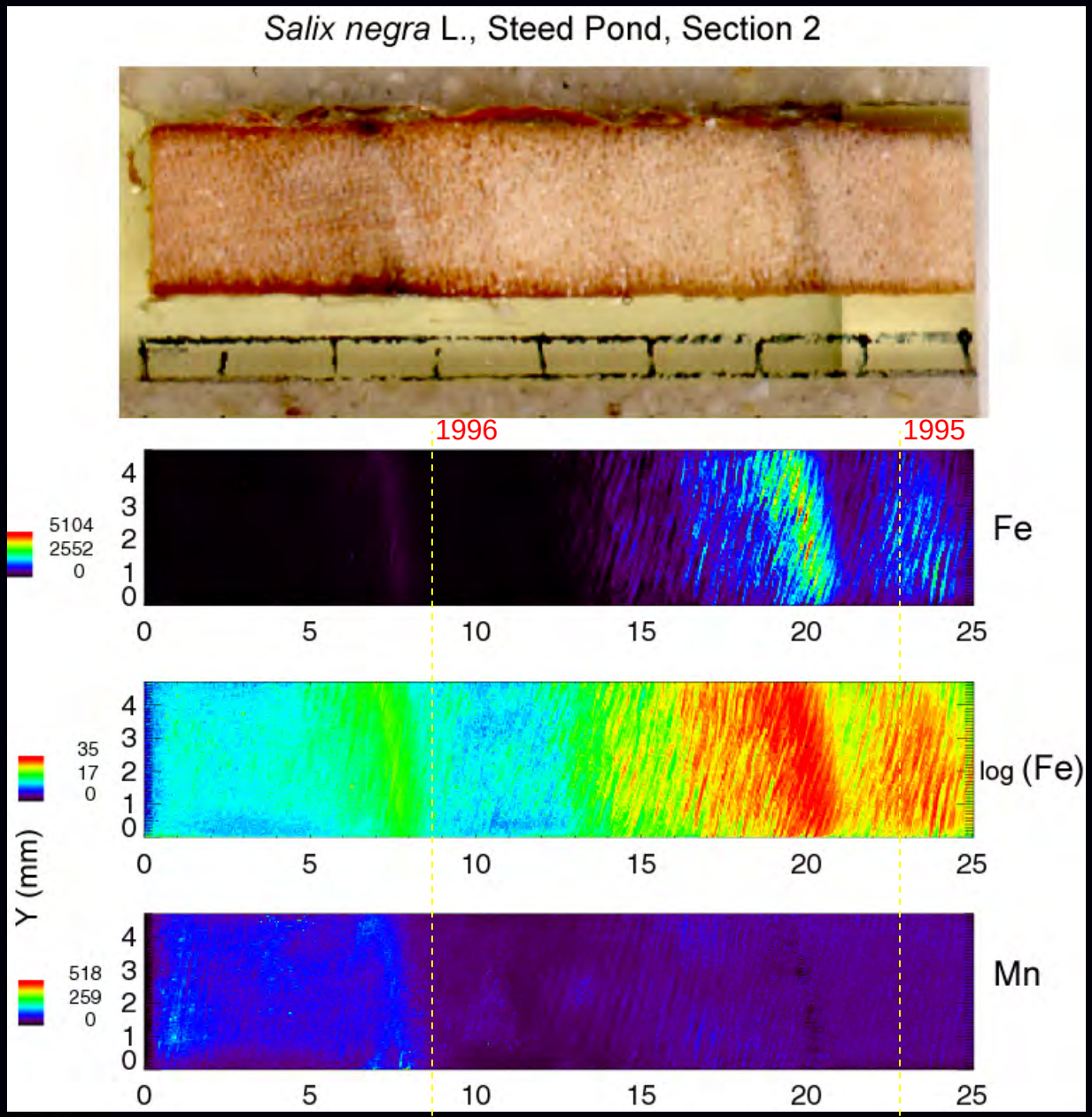
Tree cores of black willows growing at the Savannah River
DOE site record contamination from contaminated pond

