Local Atomic and Electronic Structure: X-ray Absorption Fine Structure and Other Inner Shell Spectroscopies

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National Institute of Standards and Technology

Applications of Synchrotron Techniques in Glass Research
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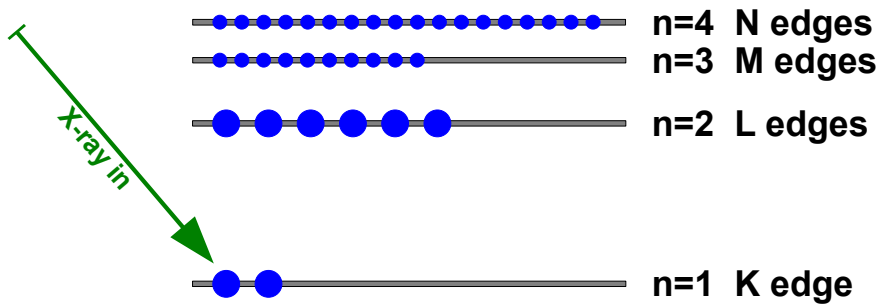
Copyright

The basic physical process in XAS and XRF



1. An incoming photon interacts with a deep-core electron. Shown here, a 1s electron is excited for a K-edge spectrum.

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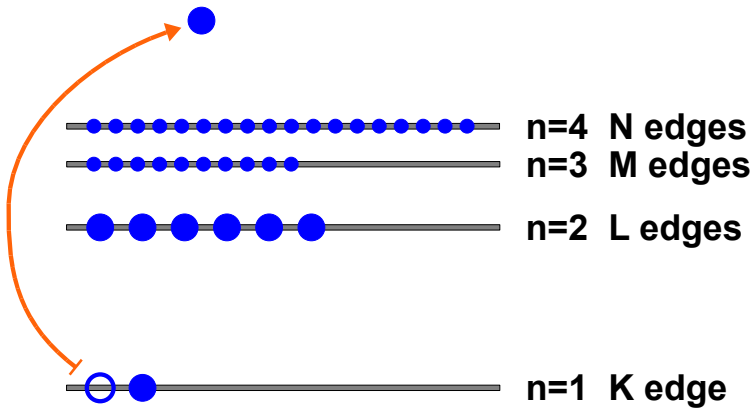

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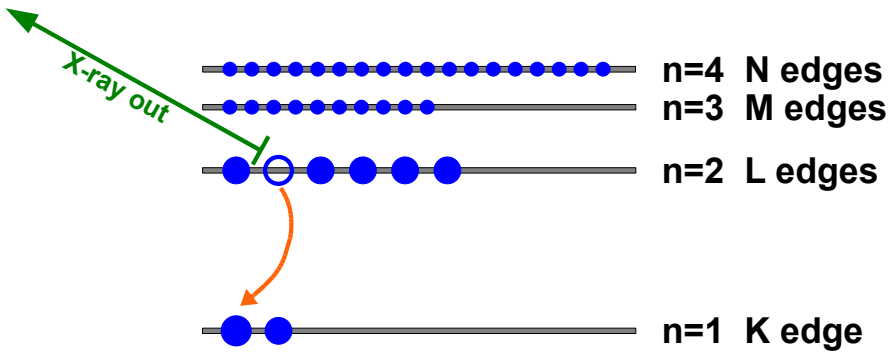

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2. The deep-core electron is promoted to some unoccupied state above the Fermi energy, propagates away, and leaves behind a core-hole.
3. A short time later (1 or 2 femtoseconds), a higher-lying electron decays into the core-hole and emits a photon.

Characteristic energies

Each element has a characteristic set of excitation and fluorescence energies. Two examples:

Iron: Z=26

Edge	Energy
K	7112
L3	706.8
L2	719.9
L1	844.6

Line	Transition	Energy	Strength
Kα_1	K-L3	6405.2	0.580
Kα_2	K-L2	6392.1	0.294
Kβ_1	K-M3	7059.3	0.082
Kβ_3	K-M2	7059.3	0.043
Kβ_5	K-M4,5	7110.0	0.001

Uranium: Z=92

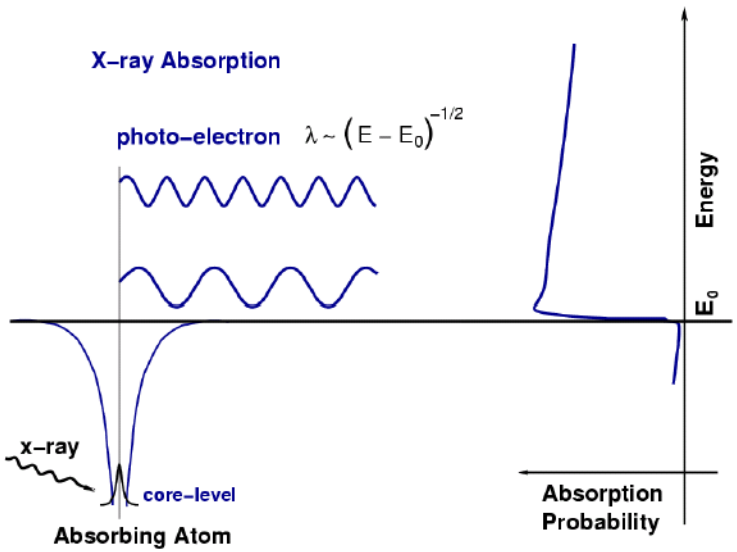
Edge	Energy
K	115606
L3	17166
L2	20948
L1	21757

Line	Transition	Energy	Strength
Lα_1	L3-M5	13614.0	0.686
Lα_2	L3-M4	13438.0	0.077
Lβ_2	L3-N4,5	16387.7	0.181
Lβ_5	L3-O4,5	17063.2	0.038
Lβ_6	L3-N1	15727.0	0.013
L$_\ell$	L3-M1	11618.0	0.005

The exact energy positions of edges and lines are sensitive to the chemical environment of the absorber.

A simple picture of X-ray absorption

An incident x-ray of energy E is absorbed, destroying a core electron of binding energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or an Auger electron.

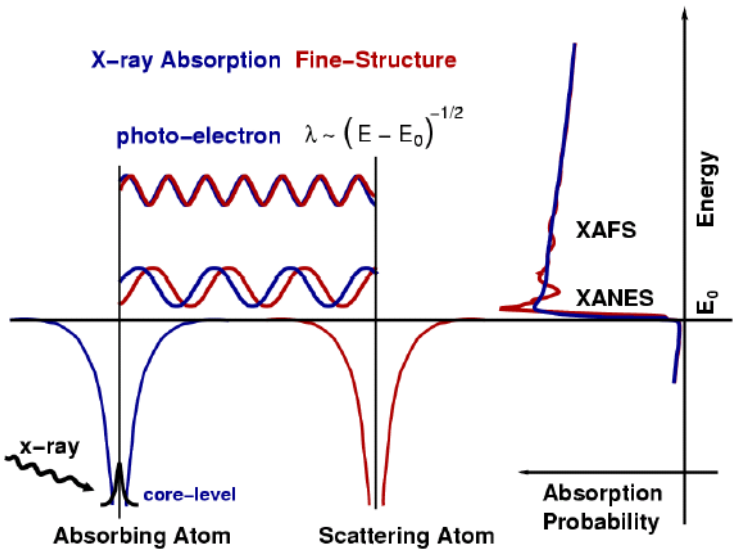


An empty final state is required.
No available state,
no absorption!
When the incident x-ray energy is larger than the binding energy, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption in condensed matter

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.

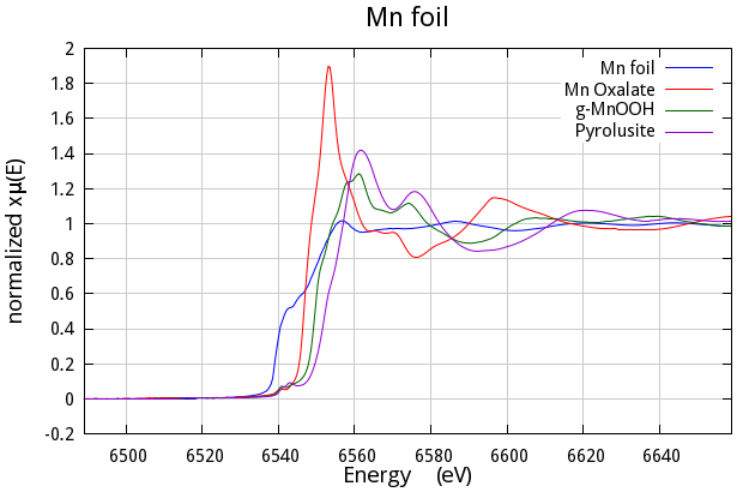


The scattering of the photo-electron wave function interferes with itself.

$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

This interference at the absorbing atom will vary with energy, causing the oscillations in $\mu(E)$.

XAS and Valence State



As the valence increases

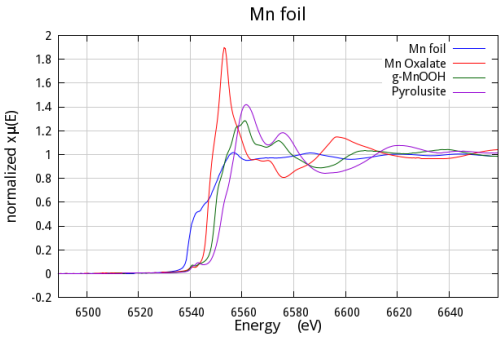
$Mn^0 \rightarrow Mn^{2+} \rightarrow Mn^{3+} \rightarrow Mn^{4+}$

the edge position shifts to higher energy.

