

Introduction to X-ray Absorption Spectroscopy

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&

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National Synchrotron Light Source II

XAS 2024: Fundamentals of XAS Data Analysis: A Hands-on Tutorial

19 March, 2024

Part 1

The basic physics and chemistry of X-ray Absorption

This Talk

This talk is an introduction to the inner-shell spectroscopies, XAS and XRF.

Outline

- An overview of the basic physics of inner shell spectroscopies
- An introduction to XAS and XRF beamline instrumentation
- A flavor of the sorts of science that can be accomplished with XAS and XRF, including examples from my own research and my beamline.

My hope is that you will leave with a sense of how XAS and XRF might be applied to **your** research.

XAS and XRF

X-ray Absorption Spectroscopy and X-Ray Fluorescence spectroscopy

These are inner shell spectroscopies.

Inner shell means that an x-ray interacts primarily with a deep-core electron rather than with a valence electron.

Spectroscopy means that some aspect of the interaction changes as a function of photon energy.

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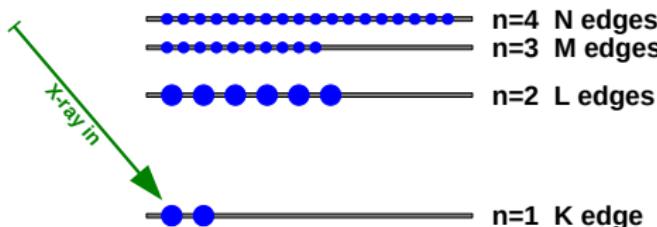
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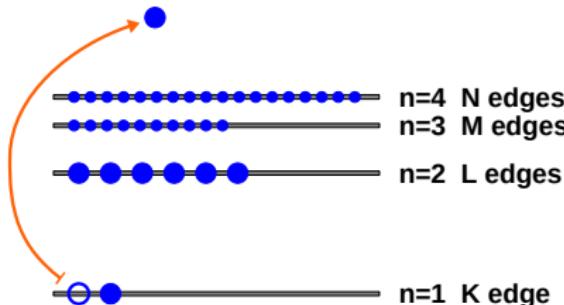
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The basic physical process in XAS and XRF



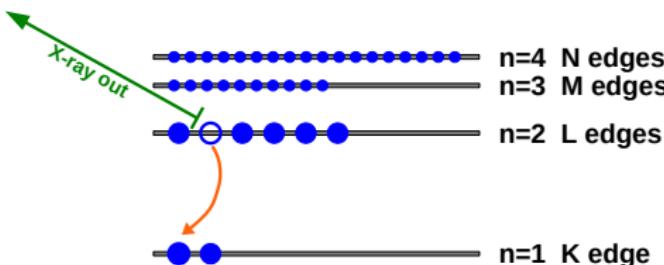
- ① An incoming photon interacts with a deep-core electron. Shown here, a 1s electron is excited for a K-edge spectrum.
- ② The deep-core electron is promoted to some unoccupied state above the Fermi energy, propagates away, and leaves behind a core-hole.
- ③ A short time later (1 or 2 femtoseconds), a higher-lying electron decays into the core-hole and emits a photon. Shown here, a $2p^{3/2}$ or $2p^{1/2}$ electron fills the 1s hole.
- ④ Alternately, the energy from the higher-lying electron can be used to emit an Auger electron.

The basic physical process in XAS and XRF



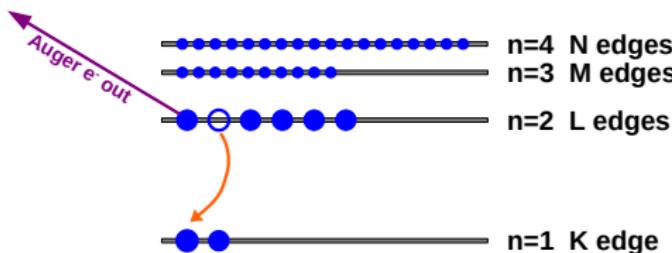
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Elements and Beamlines

*Lanthanide series

****Actinide series**

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

Elements and Beamlines

hydrogen 1 H 1.0079	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 4.003
lithium 3 Li 6.941	beryllium 4 Be 9.0122	carbon 6 C 12.011	nitrogen 7 N 14.007
sodium 11 Na 22.990	magnesium 12 Mg 24.305	phosphorus 15 P 30.974	oxygen 8 O 15.999
potassium 19 K 39.098	silicon 14 Si 28.086	sulfur 16 S 32.065	fluorine 9 F 18.998
calcium 20 Ca 40.080	chromium 21 Cr 51.996	chlorine 17 Cl 35.453	neon 10 Ne 20.180
rubidium 37 Rb 85.468	nickel 24 Ni 58.697	aristoteles 18 Ar 36.947	
strontium 38 Sr 87.62	iron 26 Fe 55.845		
cesium 55 Cs 132.91	cobalt 27 Co 58.937		
barium 56 Ba 137.35	nickel 28 Ni 58.697		
francium 87 Fr 223.024	copper 29 Cu 63.546		
	zinc 30 Zn 65.409		
	gallium 31 Ga 69.721		
	germanium 32 Ge 72.61		
	arsenic 33 As 74.933		
	sele-nium 34 Se 78.96		
	bromine 35 Br 79.947		
	krypton 36 Kr 83.91		
↑ Vanadium			
K: 5465 eV Kα_1 (K-L3): 4953 eV L₁: 627 eV Kα_2 (K-L2): 4945 eV L₂: 520 eV K$\beta_{1,3}$ (K-M3/M2): 5428 eV L₃: 512 eV Kβ_5 (K-M4,5): 5463 eV			
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K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

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rubidium 37 Rb 85.468	strontium 21 Sc 44.966	chlorine 17 Cl 35.453	neon 10 Ne 20.180
cesium 55 Cs 132.91	titanium 22 Ti 47.867	silicon 14 Si 28.086	argon 18 Ar 36.941
rhenium 75 Rf 223.01	vanadium 23 V 50.947	manganese 25 Mn 54.938	hafnium 72 Hf 178.49
lanthanide series	chromium 24 Cr 51.996	iron 26 Fe 55.845	nickel 27 Co 58.937
actinide series	nickel 28 Ni 58.693	cobalt 29 Cu 59.931	copper 30 Zn 65.39
** Actinide series	zinc 31 Ga 69.721	zinc 32 Ge 71.97	zinc 33 As 74.933
	yttrium 39 Y 88.906	yttrium 39 Zr 91.228	zinc 34 Se 86.96
	lanthanides 57 La 138.91	lanthanides 71 Lu 174.97	zinc 35 Br 87.941
	cerium 58 Ce 141.52	cerium 72 Rf 175.00	zinc 36 Kr 89.951
	lanthanides 103 Lr 192.96	lanthanides 104 Rf 196.97	
	actinides 95 Ac 222.01	actinides 99 Th 232.04	

↑ Chromium

K: 5989 eV $\text{K}\alpha_1$ (K-L3): 5415 eV
 L₁: 696 eV $\text{K}\alpha_2$ (K-L2): 5405 eV
 L₂: 584 eV $\text{K}\beta_{1,3}$ (K-M3/M2): 5947 eV
 L₃: 574 eV $\text{K}\beta_5$ (K-M4,5): 5987 eV

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

Elements and Beamlines

hydrogen 1 H 1.0079	beryllium 3 Li 6.941	boron 5 B 10.811	helium 2 He 1.0083
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praseodymium 59 Pr 144.91	nickel 28 Ni 58.697	germanium 32 Ge 71.971	seleium 34 Se 78.961
neodymium 60 Nd 144.91	copper 29 Cu 63.546	tin 33 Sn 118.700	bromine 35 Br 79.944
europium 62 Eu 152.94	zinc 30 Zn 65.409	lead 32 Pb 207.200	iodine 53 I 126.904
* Lanthanide series	lutetium 71 Lu 174.97	tin 31 Ta 182.95	thallium 53 Tl 204.97
** Actinide series	thorium 90 Th 232.03	thorium 91 Th 232.03	polonium 84 Po 210.00
	protactinium 91 Pa 231.04		

↑ Manganese

K: 6539 eV $\text{K}\alpha_1$ (K-L3): 5900 eV
L₁: 769 eV $\text{K}\alpha_2$ (K-L2): 5889 eV
L₂: 650 eV $\text{K}\beta_{1,3}$ (K-M3/M2): 6492 eV
L₃: 639 eV $\text{K}\beta_5$ (K-M4,5): 6537 eV

K- or L-edges measured at a soft-X-ray beamline

K-edges measured at a hard-X-ray beamline

L-edges measured at a hard-X-ray beamline

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K- or L-edges measure
K-edges measured
L-edges measured

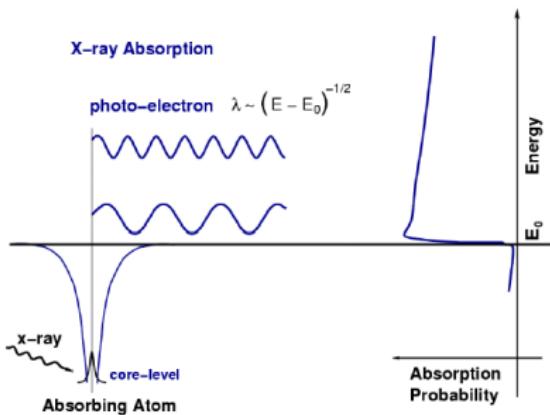
← Uranium

K: 115606 eV
L₁: 21757 eV
L₂: 20948 eV
L₃: **17166** eV

- La_1 ([L3-M5](#)), 13614 eV
- La_2 ([L3-M4](#)), 13438 eV
- Lb_2 ([L3-N4,5](#)), 16388 eV
- Lb_5 ([L3-O4,5](#)), 17063 eV
- Lb_6 ([L3-N1](#)): 15727 eV
- L_ℓ ([L3-M1](#)): 11618 eV

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.



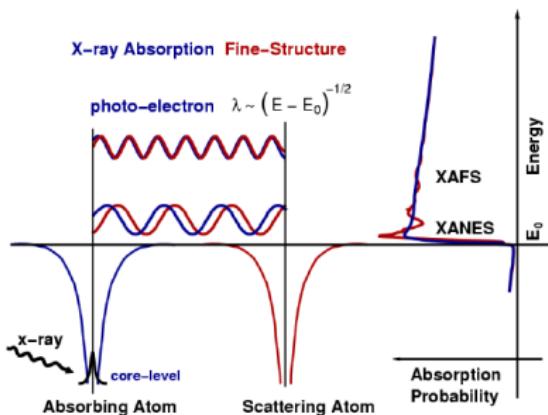
An empty final state is required.
**No available state,
no absorption!**

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.

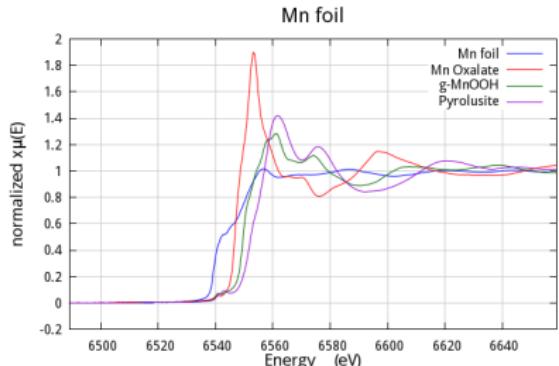


The scattering of the photo-electron wave function interferes with itself.