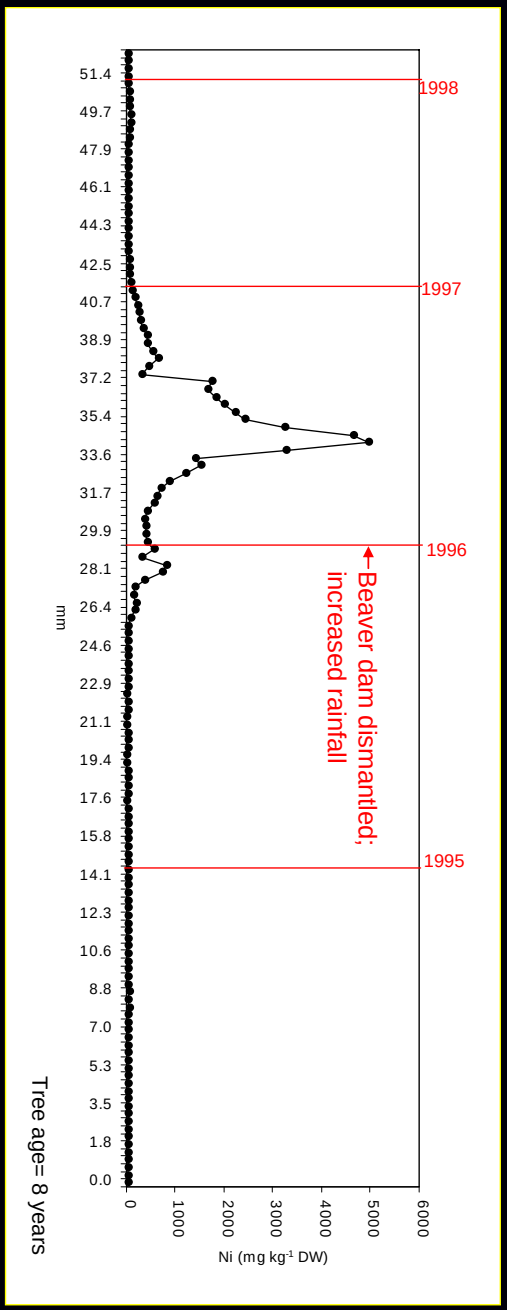




Tracy Punshon (Dartmouth) and Tony Lanzirotti, NSLS

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
Fe
log (Fe)
Mn
Y (mm)
5104
2552
0
35
17
0
518
259
0
0
5
10
15
20
25