XAS is a direct measure of valence state

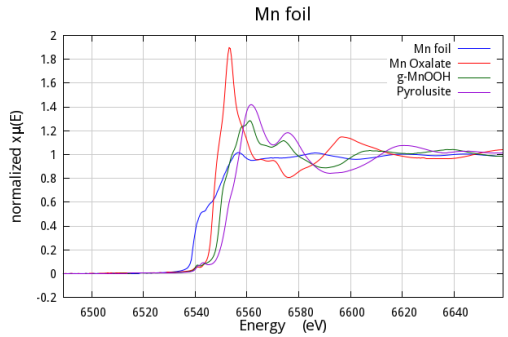
Since each element has its own edge energy, an element's valence can be measured even in a heterogeneous sample and even if it is a minority component.

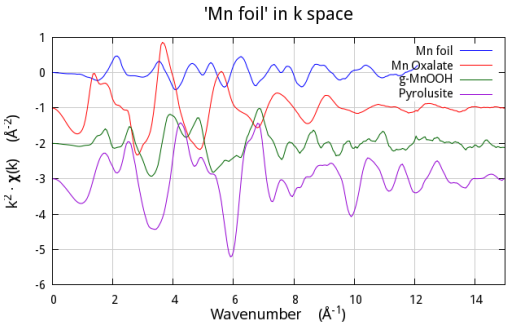
XAS and Local Atomic Structure



- The different Mn species display big differences in the fine structure beyond the edge as the valence increases (Mn^0, Mn^{2+}, Mn^{3+}, Mn^{4+}). The white line and subsequent oscillations are quite different.

XAS and Local Atomic Structure





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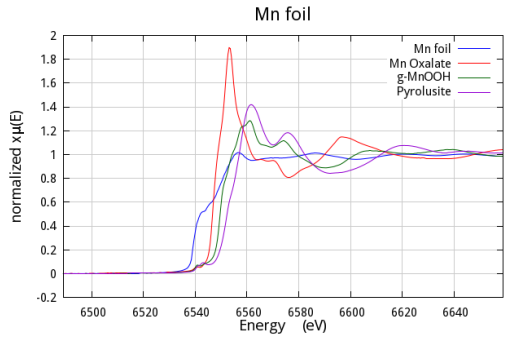
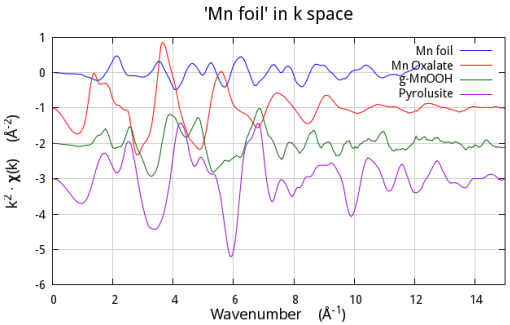
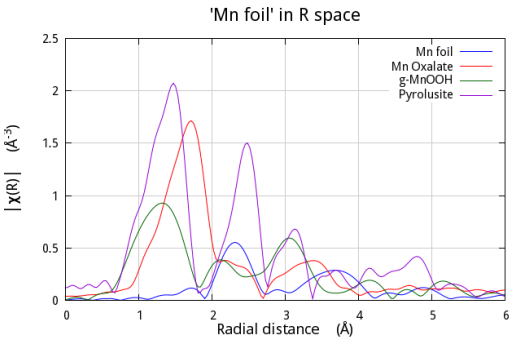
- The oscillatory portion of the spectrum can be isolated and ...

XAS and Local Atomic Structure







- The different Mn species display big differences in the fine structure beyond the edge as the valence increases (Mn^0, Mn^{2+}, Mn^{3+}, Mn^{4+}). The white line and subsequent oscillations are quite different.
- The oscillatory portion of the spectrum can be isolated and ...
- ... Fourier transformed. This FT function can be interpreted in terms of partial pair distribution functions of atoms about the absorber. The Mn-O distances are different for the Mn^{2+}, Mn^{3+}, and Mn^{4+} and clearly different from the Mn-Mn distance in Mn metal.

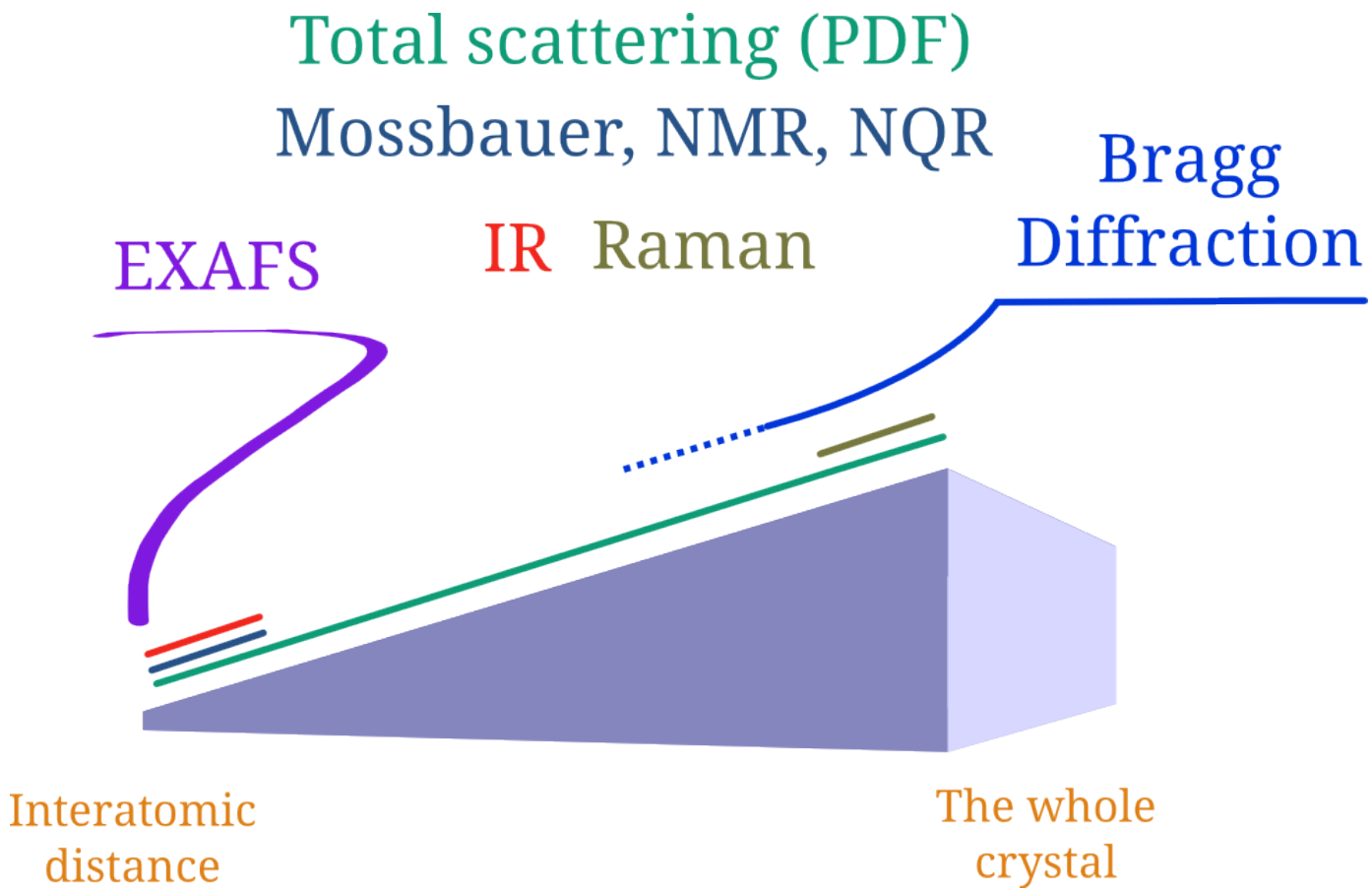
XAS is a direct measure of local structure

- Since each element has its own edge energy, an element's local structure can be measured even in a heterogeneous sample and even if it is a minority component
- No assumption of symmetry or periodicity is made, so the sample can be crystalline, amorphous, thin film, in solution, surface sorbed, $\cdots$, *whatever*
- Since x-rays are deeply penetrating into matter, minimal sample preparation is required
- Samples can be measured *in situ*, which can mean
  - cryostat or furnace
  - high pressure cell
  - electrochemistry cell or fuel cell
  - peristaltic or stop-flow pump with liquid samples
  - high field magnet
  - etc...