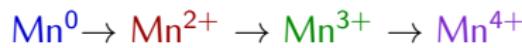
$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

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

XAS and Valence State



As the valence increases

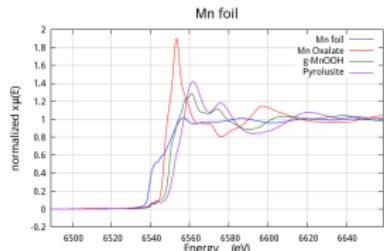


the edge position shifts to higher energy.

XAS is a direct measure of valence state

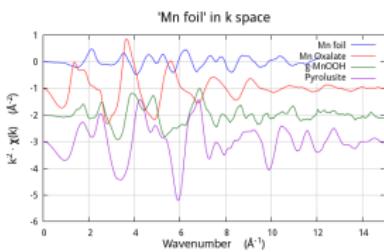
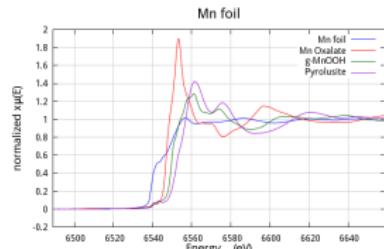
- Since each element has its own edge energy, an element's valence can be measured even in a heterogeneous sample
- Since x-rays are deeply penetrating into matter, samples often require only preparation
- No assumption of symmetry or periodicity is made, so the sample can be crystalline, amorphous, thin film, in solution, surface sorbed, . . . , whatever

XAS and Local Atomic Structure



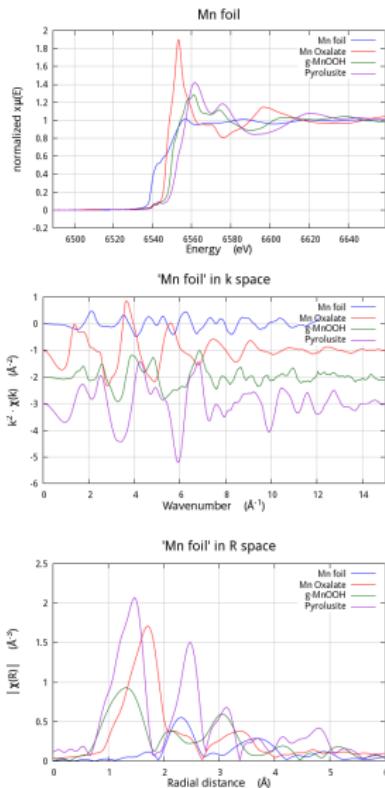
- The different Mn species display big differences in the fine structure beyond the edge as the valence increases (Mn^0 , Mn^{2+} , Mn^{3+} , Mn^{4+}). The white line and subsequent oscillations are quite different.
- The oscillatory portion of the spectrum can be isolated and ...
- ... Fourier transformed. This FT function can be interpreted to yield 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.

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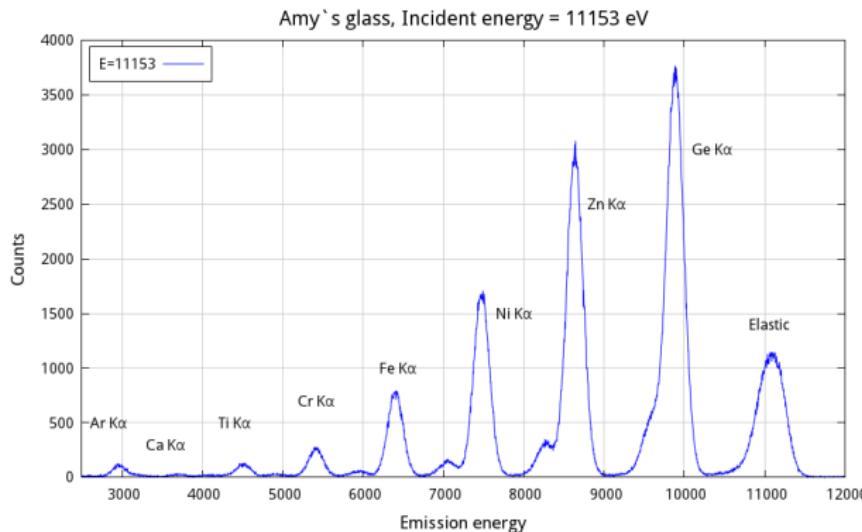
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Fluorescence from Many Elements

X-ray fluorescence is a **spectroscopy** in which the incident energy is fixed and the energy dependence of the secondary photons is measured.

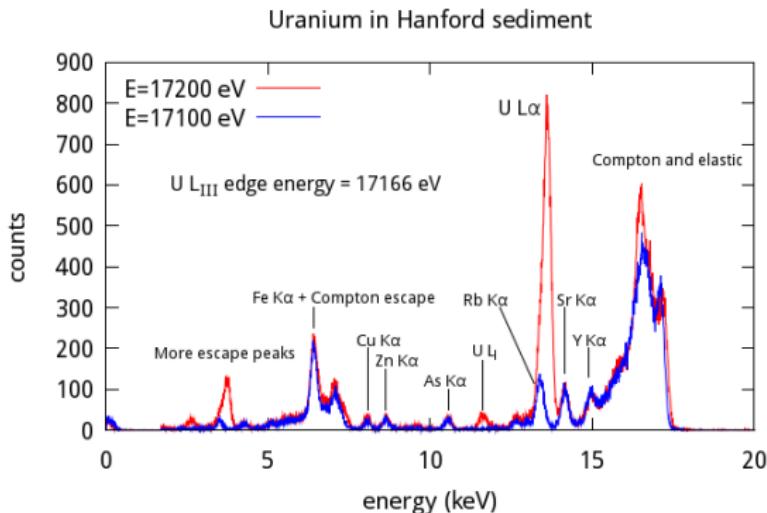
Every element with an edge **below** the incident energy will fluoresce.

Glass with every 2nd element Ca–Ge, incident energy = 11153 eV



Fluorescence from A Sediment Sample

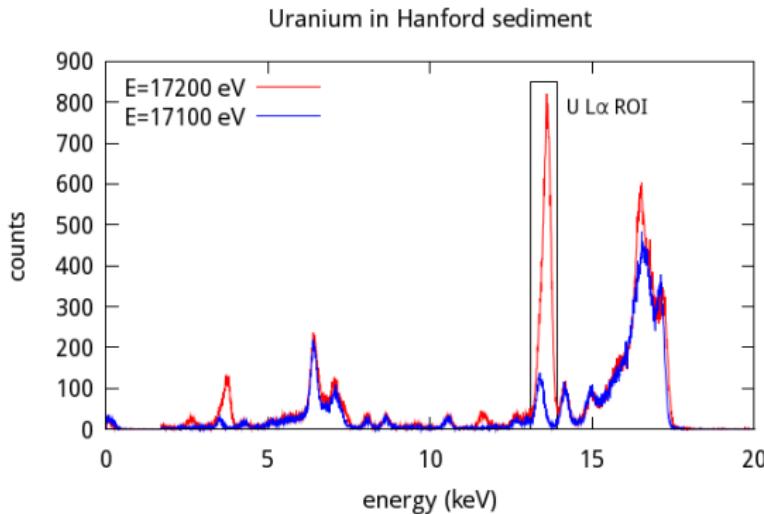
Here are the XRF spectra with incident beams **above** and **below** the U L_{III} edge for a sediment heavily contaminated with uranium.



When combined with a standard measured under identical conditions, element concentrations can be *quantified*.

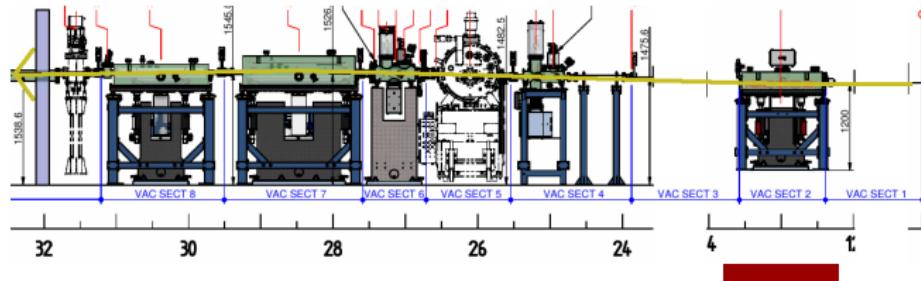
Using the Fluorescence Spectrum for XAS

We can place a **region of interest** (ROI) around the U L α peak and measure its variation as a function of incident energy.



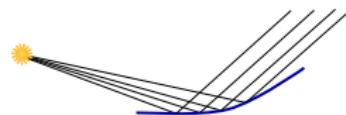
In this way, we measure signal only from the absorber and reject all other photons entering the detector.

Typical optics for an XAS beamline

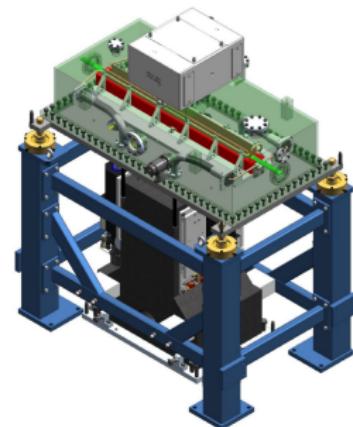


Collimating mirror

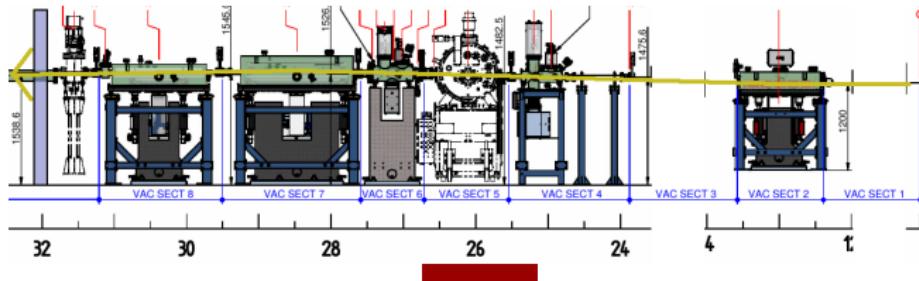
Makes the divergent rays from the source parallel, setting the beam size ($8\text{ mm} \times 1\text{ mm}$ at BMM)



Total external reflection from a paraboloid surface

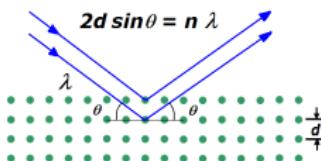


Typical optics for an XAS beamline



Monochromator

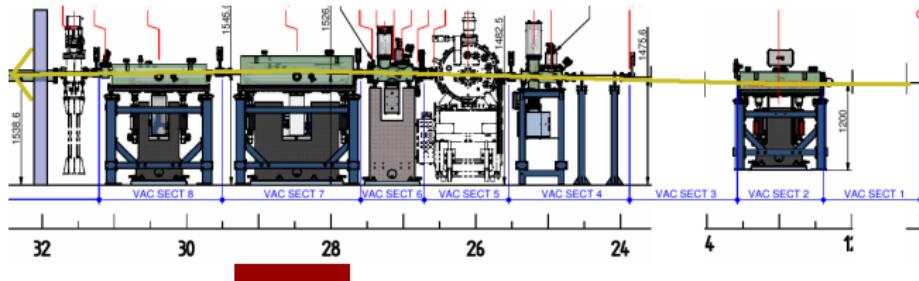
Bragg diffraction from a Si crystal to pass a narrow bandwidth from the pink beam