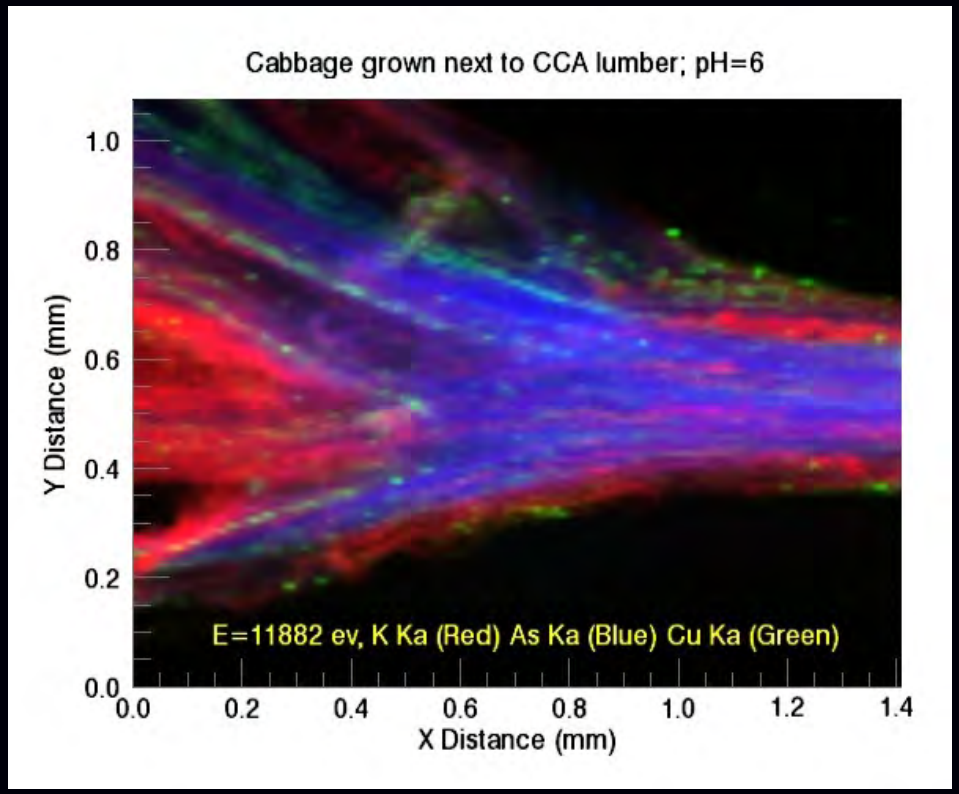

Tree age= 8 years
Ni (mg kg-1 DW)
mm
0
1000
2000
3000
4000
5000
6000
1998
1997
1996
1995
Beaver dam dismantled; increased rainfall

Environmental Hazards of Pressure Treated Lumber

- *Most woods are susceptible to attack by fungus and insects. To make wood more resistant to attack, the lumber industry embedded insecticides and anti-fungal agents.*
- *The wood is injected with an aqueous solution of Copper, Chromate and Arsenic (CCA) under pressure.*
- *A 12 foot 2 x 6 contains enough arsenic, if released, to kill about 250 adults.*
- *The EPA announced a transitional ban on the production of CCA wood for residential use in 2002.*

Environmental Hazards of Pressure Treated Lumber

Cabbage grown near degrading CCA lumber



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

Cultural Heritage

Eureka! The Archimedes Palimpsest

- In the 10th century, an anonymous scribe copied Archimedes' treatises in the original Greek onto parchment.

- Three centuries later, a monk “palimpsested” (recycled) the parchment by scraping away the Archimedes text, cutting the pages in half, turning them sideways and writing Greek Orthodox prayers onto the recycled pages.

- Forgers in the early 20th century painted religious imagery on four of the pages in an attempt to elevate the manuscript's value.