As a result, XAS is used in a very broad array of scientific disciplines

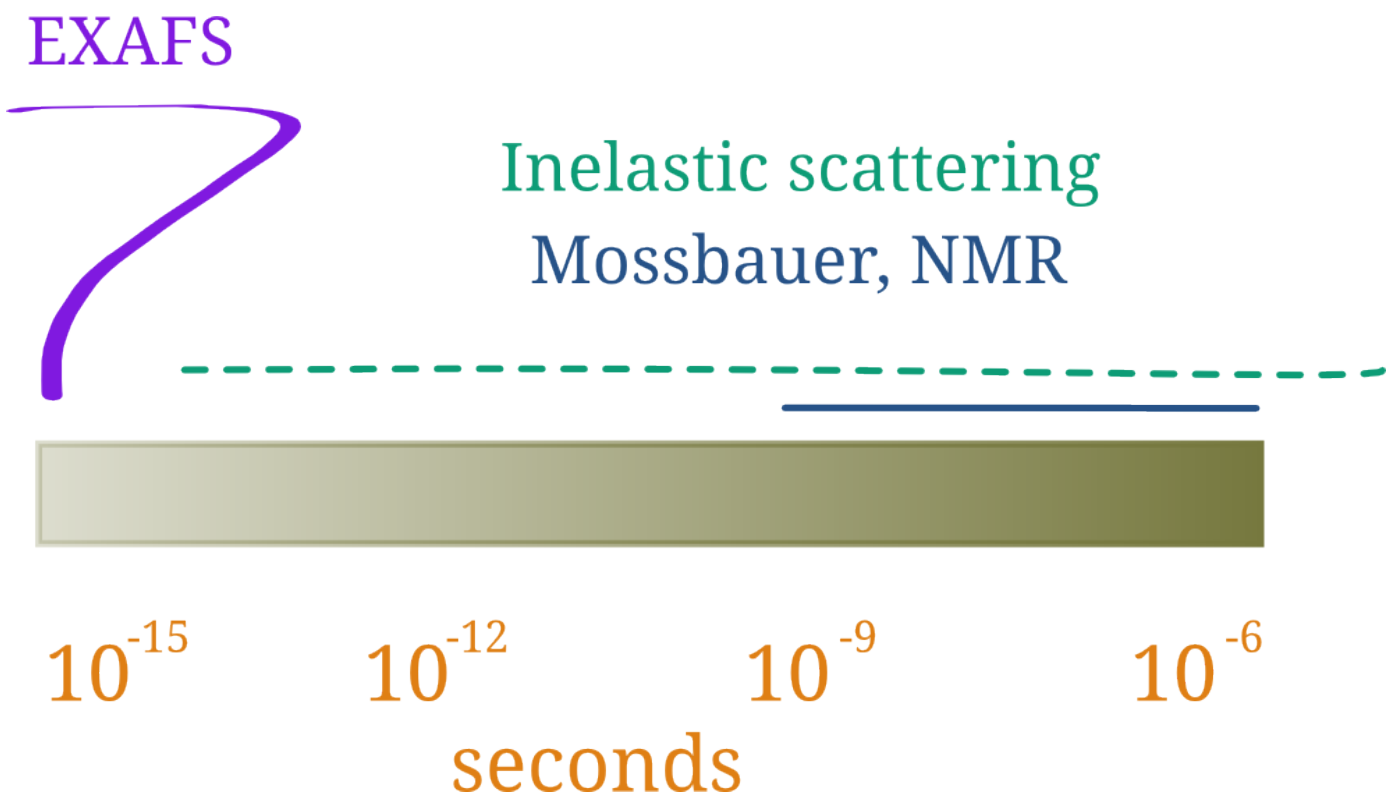
Comparing structural techniques

Part 1: Length scales



Comparing structural techniques

Part 2: Time scales



Comparing structural techniques

Part 3: Spatial resolution and disorder

Spatial Resolution

- The ultimate resolution of EXAFS is a complicated and open question. In normal practice, it is limited by the extent of the measurement to $\mathcal{O}(0.01\,\text{Å})$.
- Techniques sensitive to symmetry breaking (Bragg, Raman) may be much more sensitive that EXAFS.

Structure Disorder

- EXAFS measures disorder about inter-atomic distance.
- Diffraction and Mössbauer measure disorder about lattice position.
- In general, relating these disparate measures of disorder is very difficult.

Comparing structural techniques

Part 4: What makes EXAFS wonderful?

Element selectivity: Thus EXAFS is sensitive to small minority components of a sample

No assumptions of symmetry or periodicity: Both theory and analysis are independent to symmetry and periodicity, thus EXAFS is applicable to a very broad range of sample types.

In situ measurements: Hard x-rays are deeply penetrating, thus the sample can be maintained in exotic conditions of temperature, pressure, chemical potential, fluid flow, etc....

Ease of measurement: Good practice is required (of course), but both sample preparation and measurement are relatively straightforward.

Comparing structural techniques

Part 5: What makes EXAFS troublesome?

Near-sightedness: EXAFS is insensitive to correlations beyond a few Ångstroms.

Scatterers of similar Z: EXAFS has a hard time with neighbors that are close on the periodic table. For instance, it is very hard to distinguish As and Se neighbors.

Mixed phase or multi-site materials: EXAFS looks at all the atoms beneath the footprint of the beam. If the absorber exists in multiple phases, EXAFS interpretation can be difficult or impossible.

Quantitative analysis: Although measurement is simple, analysis can be very challenging and requires extensive training and practice.

EXAFS & this workshop

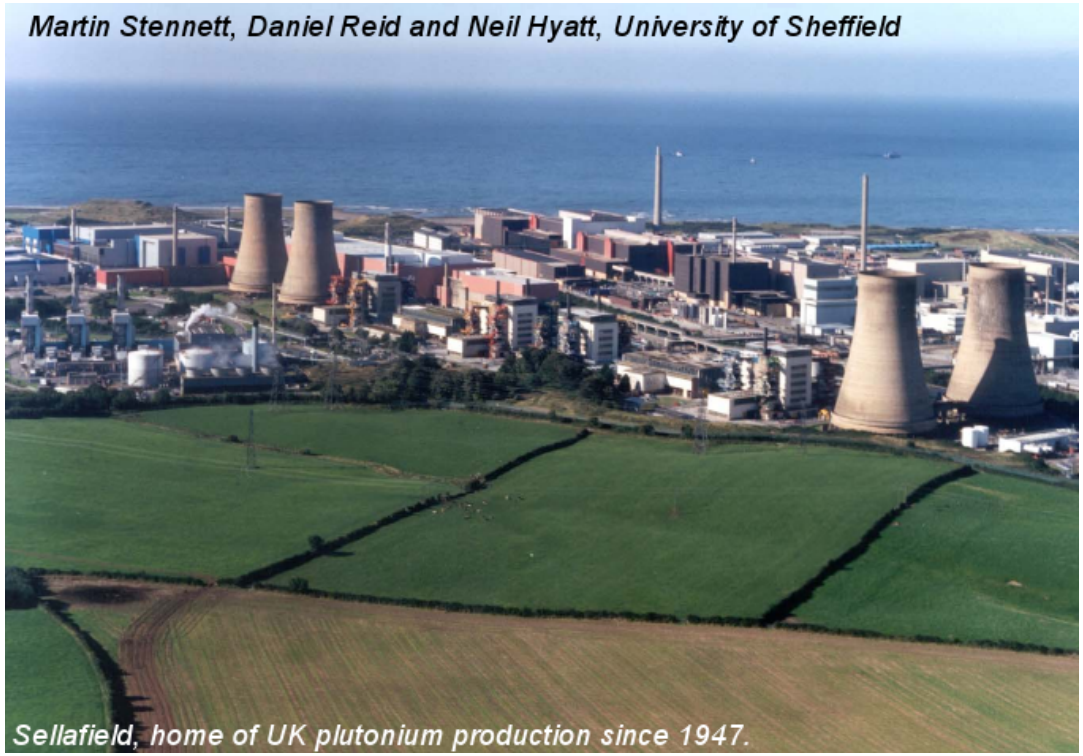
Klaus Attenkofer: ultrafast time resolved EXAFS

Faisal Alamgir: interpretation of the XANES for soft and hard X-rays

Neville Greaves: combining EXAFS with other synchrotron measurement techniques

Simon Billinge: total X-ray scattering (AKA PDF), this technique and EXAFS complement one another in several important ways

Plutonium containment



My colleagues from University of Sheffield come to X23A2 to study zirconolite glassification by ion-implantation as an analog for α-recoil damage from actinide impurities. The research is related to long-term Pu containment strategy.

Ceramic wasteform design

Minerals: Nature's wasteforms
Tool box of target synthetic phases

Parent formula: $CaZrTi_2O_7$

CN = 8 7 6+5

Zirconolite: $(Ca,Th,Ce)Zr(Ti,Nb)_2O_7$

Wasteform formulation

$(Ca,Act,Ln)(Zr,Hf,Act)(Ti,M)_2O_7$

plus TiO_2 or ZrO_2 buffer

Incorporate additives & impurities
Neutron absorbers: Gd, Hf
Impurities: e.g. Am

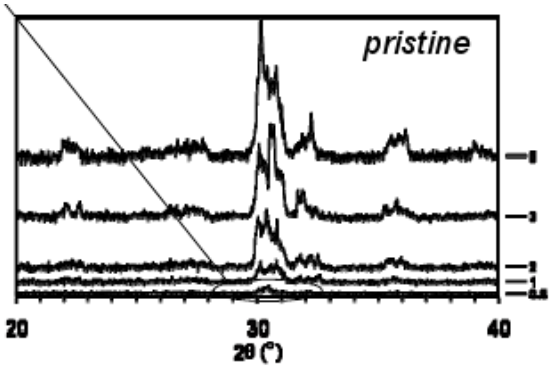
Ionic radii & co-ordination
Act^{4+} (VIII) = 0.90… 1.00 Å
Ln^{3+}: (VIII) = 0.95… 1.20 Å

Excess inert buffer
Variation in feed chemistry

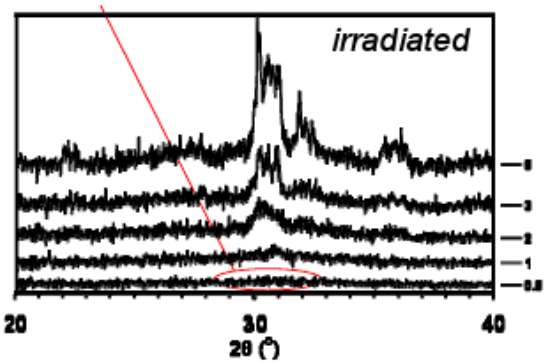
What is effect of cumulative α-recoil damage on material structure and Pu retention?

Expect material to become metamict, but what does the metamict structure look like?

Laboratory Grazing Incidence XRD



GIXRD measurements of the pristine zirconolite surface show that crystalline structure persists to the surface.