Change energy by changing angle

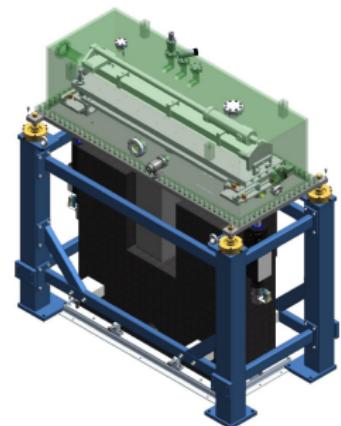


Typical optics for an XAS beamline



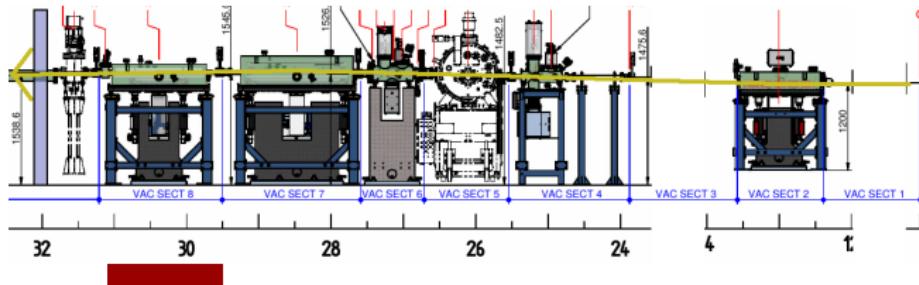
Focusing mirror

Total external reflection from a torroid surface, bent such that rays focus to a spot



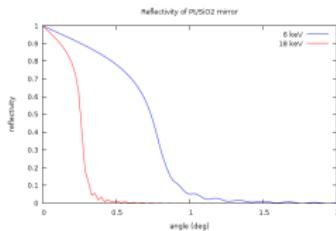
All instrumentation images are from FMB Oxford Beamlines Ltd.
Photo of mirror is from ESRF ID09B

Typical optics for an XAS beamline

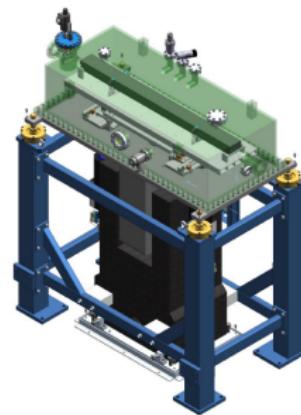


Harmonic rejection mirror

Flat mirror redirects beam from mono and M2

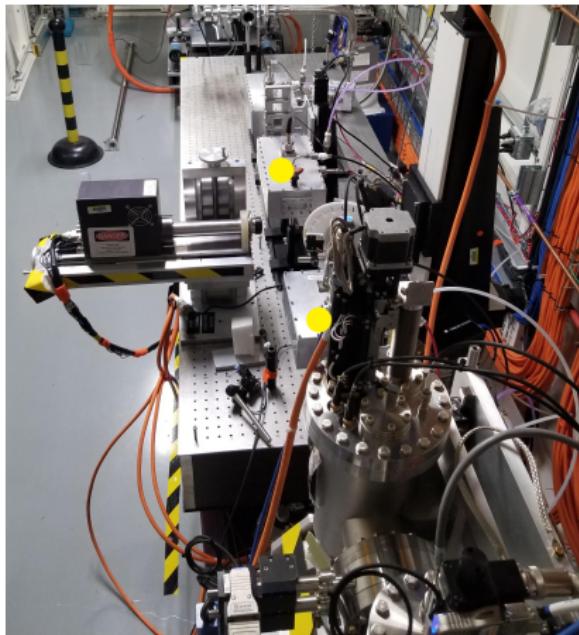


Choose an angle to pass the fundamental but absorb harmonics

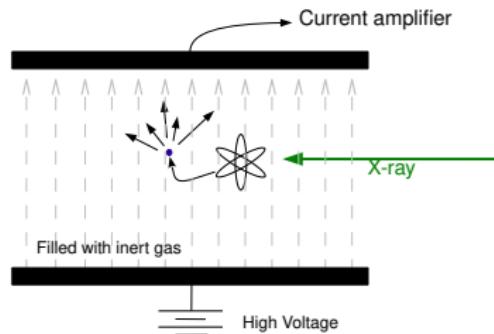


All instrumentation images are from FMB Oxford Beamlines Ltd.

A typical XAS hutch (BMM at NSLS-II)



Ionization chambers



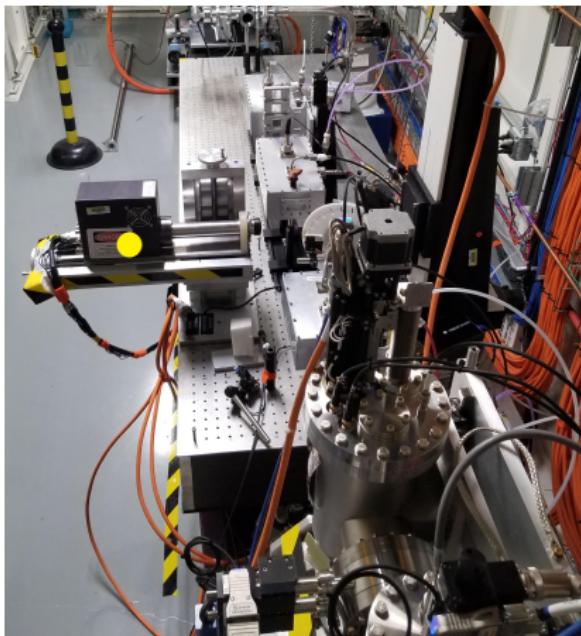
Gas-filled capacitors. Incoming photon ionizes a gas molecule. The electron cascade produces a measurable current.

Transmission XAS

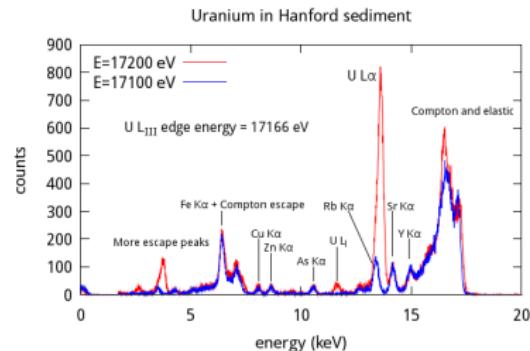
$$\mu(E) = \ln(I_0/I_t)$$

i.e. Beers' Law for X-rays

A typical XAS hutch (BMM at NSLS-II)



Energy discriminating fluorescence detector

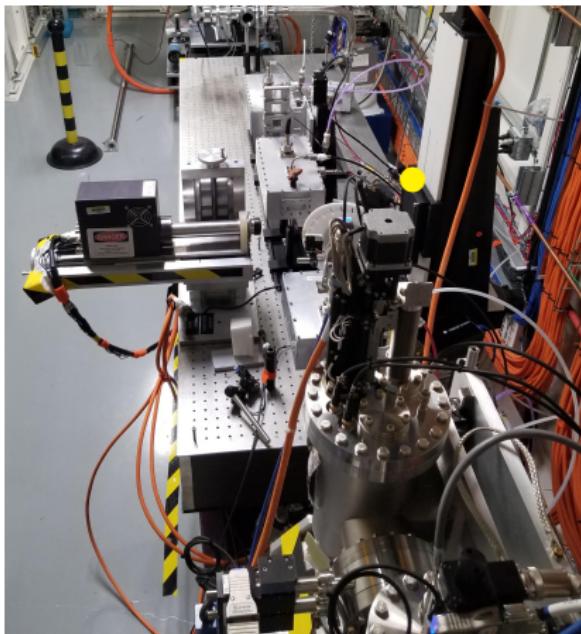


Silicon drift diode measures energy of each photon deposited

Fluorescence XAS

$$\mu(E) \propto I_f/I_0$$

A typical XAS hutch (BMM at NSLS-II)



Sample stage

Hard X-rays are deeply penetrating into matter, so the stage could be:

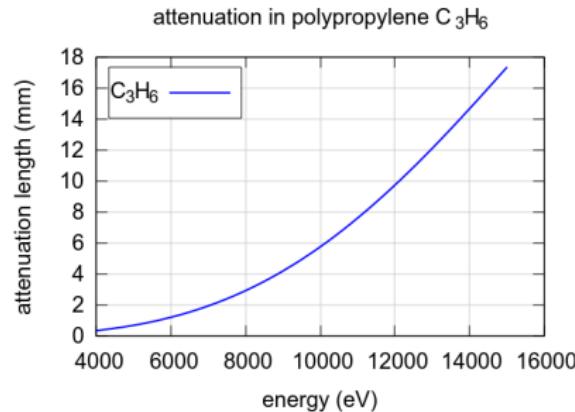
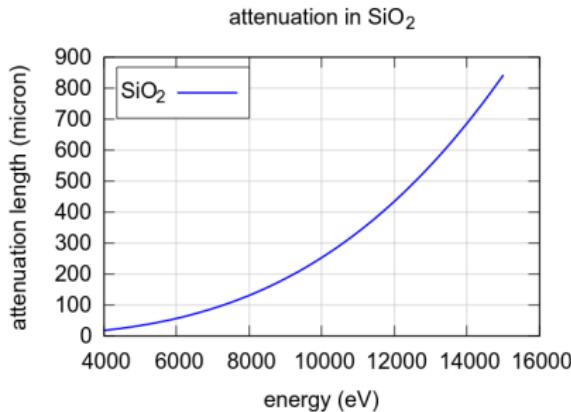
- Cryostat
- Furnace
- Pressure cell
- Electrochemistry cell
- Stop-flow cell
- Gas flow reactor
- Controlled atmosphere

etc. etc. etc.

Real samples under real conditions

What is meant by “deeply penetrating”?

The [Center for X-ray Optics](#) provides a tool for estimating the attenuation of X-rays as they pass through matter.
http://henke.lbl.gov/optical_constants/atten2.html



So, windows made of low-Z materials can be quite thick and still pass hard X-rays. This allows deployment of specialized sample environments for use in XAS experiments.

Acronyms

XANES X-ray Absorption Near-Edge Structure

NEXAFS Near-Edge X-ray Absorption Fine Structure

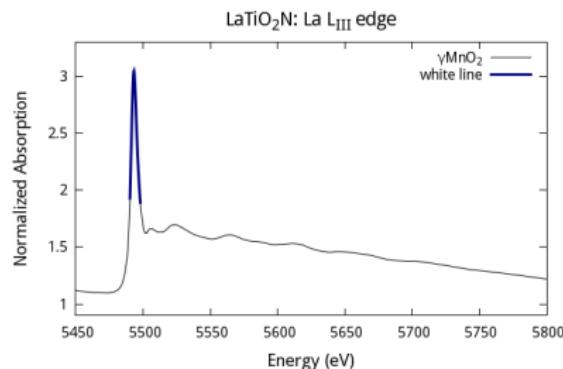
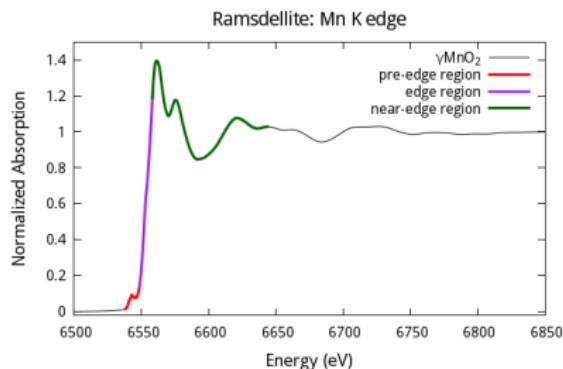
XANES and NEXAFS are exactly the same thing. Historically, the soft X-ray community says “NEXAFS” while the hard X-ray community says “XANES”.