Uwe Bergmann, SSRL
http://news.stanford.edu/news/2006/august9/arch-080906.html

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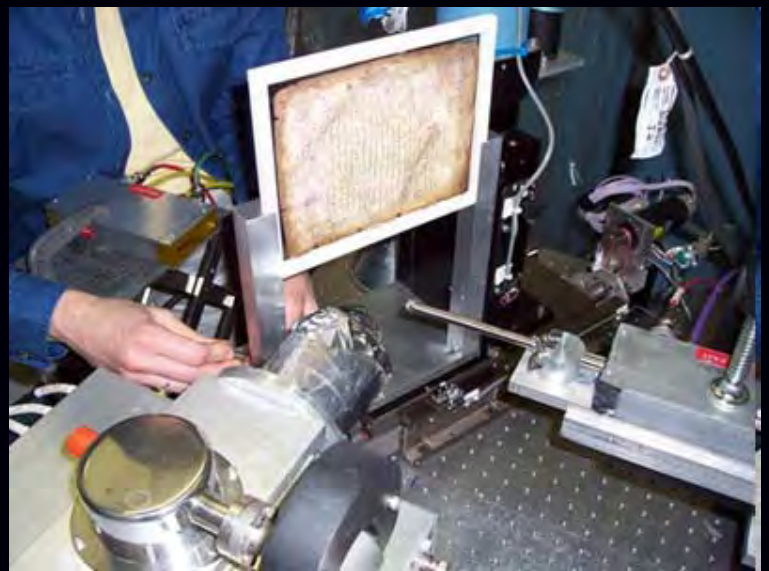
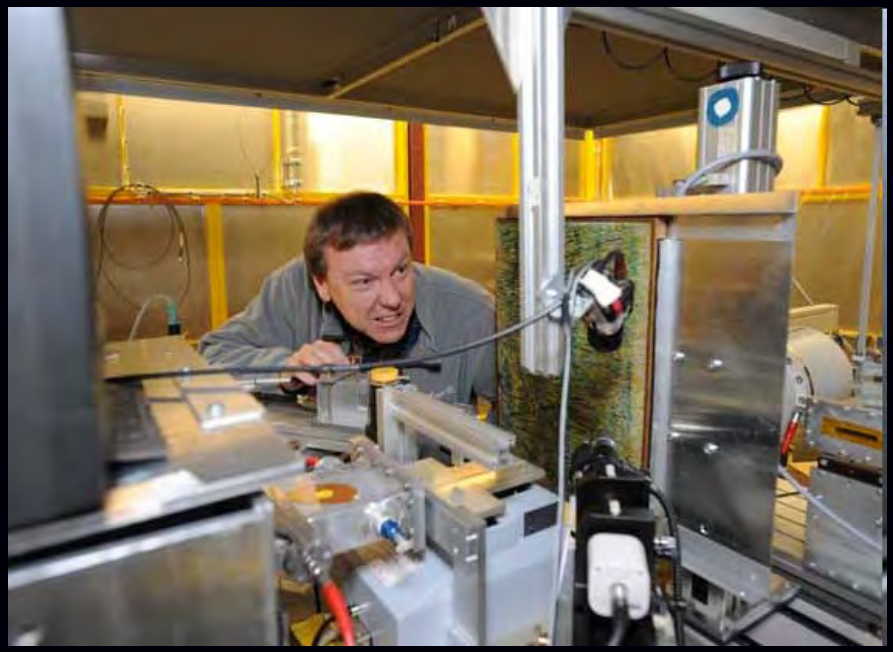


Vincent van Gogh

"Grasgrond" ("Patch of Grass"), it was painted by van Gogh in Paris in 1887



Joris Dik and Koen Janssens (U. Delft), **DESY**
http://www.vangogh.ua.ac.be/

BONES

Thermopolis Archaeopteryx

The image is a composite blend of scans of the elements phosphorus, silicon, sulfur, and iron. The bright colors in the wing areas show how part of the feather chemistry has been preserved.

Fossil of an ancient squid, X-rays image chemical traces of the animal's soft tissue left behind in the limestone; at right, the tentacles are clearly visible