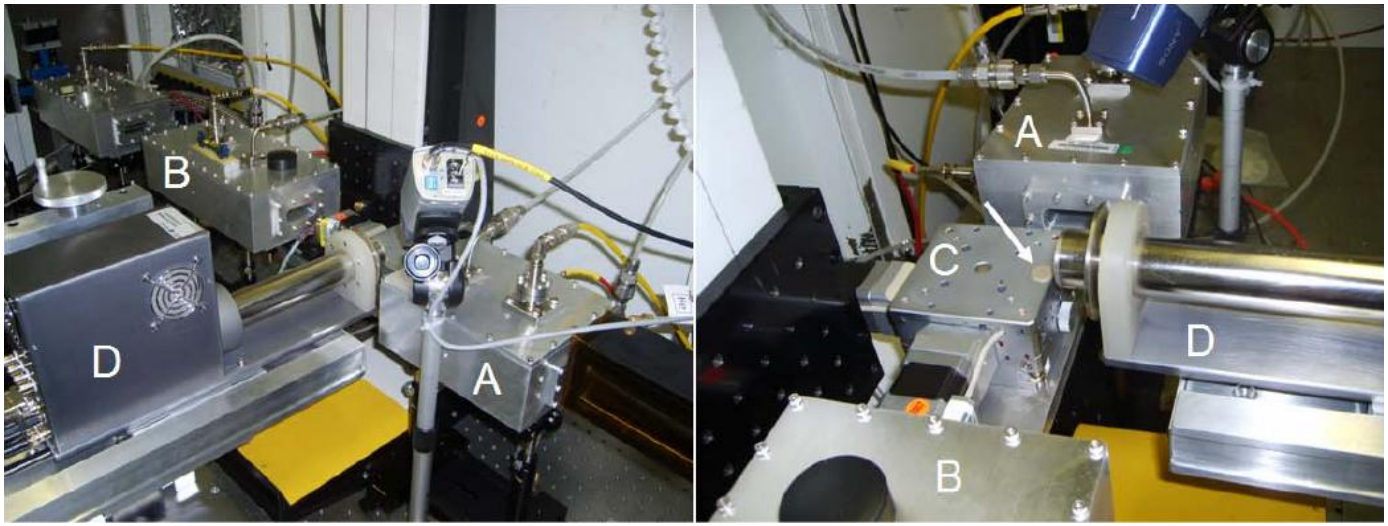


After heavy ion bombardment, the bulk crystallinity vanishes near the surface.

Can we learn anything useful about the structure of the damaged surface?

Data courtesy M. Stennett, D. Reid, N. Hyatt, unpublished

Grazing Incidence XAS



A. Incident intensity ionization chamber

B. Transmitted intensity ionization chamber

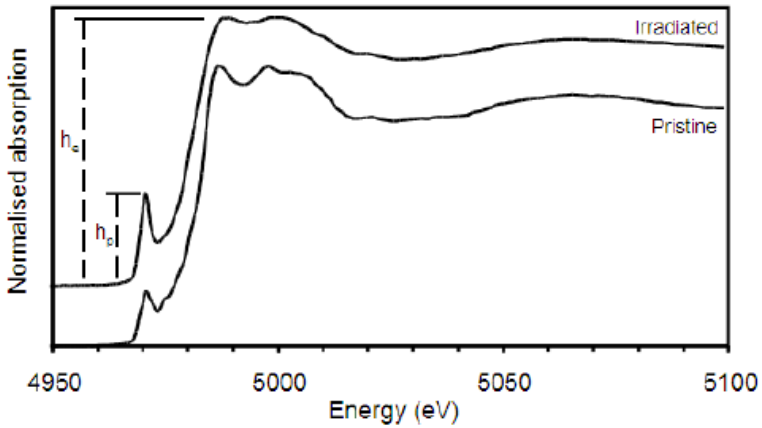
C. 5 dimensional sample stage

D. Energy discriminating fluorescence detector

And the sample is a polished zirconolite wafer. By controlling the tilt of the sample stage, we can control the penetration depth of the beam into the sample.

Ti K Edge XANES

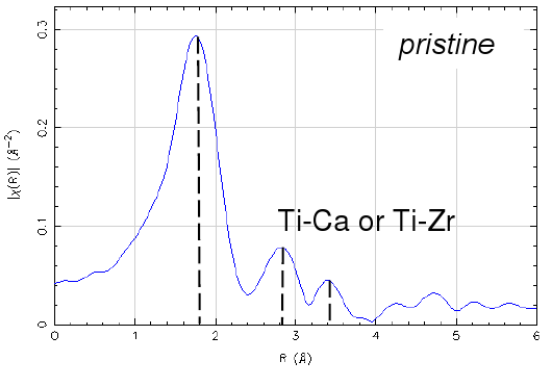
At a $\sim 0.1^\circ$ angle of incidence, we see dramatic differences in the GIXAS spectrum compared to the bulk XAS spectrum.

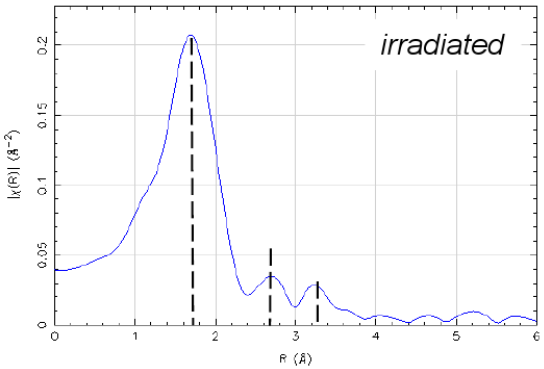


- The shift in edge position and increase in the height of the first peak indicate a change from 6-fold to 5-fold coordination.
- The dampening of the oscillations above the edge suggest an increase in local structural disorder.

Data courtesy M. Stennett, D. Reid, N. Hyatt, unpublished

Ti K Edge EXAFS



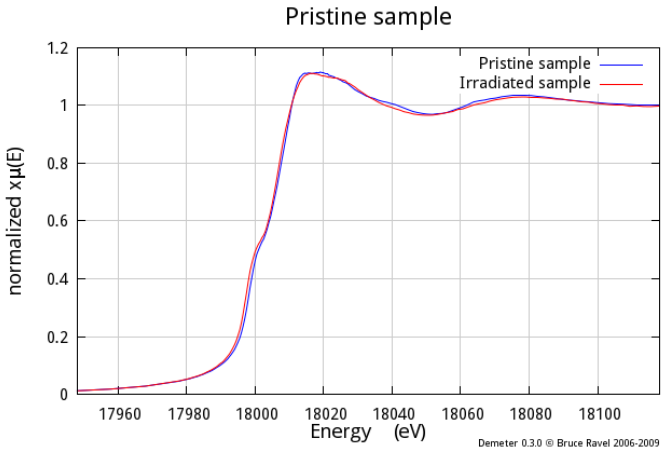


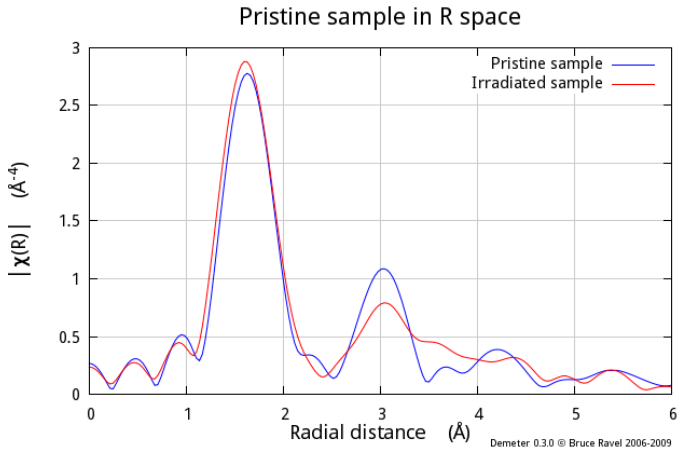
- The signal from oxygen in the first coordination shell is reduced and broadened.
- The signals from higher shells (Ca, Zr, etc.) are similarly reduced.

These data can be quantitatively analyzed to get coordination numbers of and distances to the neighboring atoms.