Both acronyms refer to the portion of the XAS (X-ray Absorption Spectroscopy) measurement in the vicinity of the absorption edge.

The Extended X-ray Absorption Fine Structure is oscillatory data extending hundreds of volts above the edge.

Some vocabulary

Words commonly used to describe specific parts of the XANES spectrum.



pre-edge Small (or large, certainly meaningful!) features between the Fermi energy and the threshold

edge The main rising part of XAS spectrum

near-edge Characteristic features above the edge

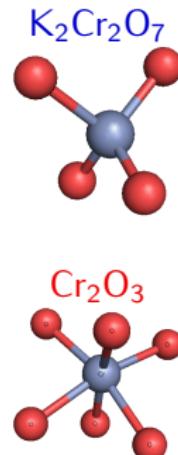
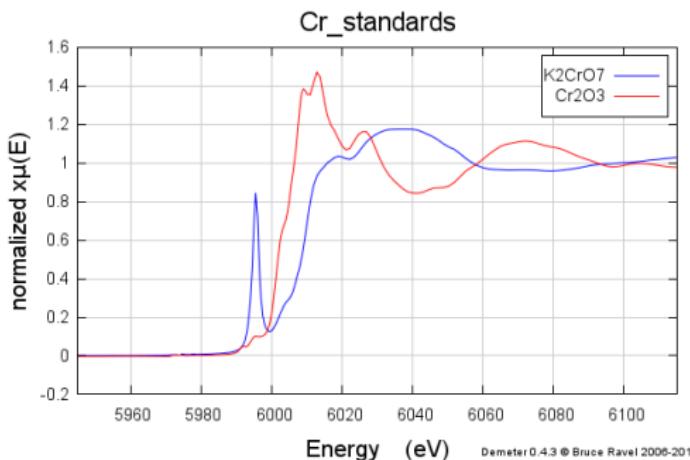
white line Large, prominent peak just above the edge, particularly in L or M edge spectra

Part 2

Understanding XANES

Speciation at a glance: Coordination

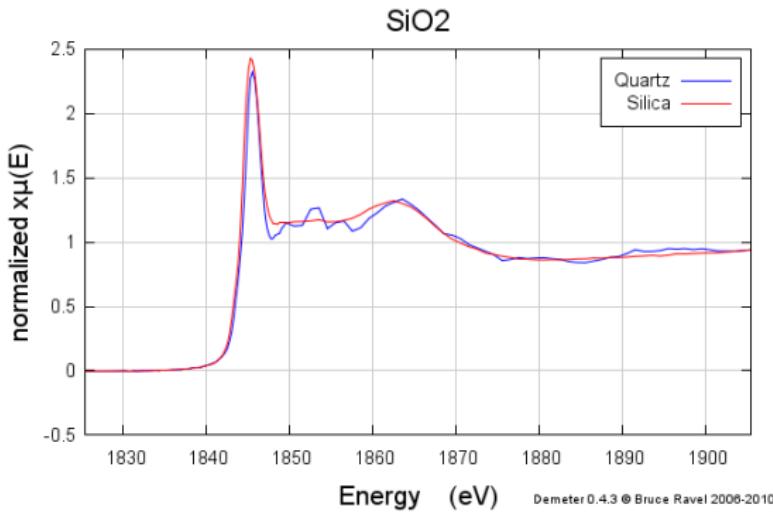
Here is Cr K edge data for tetragonally coordinated, hexavalent $K_2Cr_2O_7$ and hexagonally coordinated, trivalent Cr_2O_3 . Trivalent Cr is insoluble and non-toxic. Hexavalent Cr is readily soluble and highly toxic.



It is very easy to tell "good" Cr from "bad" Cr in a XANES measurement.

Speciation at a glance: Crystallinity

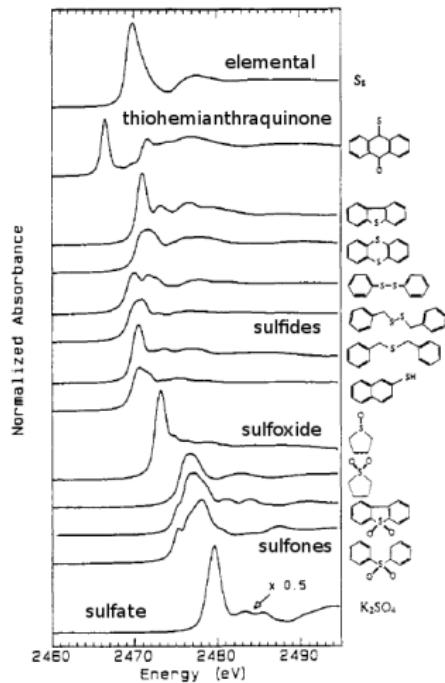
SiO_2 is found in two forms* under standard conditions: **crystalline (the mineral quartz)** and **amorphous (common glass)**.



Again, these are readily distinguished by a XANES measurement.

* Wikipedia identifies 14 other metastable, high-T, or high-P forms of SiO_2 .

Speciation at a glance: Oxidation



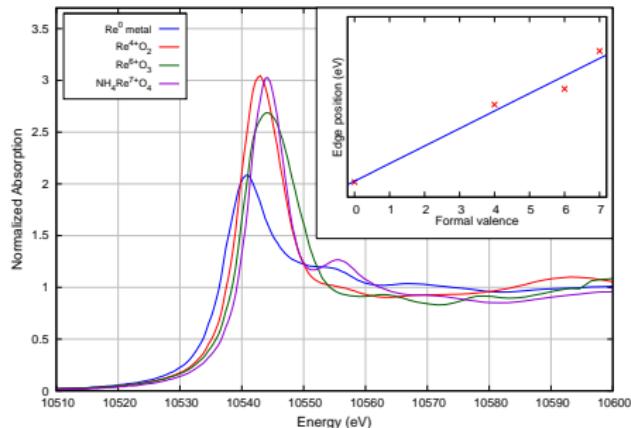
- There is an 11 eV shift from S^{2-} to S^{6+} with lots of variation among species.
- S speciation is of importance across a broad range of disciplines, including life science, catalysis, petroleum science, photovoltaics, environmental science and more.
- P and Cl are similarly rich in their XAS.

Sulfur K-edge x-ray absorption spectroscopy of petroleum asphaltenes and model compounds, G.N. George, M.L. Gorbaty, J. Am. Chem. Soc. (1989) 111:9,
3182 ↗ DOI: 10.1021/ja00191a012

Oxidation and edge position

There is a relationship between formal valence of a metal and the position of the edge in the XANES spectrum. Here is Re metal along with 4+, 6+, and 7+ oxides of Re.

The shift to higher energy is, to first order, a Coulomb effect. Less charge on the atom means less screening of the core.



Some more examples:

Mo S.P. Cramer et al. J. Am. Chem. Soc., **98**:5, pp 1287 (1976)

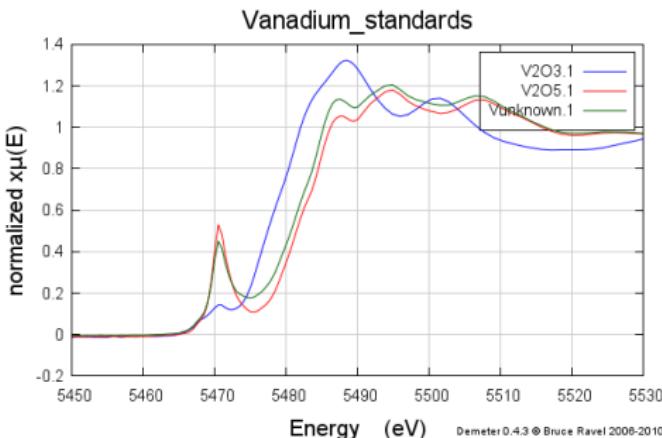
DOI: [10.1021/ja00421a053](https://doi.org/10.1021/ja00421a053)

V J. Wong et al. Phys. Rev. B**30**, 5596–5610 (1984) DOI: [10.1103/PhysRevB.30.5596](https://doi.org/10.1103/PhysRevB.30.5596)

Simultaneous XAFS measurements of multiple samples, B. Ravel, C. Scorzato, D.P. Siddons, S.D. Kelly and S.R. Bare, J. Synchrotron Rad. (2010) 17, 380–385
DOI: [10.1107/S0909049510006230](https://doi.org/10.1107/S0909049510006230)

Mixed phases

Here we see trivalent V_2O_3 , pentavalent V_2O_5 and an unknown Vanadium compound plotted together.



Like in the Cr example, we see a distinct difference between 6-coordinated and 4-coordinated V.

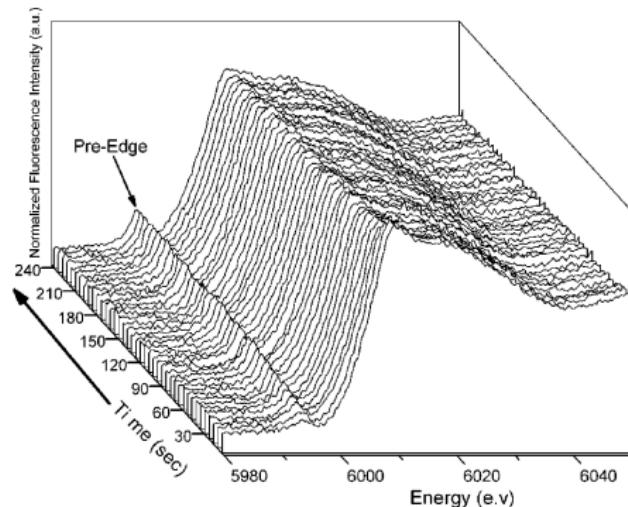
Our unknown is partially reduced, as can be seen by the reduction in pre-edge peak and the left-ward shift of the main edge.

Later we will discuss ways of determining the content of the unknown.

Evolution of redox state

The edge features are often large enough that their evolution can be measured in an *in situ* experiment.

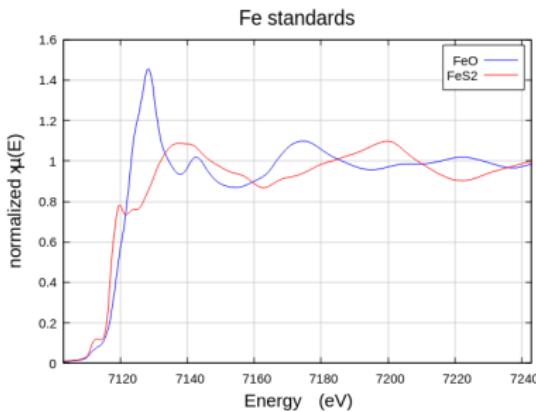
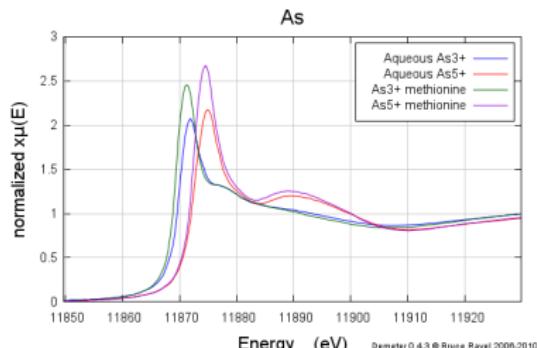
Here we see the kinetics of $\text{Cr}^{III} \rightarrow \text{Cr}^{VI}$ oxidation by Mn oxide over the course of four minutes of reaction time. Each scan was measured in 3 second.