Uwe Bergmann, SSRL

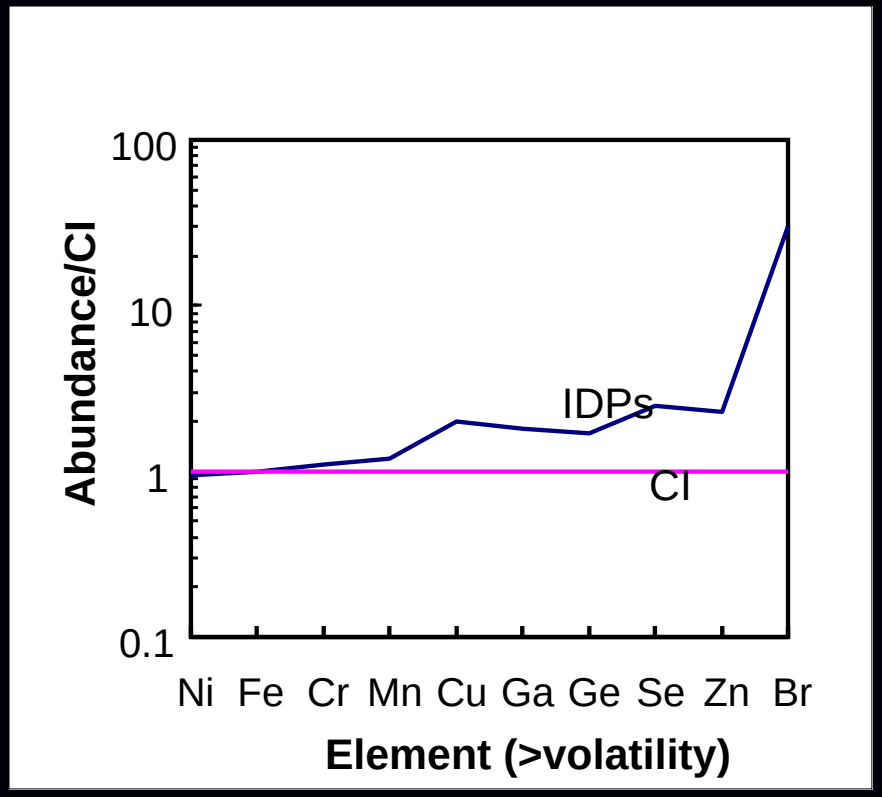
Space Dust

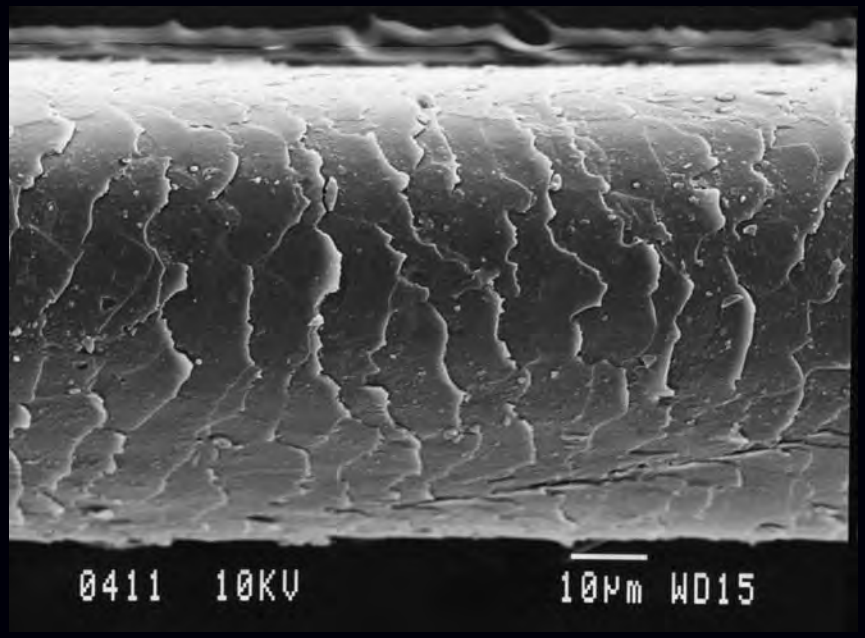
Interplanetary Dust Particles

They may be some of the earliest and most primitive solar system samples ever collected.

Many tons of dust grains, including samples of asteroids and comets, fall from space onto the Earth's atmosphere each day.