Data courtesy M. Stennett, D. Reid, N. Hyatt, unpublished

Zr K Edge EXAFS





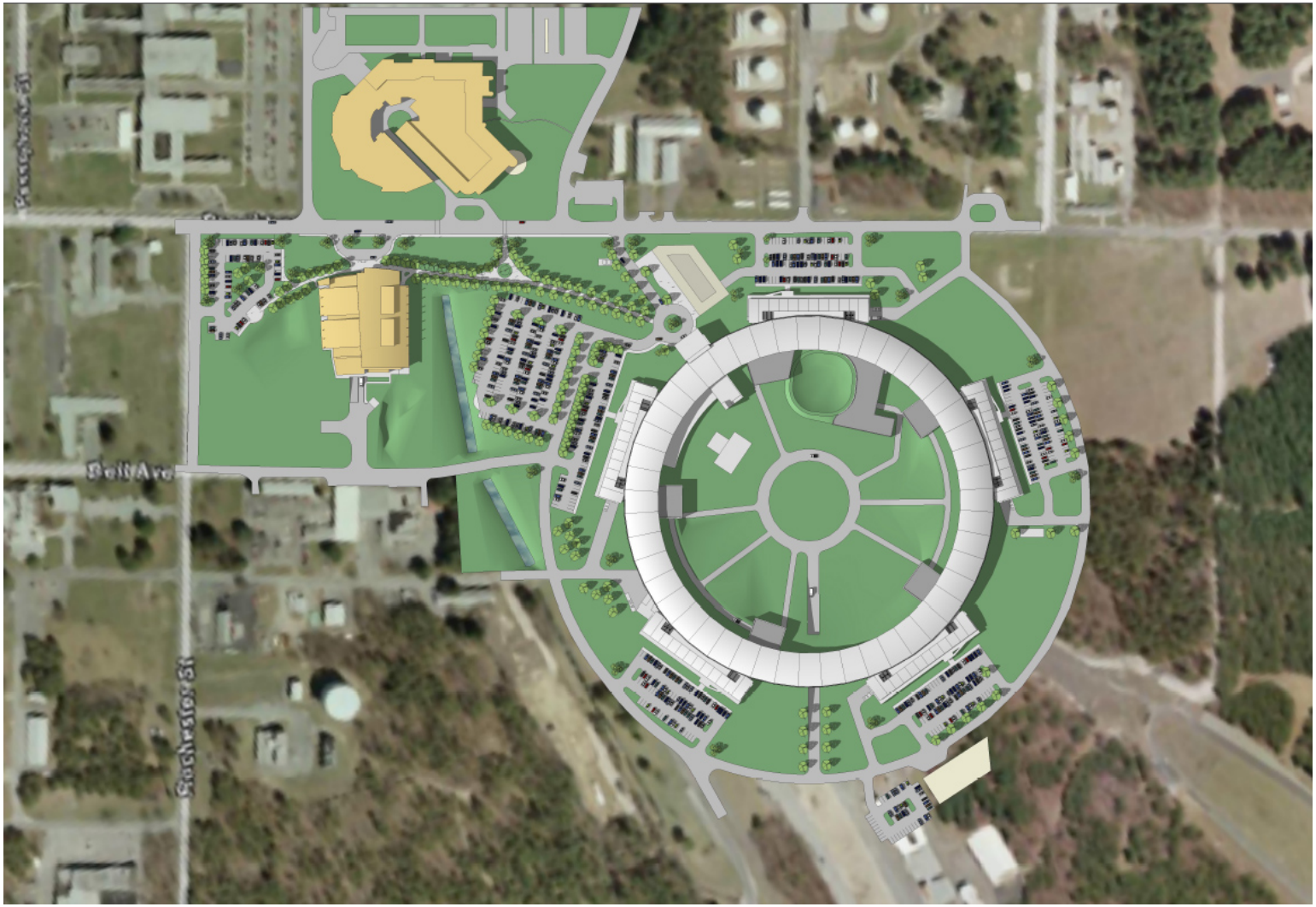
The structural changes observed at the Zr K-edge are much more subtle. There is a slight red-shift of the edge energy, a slight shortening of the Zr–O bond, and an increase in higher shell disorder.

Moving Forward

I have only sketched the outline of how XAS is applied to this problem. The next step is, of course, quantitative analysis of the Ti and Zr EXAFS data.

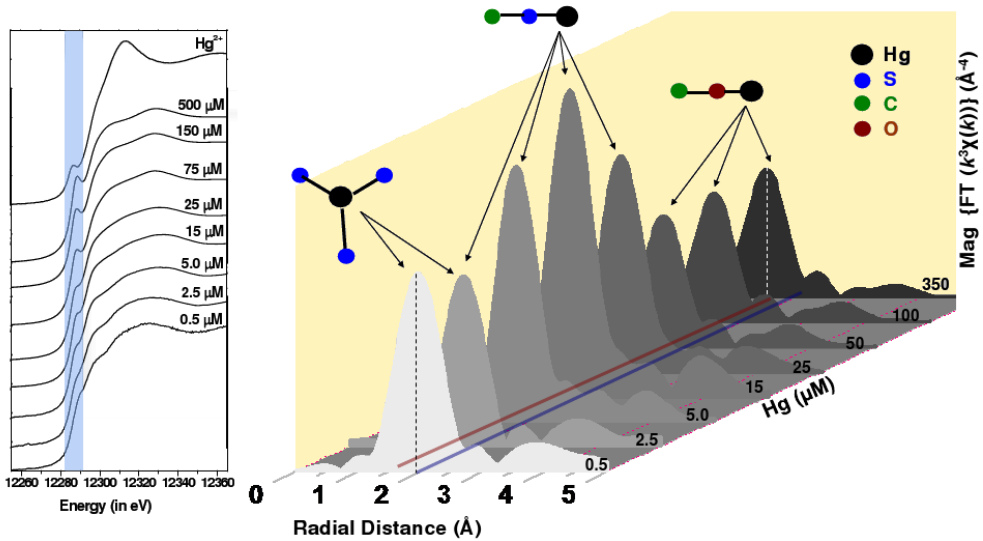
The Sheffield group is returning to X23A2 later this month to continue this work. Stay tuned for results....

Our future!



How can we use high flux?

Low concentrations: Higher flux allows us to push down our measurement sensitivity limits, as in this experiment of Hg^{2+} adsorbed on biomass at concentrations from 350 μM down to 0.5 μM:



Photon-starved experiments: Focusing optics and specialized detection technology are necessarily inefficient.

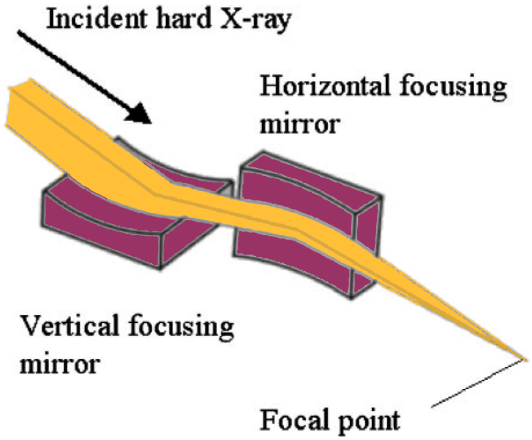
Mercury data courtesy B. Mishra and S. Myneni, measured at APS 10ID, unpublished

Focussing optics

Different types of focussing optics can be matched to the relevant length scales of different samples

Focusing mirrors A total external reflection mirror is bent to condense the x-rays vertically or toroidally. Slits may be used to define the horizontal extent. ($> 50\,\mu$m)

Kirkpatrick-Baez mirrors Short mirrors with excellent figures are used in both directions to define a small spot. (1–25 μm; $< 1\,\mu$m at NSLS-II)

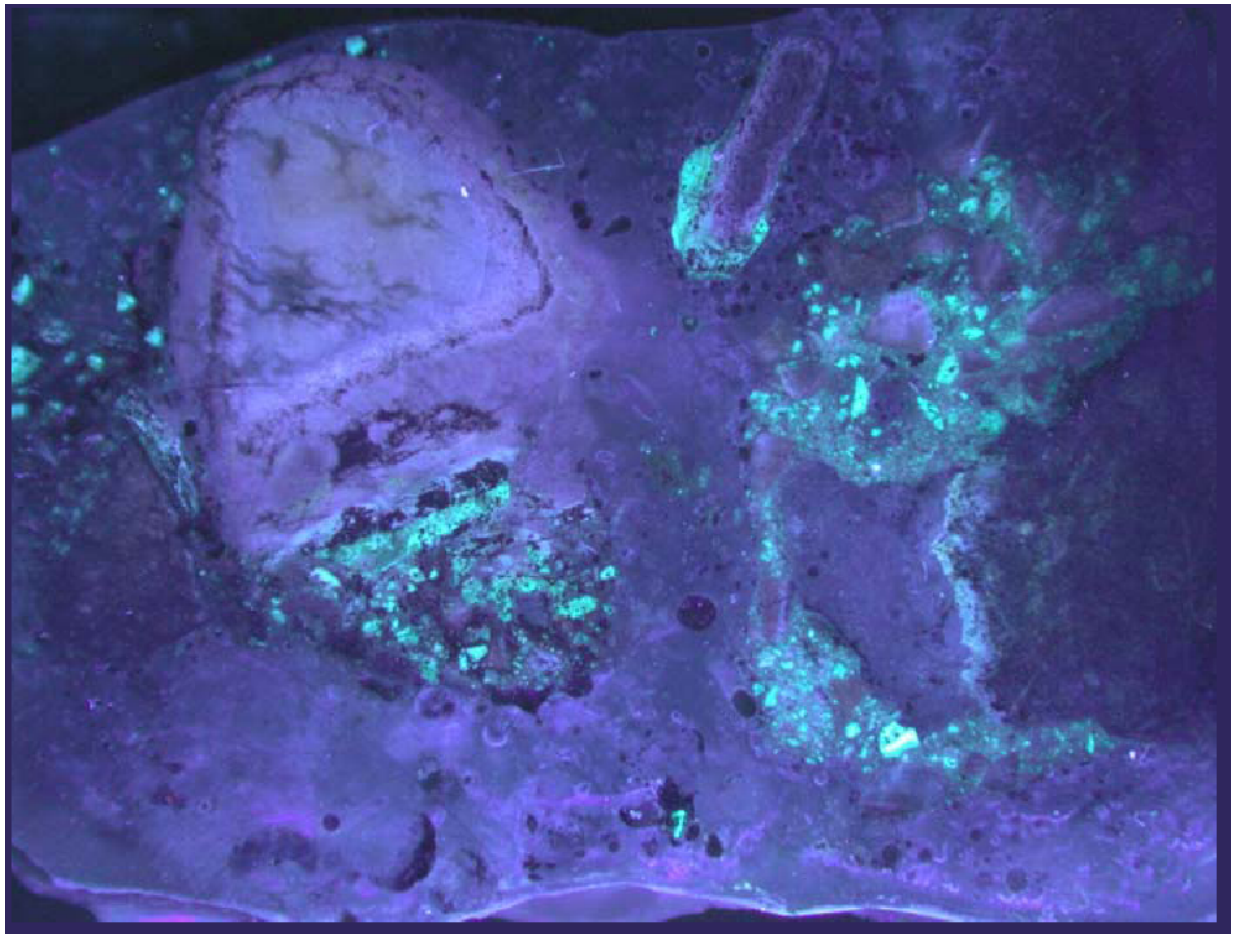


Refractive optics Fresnel zone plates — or other types of refractive lenses — define a small first order spot ($< 1\,\mu$m; $<$ 100nm at NSLS-II)

Gravel Contaminated with U

Gravel embedded in epoxy with a polished surface

Under a UV lamp, U glows greenish.