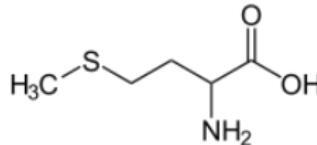
The *in situ* experiment could involve a chemical reaction, a change in temperature, electrochemical cycling, and so on.

Kinetics of Chromium(III) Oxidation by Manganese(IV) Oxides Using Quick Scanning X-ray Absorption Fine Structure Spectroscopy (Q-XAFS), G. Landrot, M. Ginder-Vogel, and D.L. Sparks, Environ. Sci. Technol., (2010) 44:1, pp 143-149
DOI: 10.1021/es901759w

Ligands



We see a significant edge shift between aqueous As³⁺ and aqueous As⁵⁺, as we expect. Note that the As³⁺ and As⁵⁺ methionine solutions are similar, but shifted to lower energy.



The same shift is seen between divalent wüstite (FeO) and divalent pyrite (FeS₂).

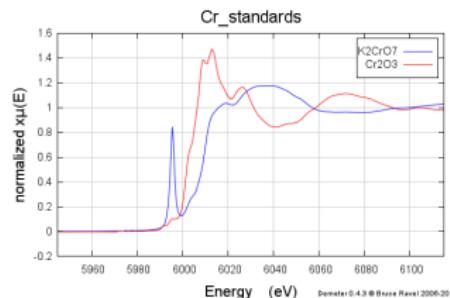
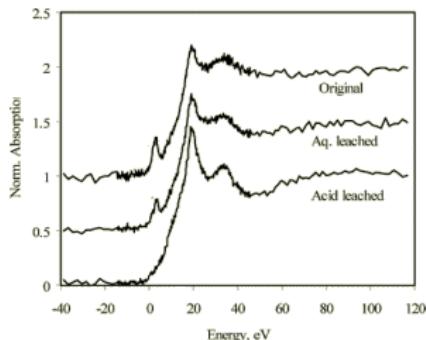
Fingerprinting

Fingerprint, tr.v.

To identify by means of a distinctive mark or characteristic.

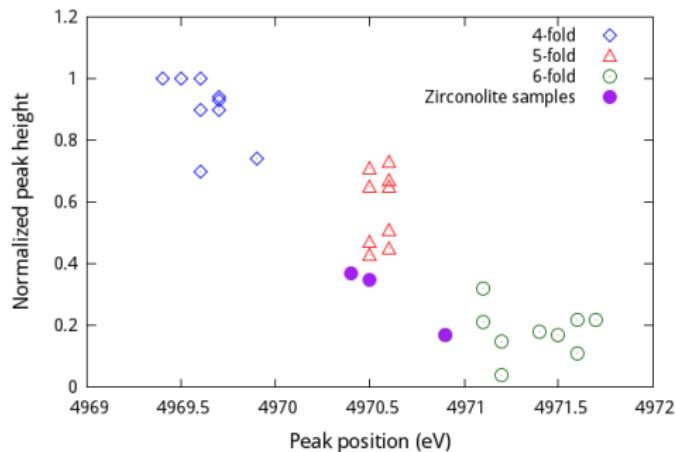
One of the most powerful uses of XANES data is to simply identify what is in front of the beam.

Looking back at the Cr^{III}/Cr^{VI} example, what might you say about the valence of the chromium contained in coal combustion residue?



Categorizing spectra

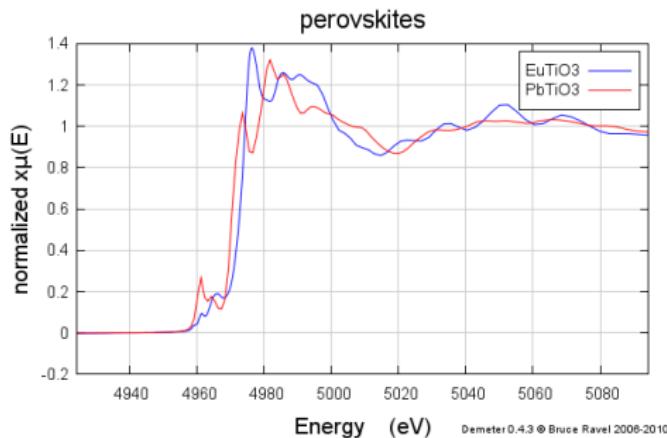
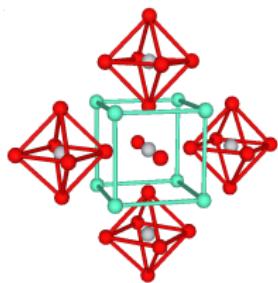
In a study of Ti-containing standard materials, the different coordination environments were found to aggregate when plotting pre-edge peak height v. peak position.



Here we see the data from the reference below along with Ti K-edge data from various Zirconolite ($\text{CaZrTi}_2\text{O}_7$) samples.

XANES and disorder

The details of the XANES can often give information about structural disorder about the absorbing atom.



EuTiO_3 is a true cubic perovskite. PbTiO_3 is a tetragonally distorted perovskite with substantial disorder in the oxygen octahedron. Consequently, the pre-edge peak is much larger for PbTiO_3 .

Why are local disorder and the pre-edge peak related?

- XAS is a dipole transition. The photoelectron changes angular momentum by 1: $\ell \pm 1$.
- For a K-edge spectrum, the initial state is s : $\ell = 0$. Thus the final state must be $\ell = 1$.
- Ti has a filled p shell but a completely empty d shell.
- With centro-symmetry, as in a true perovskite, the p and d states cannot hybridize. Broken symmetry leads to mixing of p and d states around the Fermi level.
- Disorder-driven admixture of d character results in an enhanced pre-edge peak.

Analysis

There are a number of ways to get quantitative results from XANES spectra. Here's an incomplete list:

Linear Combination Fitting

Interpret data by comparison with standards

Peak Fitting

Fit peak-like and step-like line-shapes to the XANES data

Principle Components Analysis

Decompose an ensemble of data into a mathematical basis

Difference Spectra

Subtract one normalized spectrum from another

LCF

The working assumption of LCF

The spectrum from an unknown sample can be understood as a linear superposition of the spectra of two or more known samples.

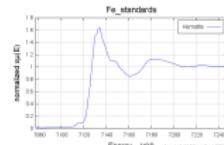
That is:



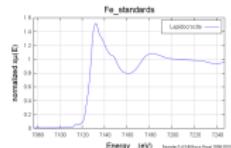
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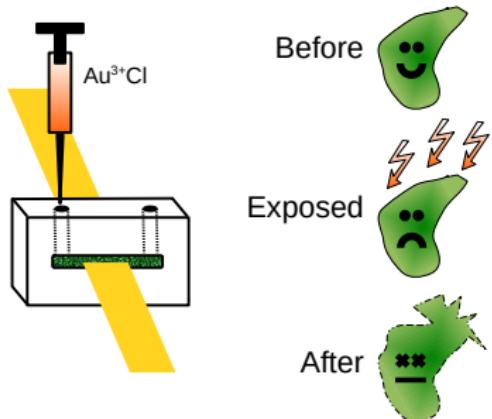


+



Economic geology (I)

One way that gold deposits form is by having Au chloride fluids rise from the deep earth, wash over cyanobacteria colonies, and reduce to metallic gold.



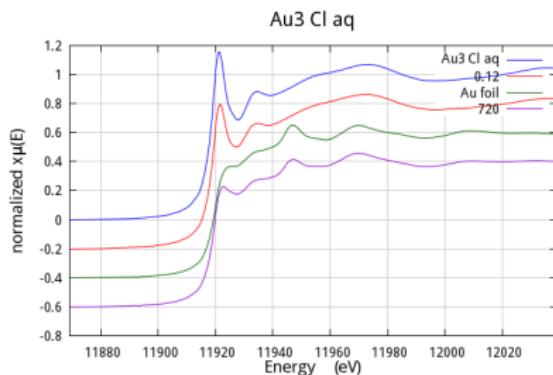
We simulated this process at the beamline by exposing cyanobacteria to an Au^{3+} solution and “watching” the evolution of the Au XAS from Au^{3+} to Au^0 .

Questions

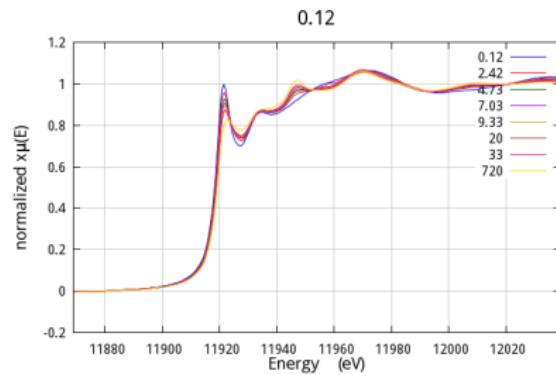
- What is the rate constant?
- Is there an intermediate species?

Economic geology (II)

We see that **7 minutes** after injection, the data strongly resemble the Au^{3+}Cl . After **one week**, the data resemble **Au metal**.

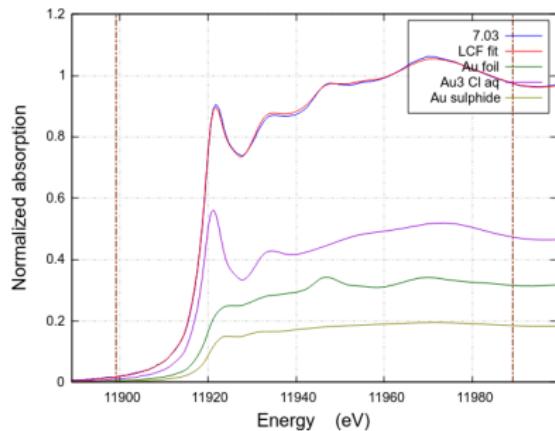


Over the course of the time series, the white line ~ 11921 shrinks while the bump ~ 11945 grows, suggesting the reduction to Au metal.

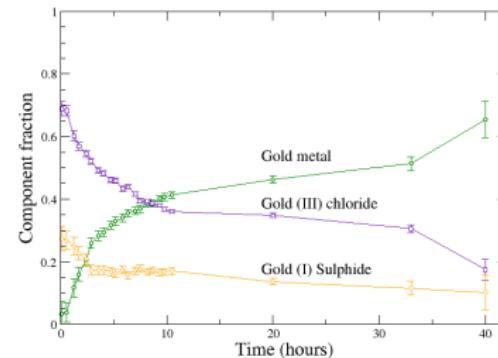


Economic geology (III)

We can analyze these data as a linear combination of species, including Au^{3+}Cl , Au metal, and Au^{1+} sulfide.



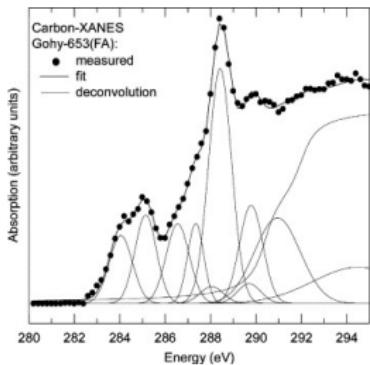
We can plot out the contributions from these species as a function of time to get a sense of reaction rates.