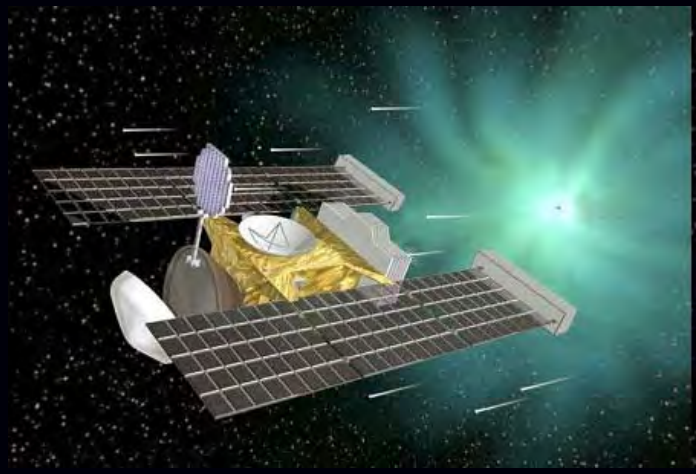
Except…



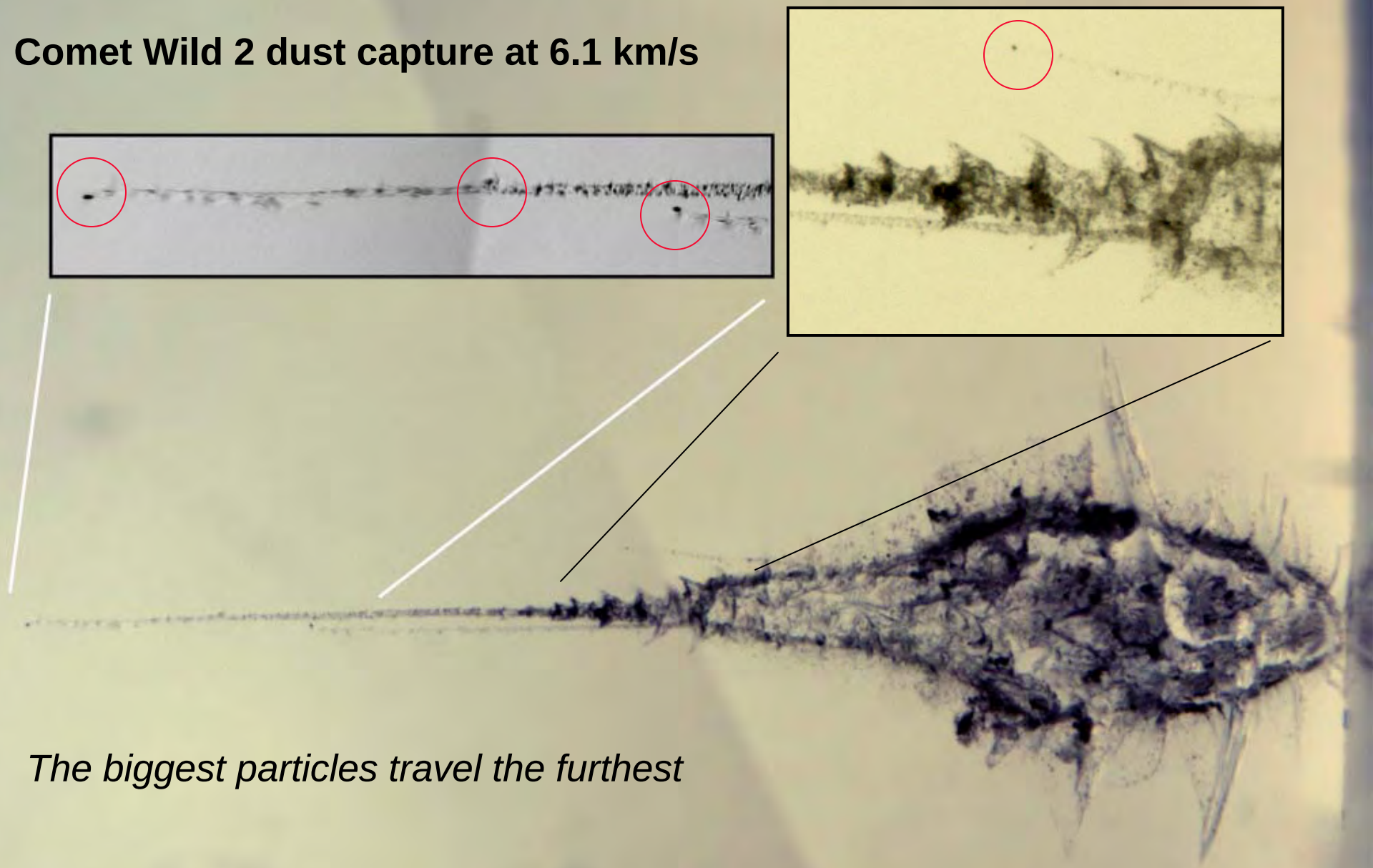


Stardust – NASA's Cometary Sample Return Mission

- *The Stardust spacecraft was launched on February 7, 1999*
- *On January 2, 2004 Stardust successfully encountered comet Wild 2, collecting samples of cometary dust*
- *On January 15 2006, Stardust successfully returned to Earth by parachuting a reentry capsule weighing approximately 125 pounds.*