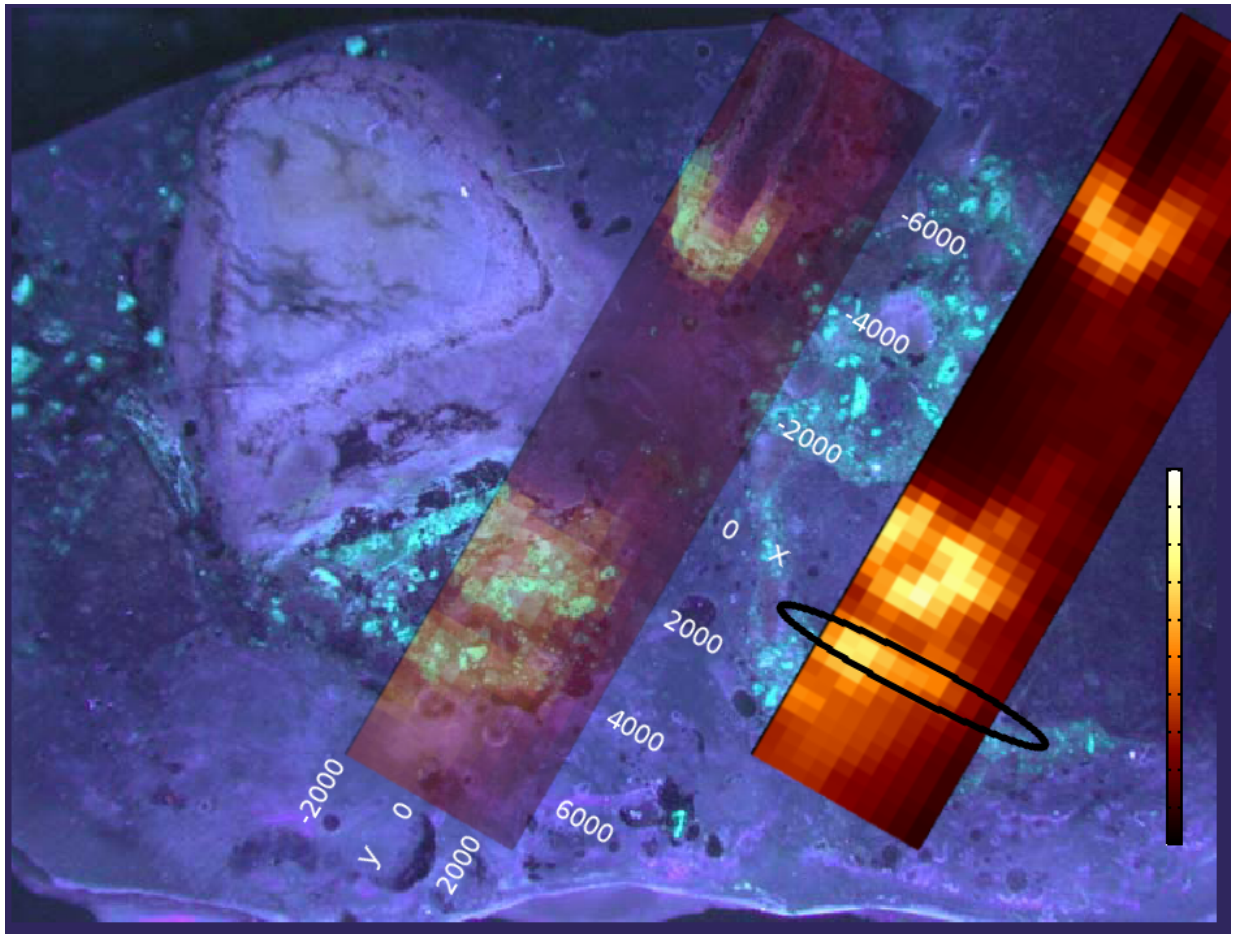


D. Phillips et el., Environ. Sci. Technol., **42**:19, pp. 7104–7110 (2008)

Gravel Contaminated with U

Gravel embedded in epoxy with a polished surface

UV photo + superposed U map — 200 μm probe at APS 10ID.



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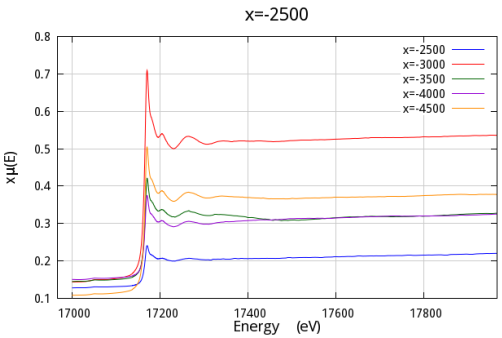
μ-EXAFS



- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.

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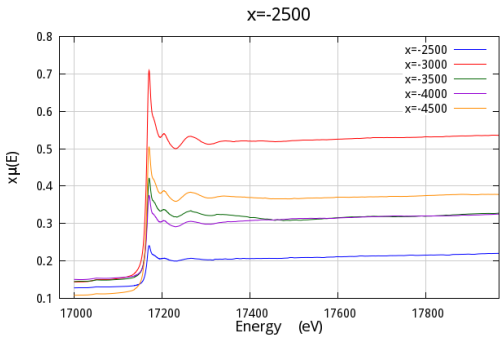

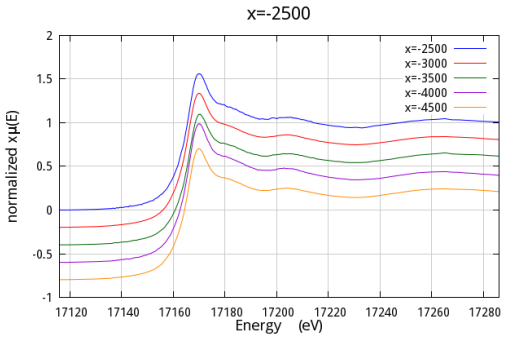

- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.
- Normalizing the data, we see variability in the XANES, indicating spatial heterogeneity in U speciation.

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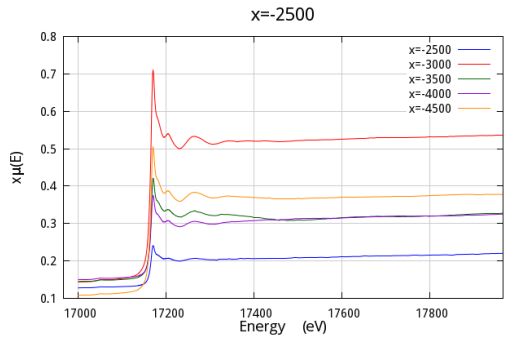
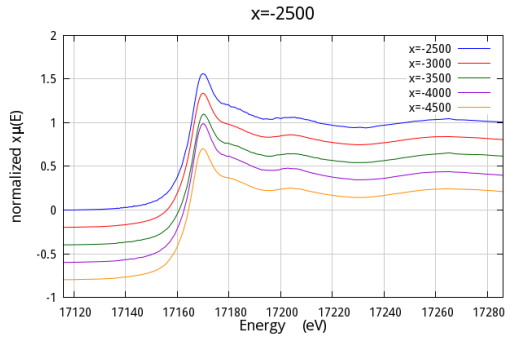
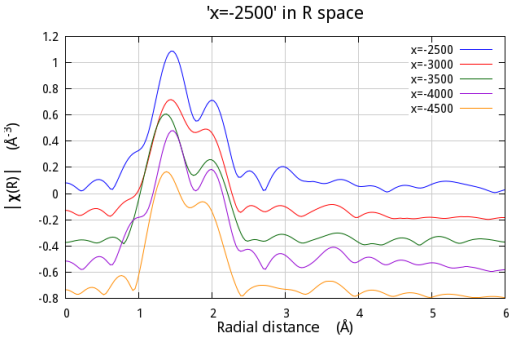
μ-EXAFS





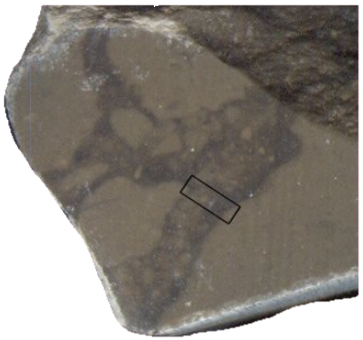


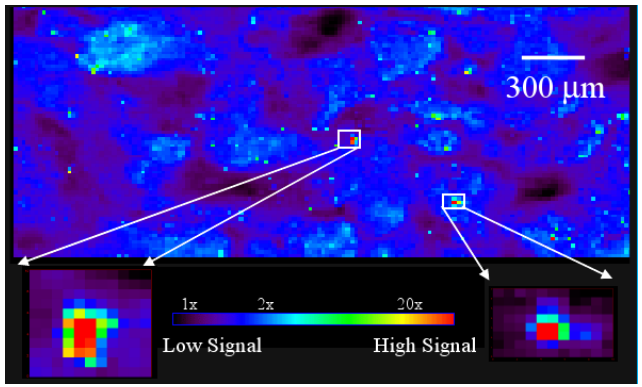
- High quality XAS data is measured with the 200 μm probe. We can see the variation in U quantity under the spot in the XAS step size.
- Normalizing the data, we see variability in the XANES, indicating spatial heterogeneity in U speciation.
- The EXAFS is of high quality and can be analyzed to uncover the different structural environments around the U at the various locations.