Peak fitting

The working assumption of peak fitting

A spectrum can be meaningfully deconstructed into a set of step-like (atan or erfc) and peak (Gaussian, Lorentzian, Voight) functions.

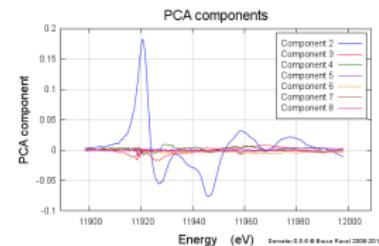
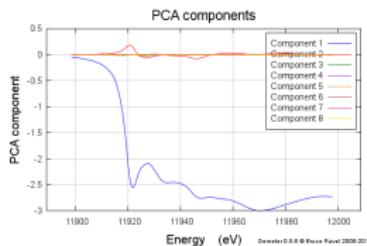
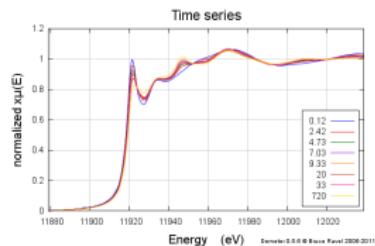


In this case, various Gaussians are interpreted as the main $1s-\pi^*$ or Rydberg/mixed valence transitions and two higher energy ($1s-2\pi^*$) transition in the C K-edge XANES of a sediment.

This sort of analysis is most meaningful when performed across an ensemble of related data. The drawback is that the physical significance of the line-shapes is sketchy, at best.

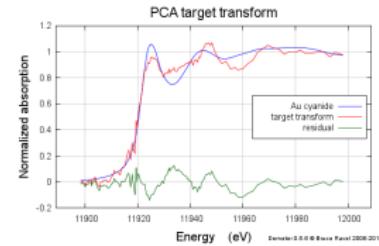
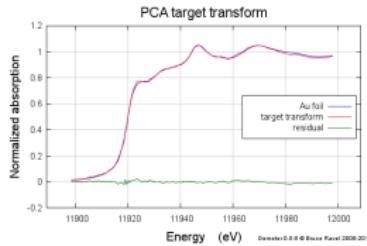
XANES: Principle Components Analysis

PCA is a bit of linear algebra which breaks down an ensemble of related data into abstract components.



The components can then be used to try to construct a standard as a test to see whether that standard is present in the ensemble.

The number of species represented in the ensemble is related to the number of statistically significant components.



S.R. Wasserman, J. Phys. IV France (1997) C2-203-C2-205; [DOI: 10.1051/jp4/1997163](https://doi.org/10.1051/jp4/1997163)

S.R. Wasserman et al., J. Synchrotron Rad. (1999) 6, 284-286; [DOI: 10.1107/S0909049599000965](https://doi.org/10.1107/S0909049599000965)

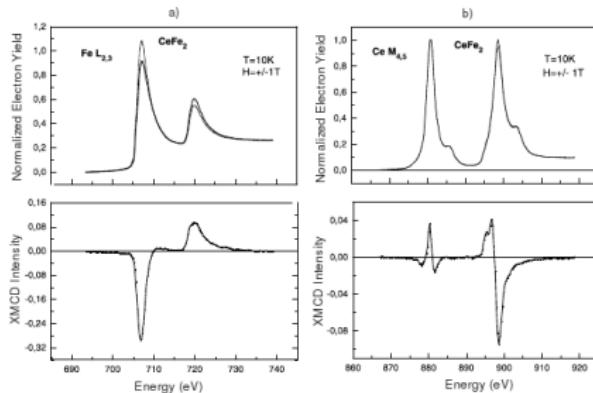
+ references therein

Difference Spectra

Difference spectra

Subtract one spectrum from another.

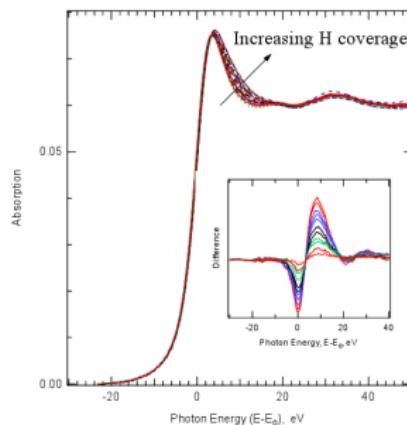
The most common use is for X-ray Magnetic Circular Dichroism (XMCD)



The areas under the difference spectra tell you about moment and magnetic ordering.

X-ray magnetic circular dichroism study on CeFe₂, A. Delobbe, et al., Europhys. Lett. 43 320 (1998), DOI: 10.1209/epl/i1998-00359-2
Pt data courtesy of Simon Bare

Difference spectra can also be used to highlight a subtle change in a data sequence.



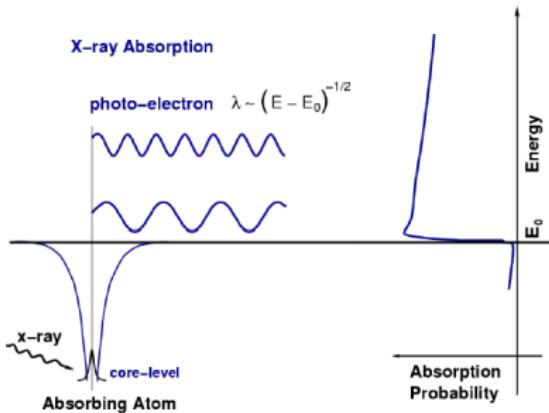
Here, hydrogenation of the Pt nanoparticles alters the Pt DOS

Part 3

Understanding EXAFS

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.



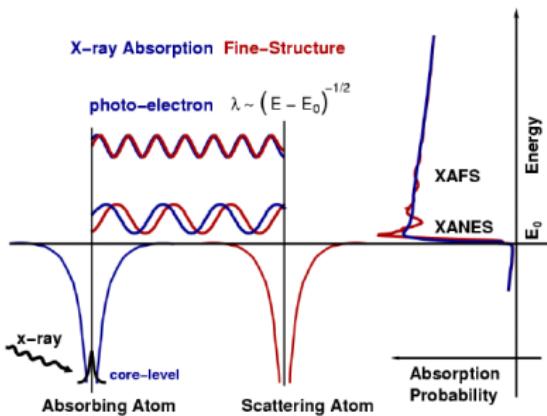
An empty final state is required.
**No available state,
no absorption!**

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 $\mu(E)$.

The EXAFS equation

For each kind of path, we evaluate the EXAFS equation:

$$\chi(k, \Gamma) = \frac{(N_\Gamma S_0^2) F_\Gamma(k) e^{-2\sigma_\Gamma^2 k^2} e^{-2R_\Gamma/\lambda(k)}}{2 k R_\Gamma^2} \sin(2kR_\Gamma + \Phi_\Gamma(k)) \quad (1)$$

$$\chi_{\text{theory}}(k) = \sum_{\Gamma} \chi(k, \Gamma) \quad (2)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \quad (3)$$

$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$

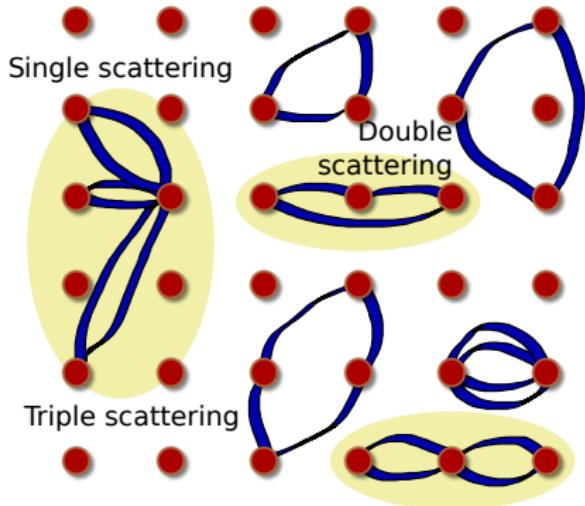
The terms in blue come from theory. (I use a thing called **FEFF**).

FEFF treats SS and MS paths equivalently. F_Γ and ϕ_Γ are the effective scattering amplitude and phase shift for the path.

The strategy of EXAFS analysis

In **FEFFIT** the terms in red are not themselves the fitting parameters. They are written in terms of the actual fitting parameters.

Real space multiple scattering in pictures



Here are some examples (in two dimensions) of single, double, and triple scattering paths.

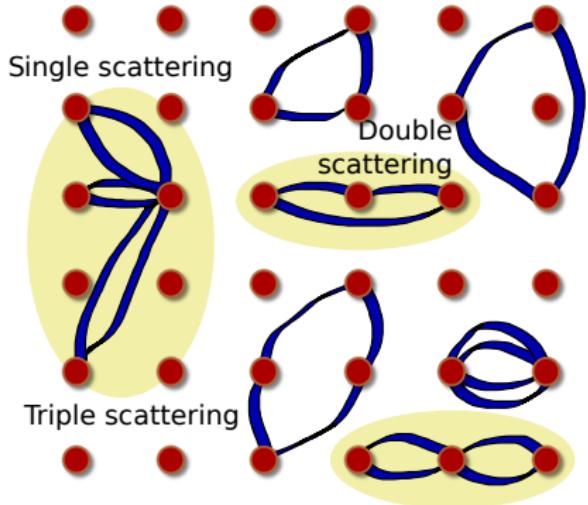
For SS, FEFF computes the three SS paths shown and all others (up to some maximum length).

SS and *collinear* MS paths tend to be the dominant contributions to the EXAFS.

The trick to EXAFS analysis

Somehow evaluate each path and choose which ones to include in a fit.

Real space multiple scattering in pictures



Here are some examples (in two dimensions) of single, double, and triple scattering paths.

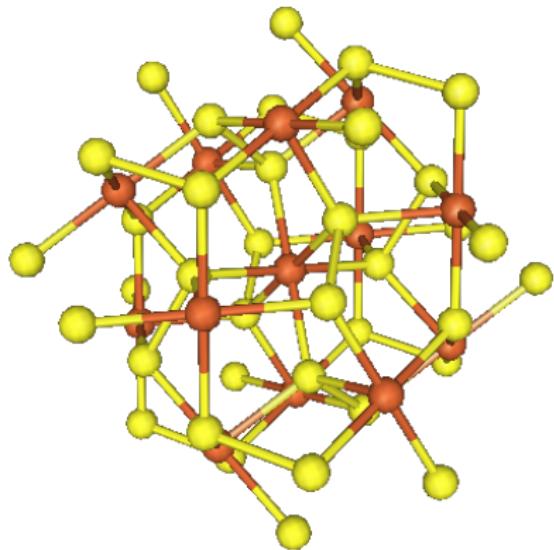
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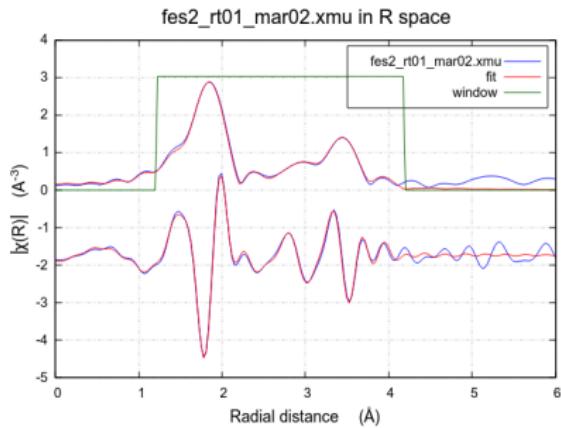
FeS₂ structure



Somehow add up the contributions from each of the scatterers **and** from all the MS paths involving those scatterers.