- *Comets are made up of material left over from the solar nebula after the planets were formed. Unlike the planets, most comets have not changed very much since the formation of the solar system. Therefore, comets may hold the key to understanding the early development of the solar system.*
- *Wild-2: only 5 solar passes; right place at right time*



Comet Wild 2 dust capture at 6.1 km/s



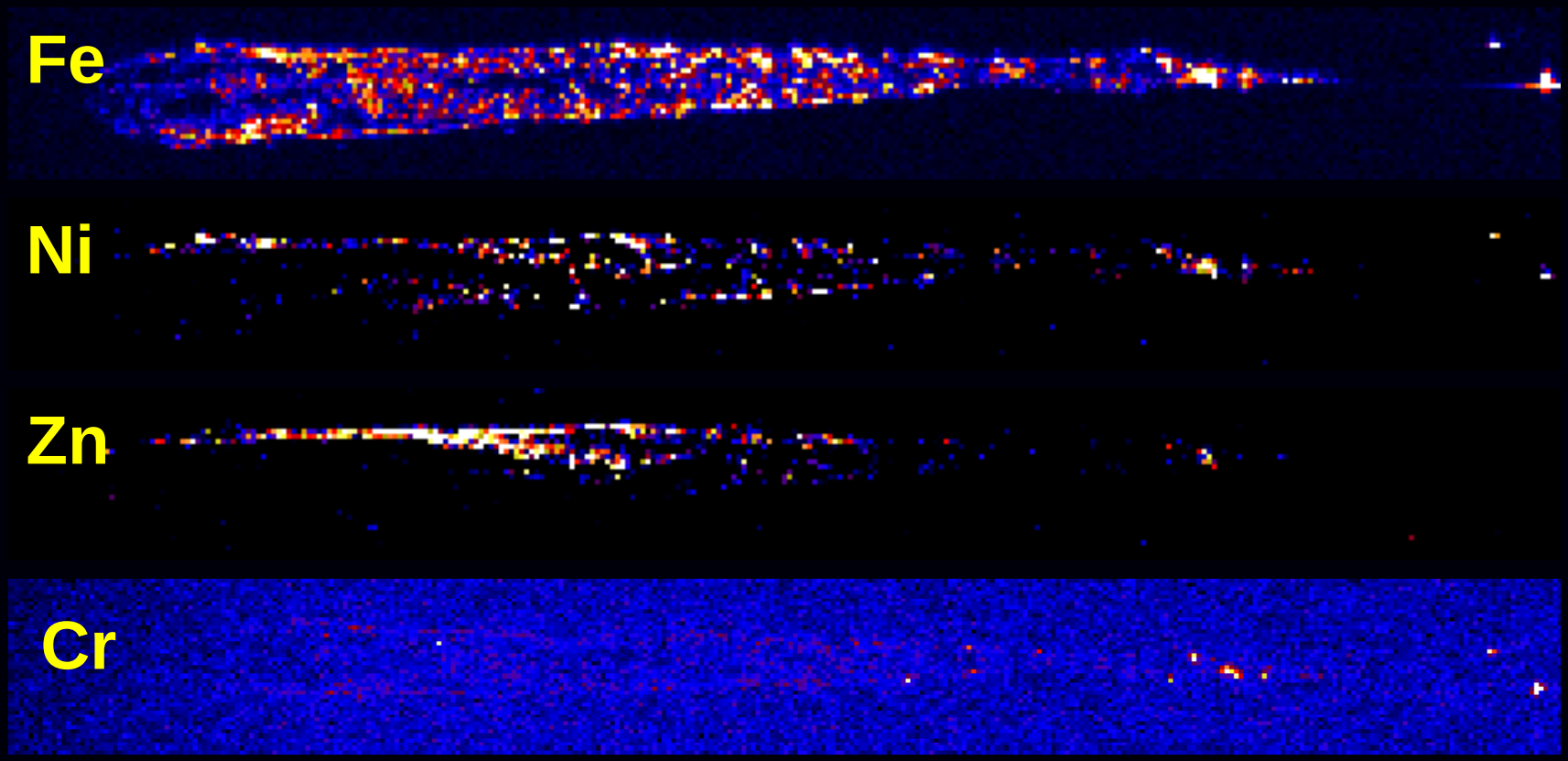
The biggest particles travel the furthest