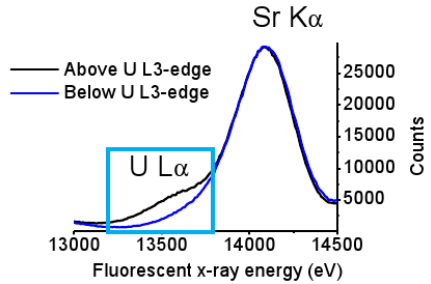
D. Phillips et el., Environ. Sci. Technol., **42**:19, pp. 7104–7110 (2008)

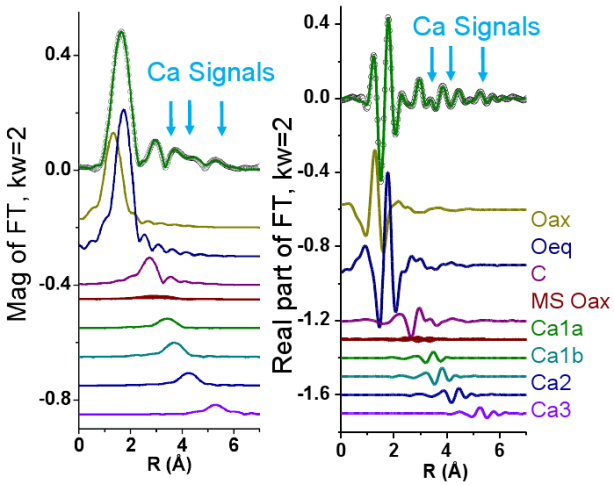
Uranyl incorporation in calcite

μXAS at APS beamline 10ID was used to quantify the structure of uranyl incorporation into an ancient calcite. This identifies a plausible strategy for uranium sequestration.









S.D. Kelly, et al, Environ. Sci. Technol. (2006) **40**:7, 2262–2268

2x10^{16} total photons

10 μm spot; 10^{11} ph/sec for 2.5 continuous days:

Flux is very significant for XAS

Exps. at relevant concentrations that cannot be done at NSLS will become routine at NSLS-II.

Sub micron probes at NSLS-II

The SRX Beamline: A KB-mirror-based μ-XRF, μ-XRD, and μ-XAS beamlline with a spot size of $\mathcal{O}(100\,\mathrm{nm})$.

The Nanoprobe: One of the NSLS-II flagship beamlines using refractive optics to attain a spot size as small as 1 nm.

Possible uses in glassy materials

- Study individual crystallites with μm- or nm-scale XRF, XRD, and XAS
- Study inclusions with the micro/nano probe
- Study segregated phases with the micro/nano probe
- ...

Various time scales

Time-resolved measurements are inherently photon-starved

In general, the more photons you have, the more you can do.

Slew scanning: Sub-minute XANES and EXAFS scans could be performed at any conventional, step-scan XAS beamline given certain upgrades to the hardware and software. This mode of measurement is routine at APS 10ID and elsewhere.

Cam driven mono: Sub-second XANES and EXAFS scans are routine at NSLS X18B, SLS SuperXAS, and elsewhere.

Laser initiated time resolution: See Klaus's talk!

Wavelength dispersive detection

Many novel possibilities become available with detection strategies that have energy resolution superior to silicon or germanium based detectors.

Bent Laue analyzers

Superior energy resolution for XRF mapping and lifetime suppression for XANES

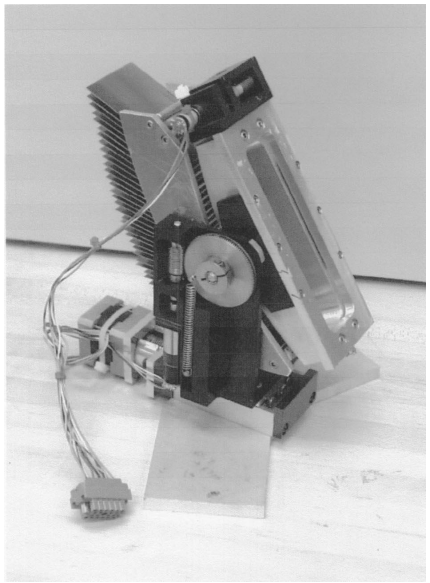
Emission spectrometry

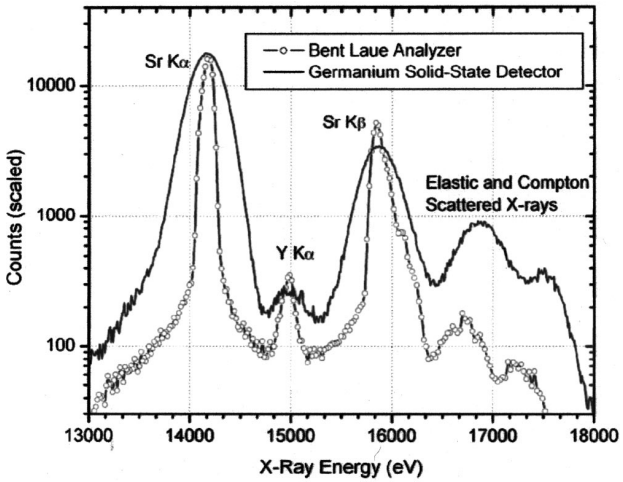
Study electronic structure by careful measurement of fluorescence lines

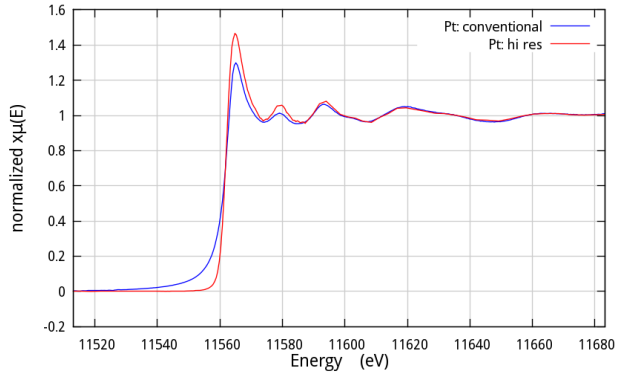
Inelastic scattering spectrometry

Low energy edges measured using high energy, deeply penetrating photons

Spectrometers: Bent Laue analyzers





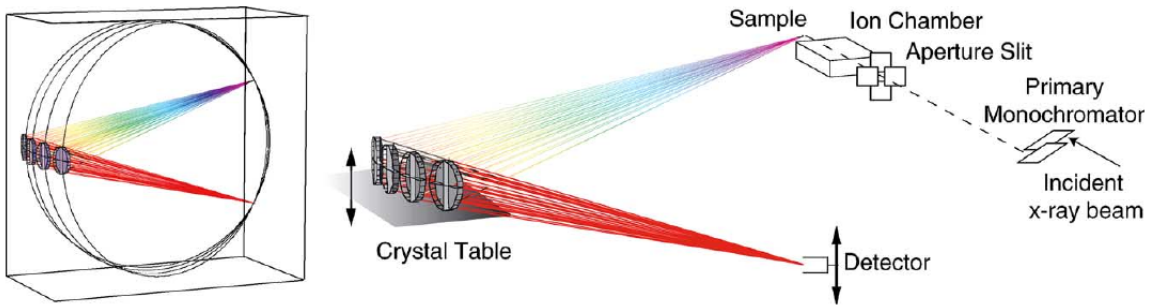


See A.J. Kropf, et al, Rev. Sci. Instrum. 74 (2003) 4696- 4702.
Hi-res XAS courtesy A.J. Kropf

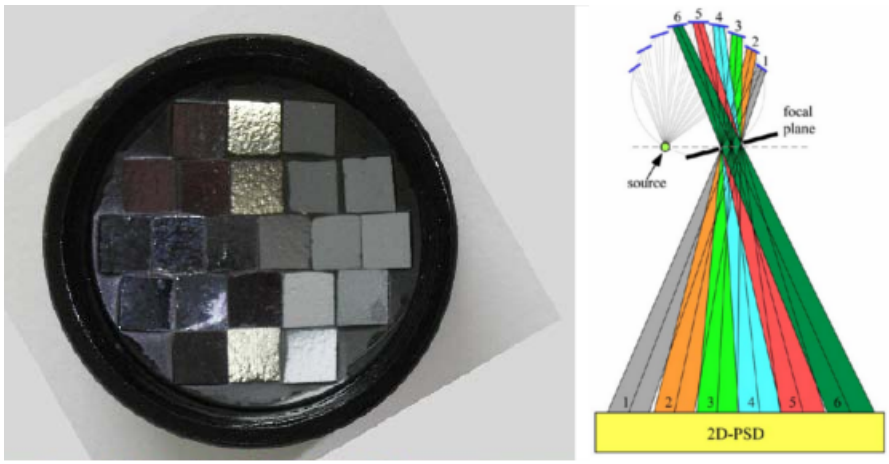
Spectrometers: XES & RIXS

Instrumentation

Johann-Rowland – ESRF ID26, NSLS X3(?)