The **Fe atom** is surrounded by an octahedron of **S atoms**

- 6 **S nearest neighbors** at 2.257 Å
- 6 **S next nearest neighbors** at 3.445 Å
- 2 **S scatterers** at 3.594 Å
- 12 **Fe scatterers** at 4.167 Å



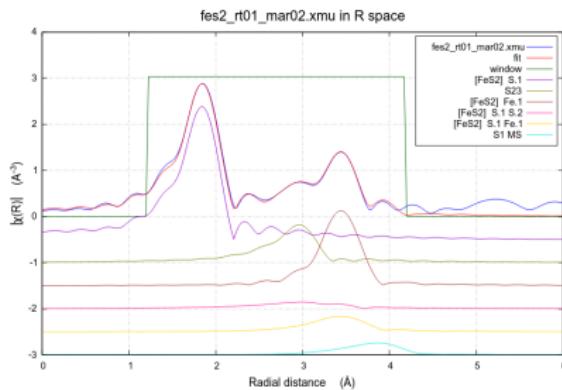
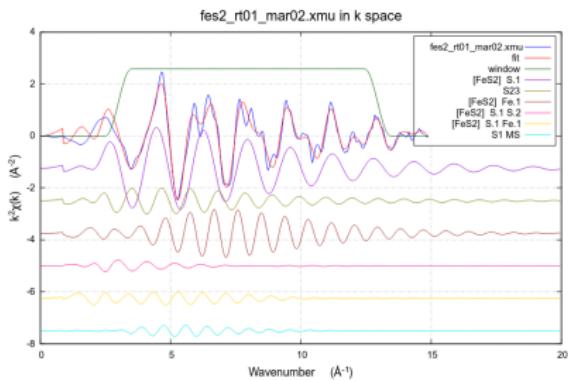
Path expansion

$$\chi(k, \Gamma) = \frac{(N_r S_0^2) F_\Gamma(k) e^{-2\sigma_\Gamma^2 k^2} e^{-2R_\Gamma/\lambda(k)}}{2 k R_\Gamma^2} \sin(2kR_\Gamma + \Phi_\Gamma(k)) \quad (1)$$

$$\chi_{\text{theory}}(k) = \sum_{\Gamma} \chi(k, \Gamma) \quad (2)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \quad (3)$$

$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$



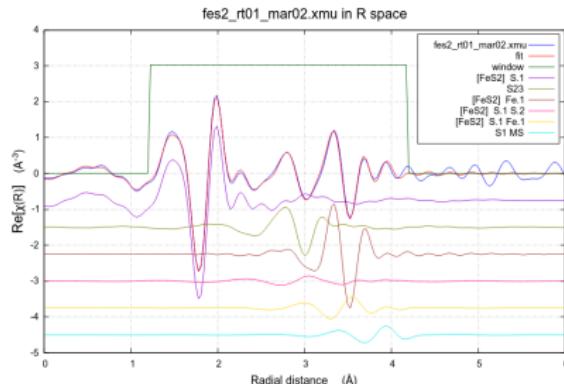
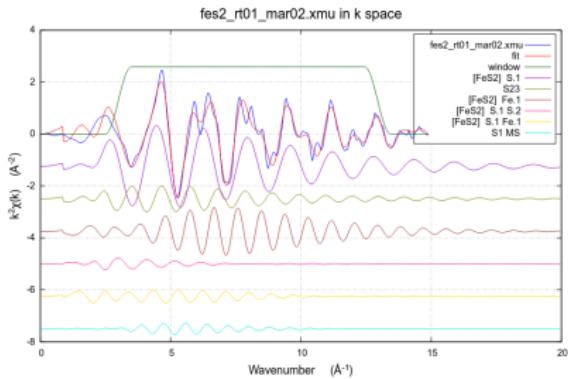
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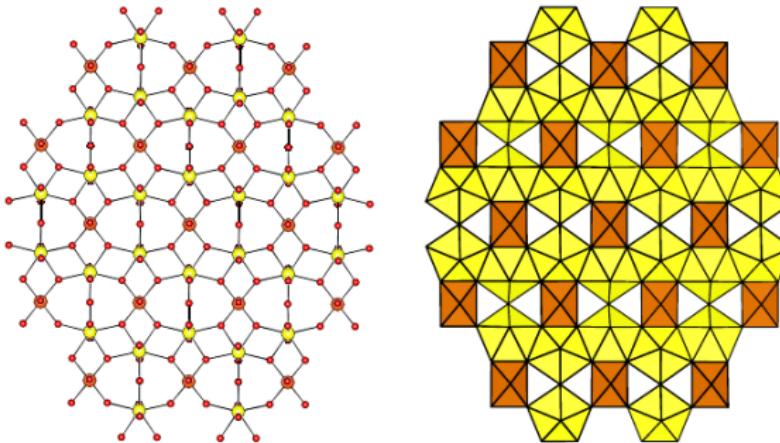
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$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$



Minerology (I)

A deep understanding of the nuclear fuel cycle requires study of “exotic” pentavalent uranium minerals that can form under specific mine or storage facility conditions. One such mineral, $\text{U}^{\text{V}}(\text{H}_2\text{O})_2(\text{U}^{\text{VI}}\text{O}_2)_2\text{O}_4(\text{OH}) + 4 \cdot \text{H}_2\text{O}$, has recently been synthesized.



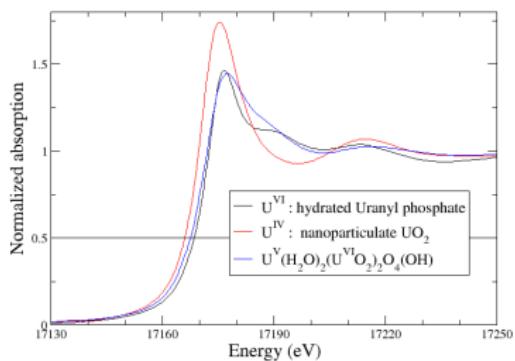
XRD is an indirect measure of valence — XAS is a direct measure!

N. Belai et al., *Pentavalent Uranium Oxide via Reduction of $[\text{UO}_2]^{2+}$ Under Hydrothermal Reaction Conditions*, Inorg. Chem., 2008, 47 (21), pp 10135–10140, DOI: 10.1021/ic801534m

Minerology (II)



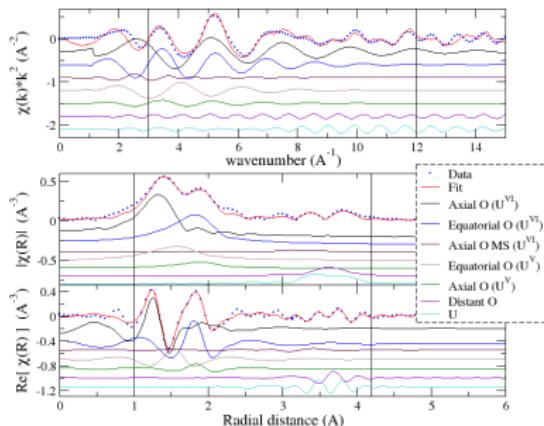
XANES data



We see evidence of U^{V} by the intermediate edge position between our U^{IV} and U^{VI} standards.

N. Belai et al., *Pentavalent Uranium Oxide via Reduction of $[\text{UO}_2]^{2+}$ Under Hydrothermal Reaction Conditions*, Inorg. Chem., 2008, 47 (21), pp 10135–10140, DOI: 10.1021/ic801534m

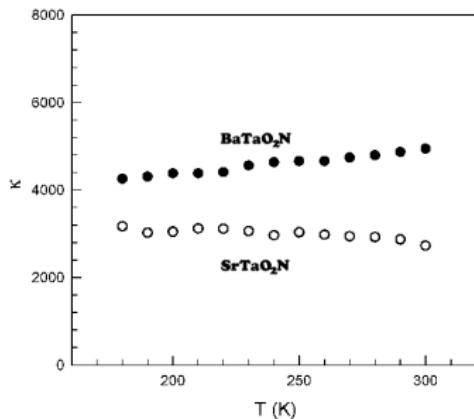
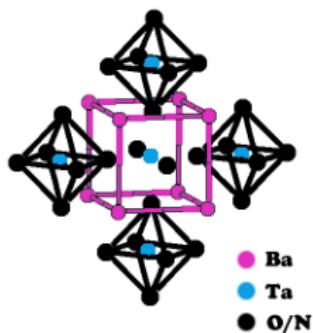
EXAFS analysis



The crystal structure refined from the XRD is consistent with the EXAFS data.

Dielectric materials (I)

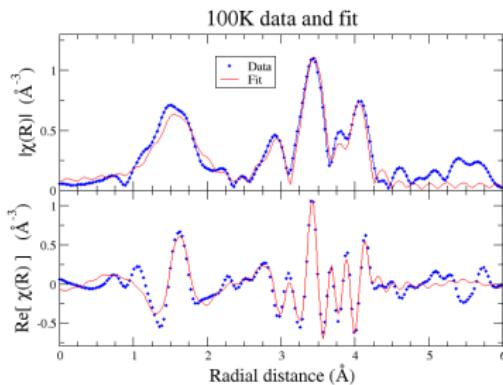
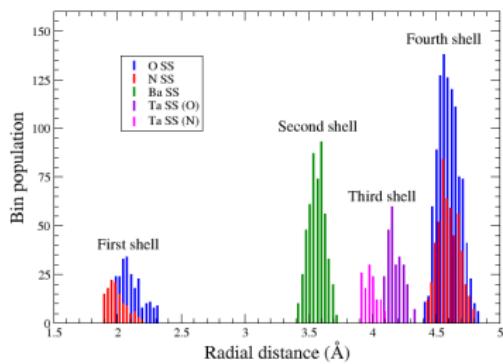
Tantalum oxynitrides are a class of dielectric materials with high K which is tunable by selection of the A cation. By mixing A cations, a temperature-constant dielectric is possible.



First principles DFT on BaTaO₂N suggests that the different ionic radii of O and N introduce substantial disorder around the Ta atom.

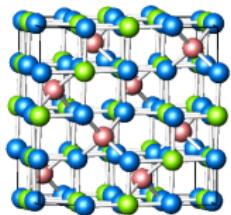
Dielectric materials (II)

The DFT results in a rather complex coordination environment about the Ta atom — much more complex than the simple perovskite structure.

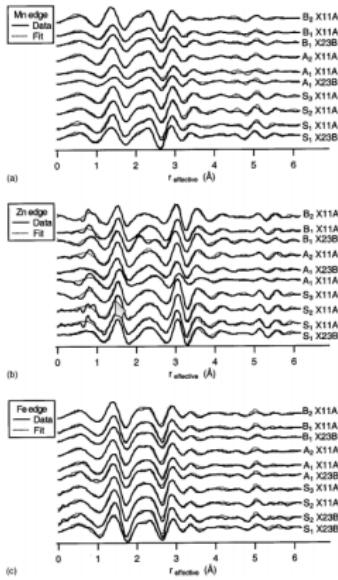


With some effort, this complexity can be incorporated into the data analysis. The EXAFS data are shown to be (mostly) consistent with the DFT results.