< coarse grained fraction >

< fine-grained fraction >

Probably, finer-grained materials have been preferentially abraded away during capture, and are sitting along the tracks, leaving the largest grains at the end

Synchrotron µXRF Mapping in-situ in aerogel

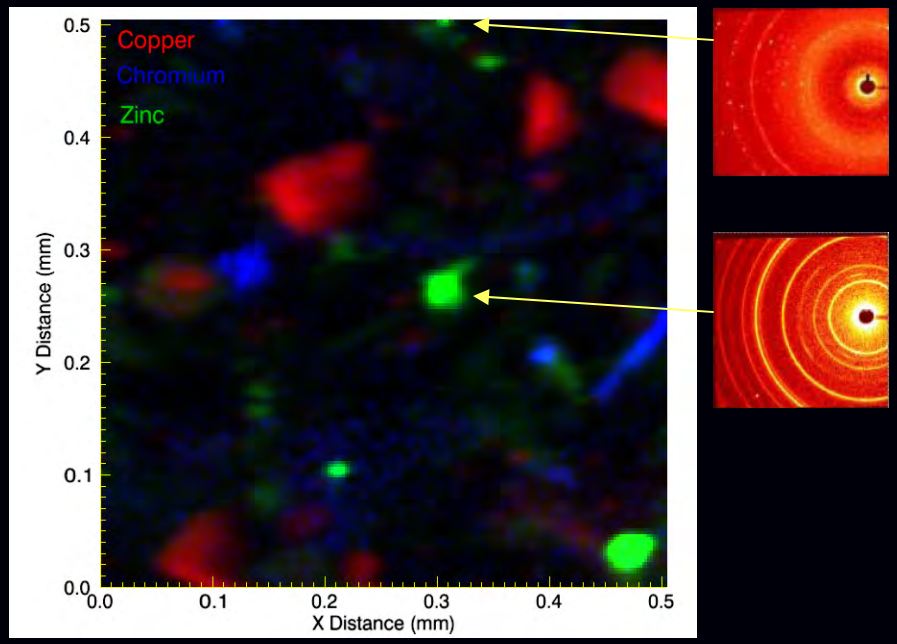


Similar primitive chemistry to what we've observed from IDP's
Surprising number of high T minerals observed

OK, teachers and students likely won't have access to space dust
But…

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

Analyzing Dust Bunnies



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

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

Conclusions

- *X-ray microprobes are incredibly versatile instruments for trace element and mineral analysis of materials in as "as-collected" state.*
- *They can be designed to be very easy to use and data interpretation can be straight-forward*
- *Very well-suited to remote experiments (as we will show you later)*
- *X-ray microprobes will be one of the first sets of beamlines made available through the InSync program.*

Introducing Synchrotrons into the Classroom