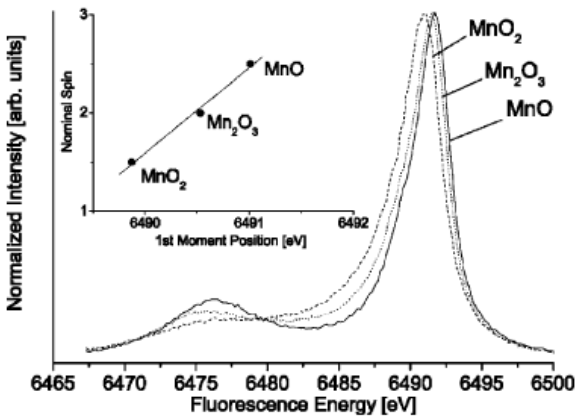
Short working distance – APS 20ID



P. Glatzel, U. Bergmann, Coord. Chem. Rev. **249** (2005) 6595;
B. Dickinson, et al. Rev. Sci. Instrum. **79**, 123112 (2008)

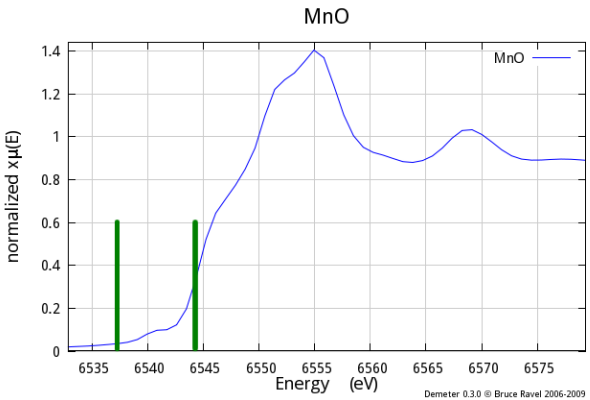
Spectrometers: XES & RIXS

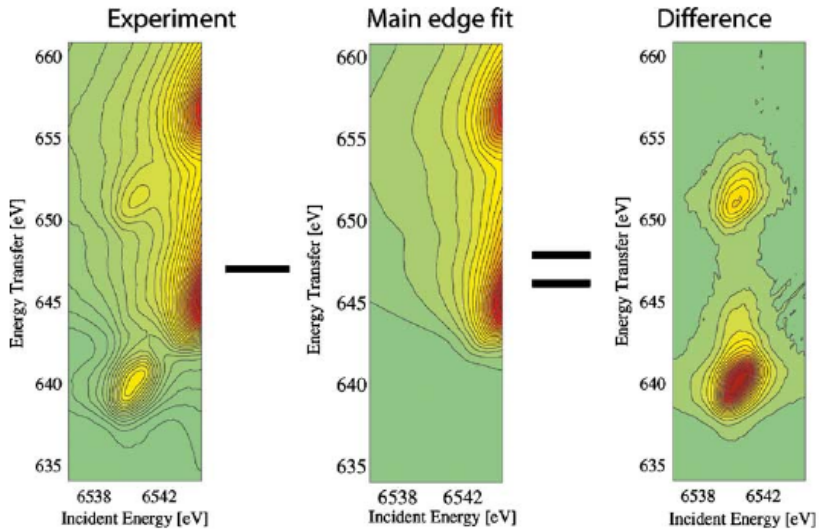
Science examples



Energy analyzing the fluorescence lines yields information about the electronic structures of different chemical states.

Combining this with a scanning monochromator, the RIXS plane is measured, elucidating the conventional XAS spectrum.



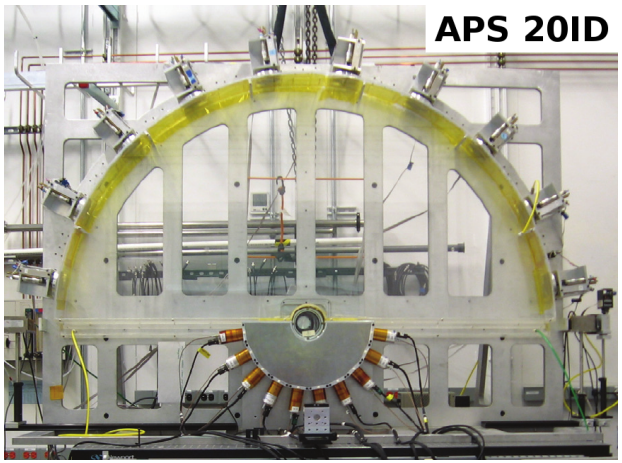


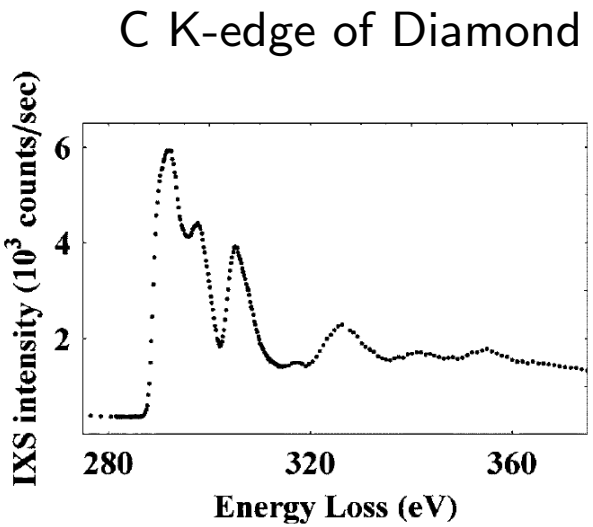
XES and RIXS data: P. Glatzel, U. Bergmann, Coord. Chem. Rev. **249** (2005) 6595;
XAS data: BR, unpublished

Spectrometers: LERIX

Lower Energy Resonant Inelastic Scattering

Probe the sample with hard x-rays and use the crystal analyzers to resolve the energy loss in the nearly-elastically scattered radiation due to absorption by low-energy edges.





Soft x-ray edges measured with hard x-rays!

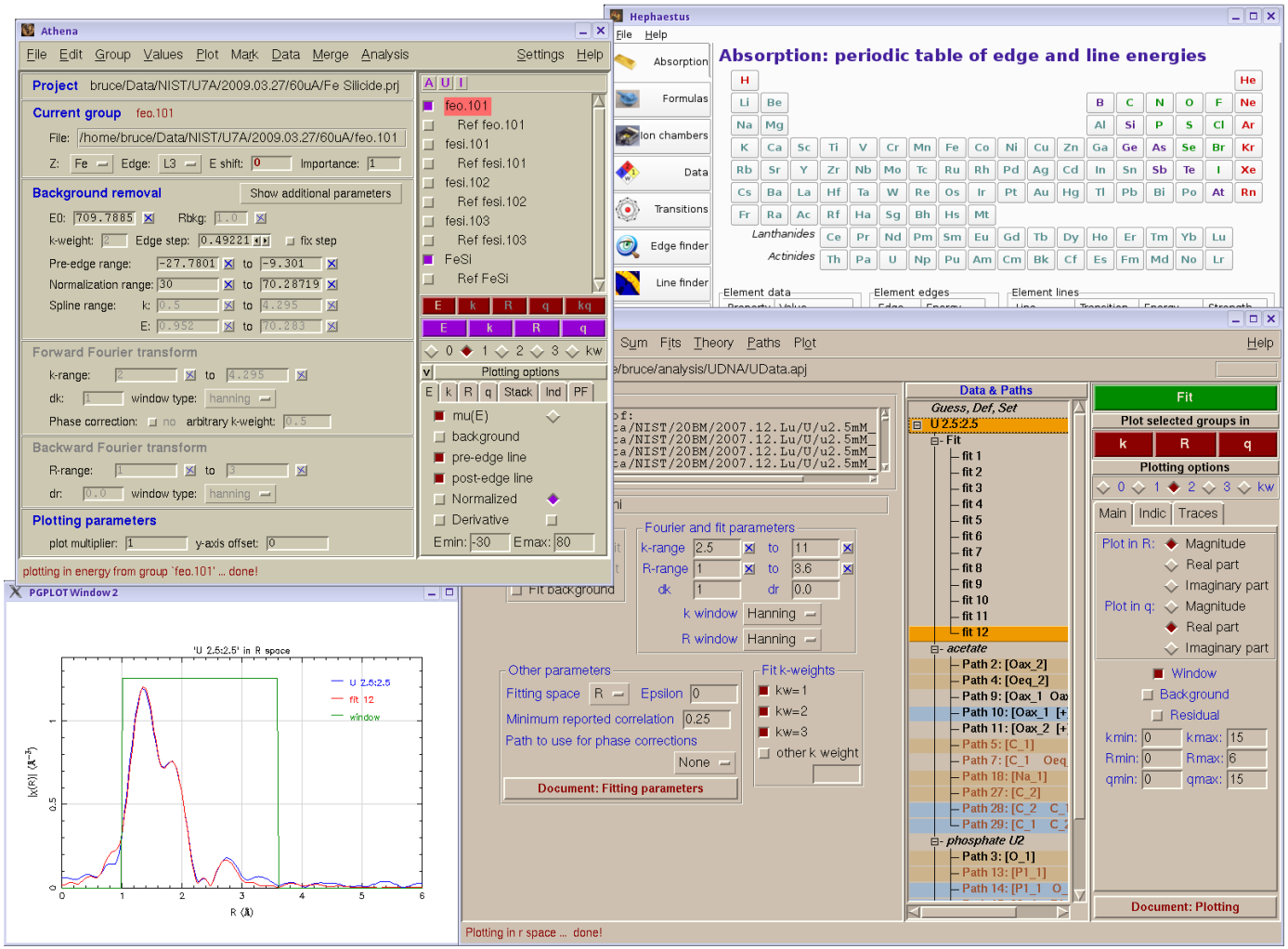
Consider, say, a C K-edge of a buried layer.

T.T. Fister et al, *Rev. Sci. Instrum.* **77**, 063901 2006 and G.T. Seidler, et al, AIP Conf. Proc. 882, p. 911 (2006).

Learning more about XAS

- http://xafs.org is a splendid resource. The "Tutorials" and "Workshops" pages are particularly useful for the newcomer to XAS.
- The IFEFFIT mailing list is an archived place to ask questions about XAS in general and the IFEFFIT software in specific. http://millenia.cars.aps.anl.gov/mailman/listinfo/ifeffit/
- There will be an XAFS Summer School at the APS in July. http://xafs.org/Workshops/APS2009
- The NSLS XAFS Online Orientation is an exciting work-in-progress. http://www.nsls.bnl.gov/users/access/modules/xafs/

Software



http://cars9.uchicago.edu/iffwiki/Ifeffit

For other software options: http://xafs.org/Software

My final comment

To the university faculty among us

NSLS-II (and other synchrotrons) needs good staff scientists. Encourage some of your students to fall in love with synchrotron radiation.