EXAFS analysis can be quite elaborate...



Oxygen
Octahedral site
Tetrahedral site



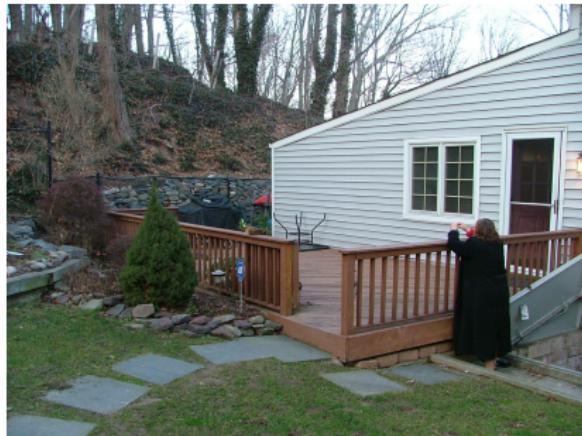
- Manganese zinc ferrite nanoparticles
- Each element can occupy each either metal site
- Oxygen vacancies can exist
- Data collected at 3 edges and on various sample preparations
- A fitting model was created using all the data simultaneously and considering occupancies of each metal on each site, oxygen vacancy, and nanoparticle undercoordination

Part 4

A real-world example

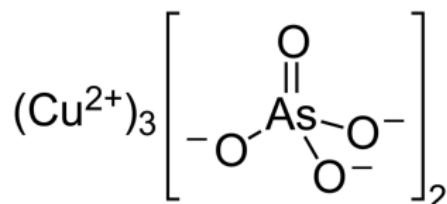
My vegetable garden

When I bought my house, there was a wooden deck off the dining room. I replaced this with a paving stone patio and converted the adjacent plot of ground into a vegetable garden.



Wood preservative

The wood used to make the deck was treated with the wood preservative chromated copper arsenate (CCA), which is chromium-bearing analogue of copper orthoarsenate, $\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$.

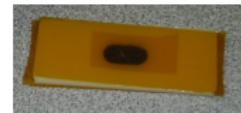


CCA-treated wood is known to leach all three elements into surrounding soils. I had some questions:

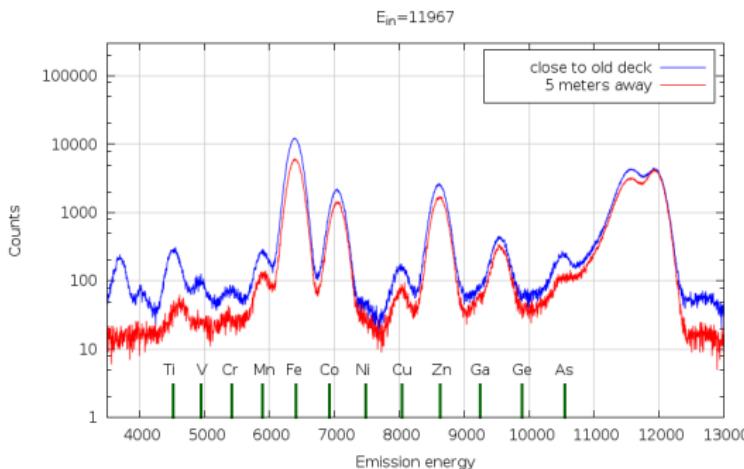
- ① How much As is in the soil? Is it higher near the patio than elsewhere in the garden? (Use XRF)
- ② What chemical species is the As in the soil? (Use XAS)

XRF spectra

I took soil samples from a few centimeters below the surface from a spot adjacent to the old deck and from a spot 5 meters away and slightly uphill.



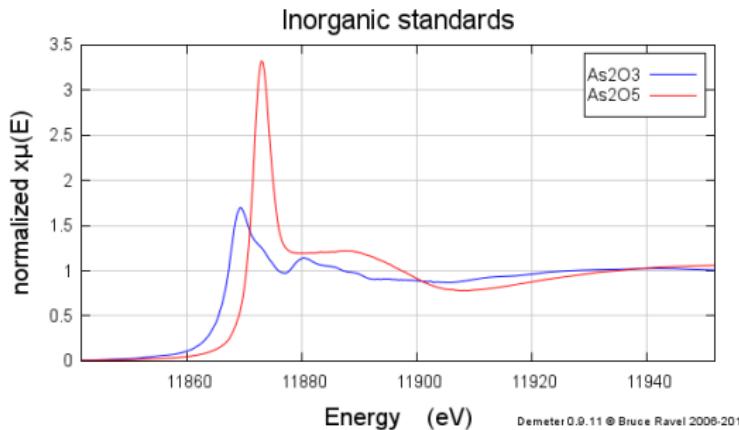
Here are the XRF spectra from those two spots:



There is a clear enhancement of both As and Cr in the soil adjacent to the old deck. The As is enhanced roughly two-fold.

As standards

As a point of reference, here are the XAS spectra from two inorganic As standards, $\text{As}_2^{3+}\text{O}_3$ and $\text{As}_2^{5+}\text{O}_5$.



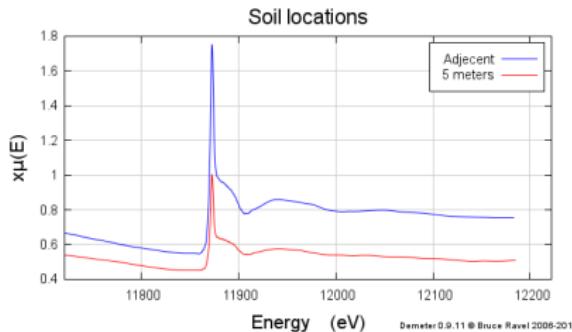
Note that the edge of As^{5+} standard is shifted substantially to higher energy and that the first peak is much enhanced.

As^{5+} is water soluble, thus more mobile than As^{3+} .

Also As^{5+} is quite toxic.

XAS from the soil samples

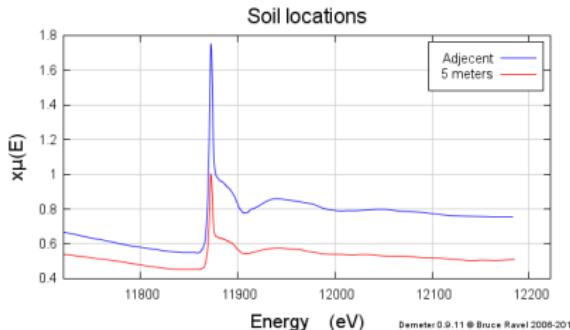
Here are the raw $\mu(E)$ data from the two soil locations. Sure enough, the signal from the site adjacent to the old deck is enhanced by about a factor of 2.



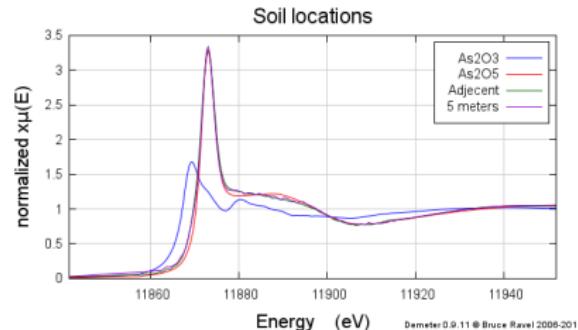
Should I be worried about eating produce from my garden?

XAS from the soil samples

Here are the raw $\mu(E)$ data from the two soil locations. Sure enough, the signal from the site adjacent to the old deck is enhanced by about a factor of 2.



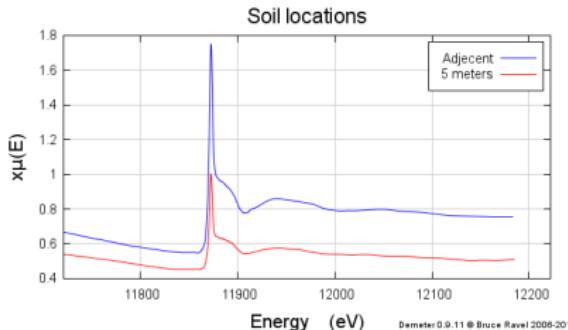
Here are the normalized data compared to standards. The As is slightly reduced, but predominantly As^{5+} . As in soil is well known to bind to soil particles as As^{5+} .



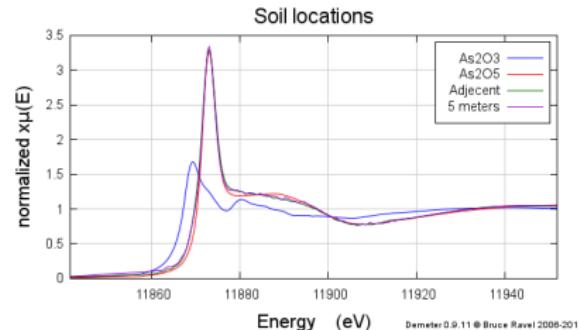
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XAS from the soil samples

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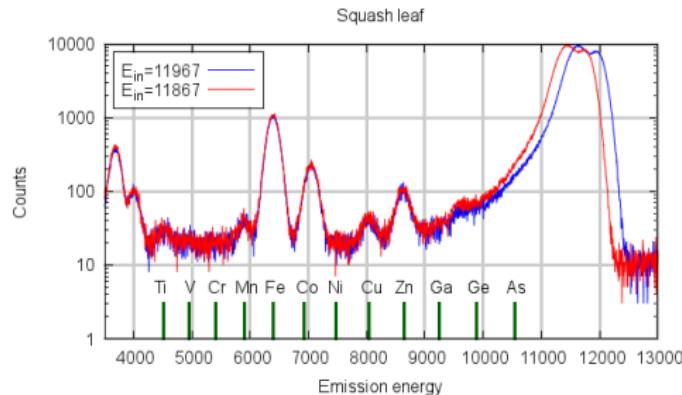
Here are the normalized data compared to standards. The As is slightly reduced, but predominantly As^{5+} . As in soil is well known to bind to soil particles as As^{5+} .



Should I be worried about eating produce from my garden?

XRF spectra from plant leaves

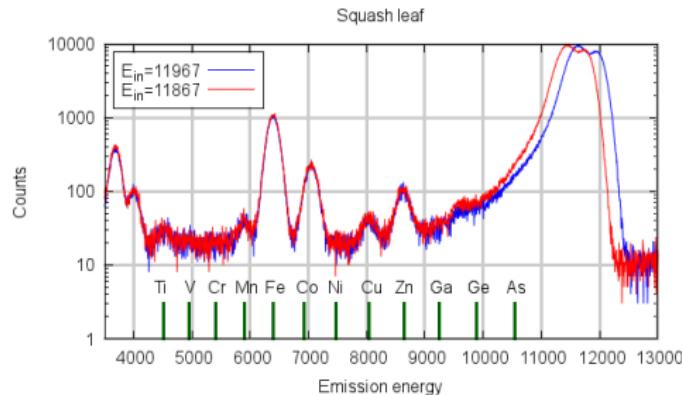
Here are XRF spectra from the leaf of a squash plant growing in the soil adjacent to the old deck.



Although toxic As^{5+} is present in the soil in elevated quantities, very little is taken up by the plants growing that soil.

XRF spectra from plant leaves

Here are XRF spectra from the leaf of a squash plant growing in the soil adjacent to the old deck.



Although toxic As^{5+} is present in the soil in elevated quantities, very little is taken up by the plants growing that soil.



The squash were delicious!

More information

About NSLS-II

↪ <http://www.bnl.gov/nsls2>

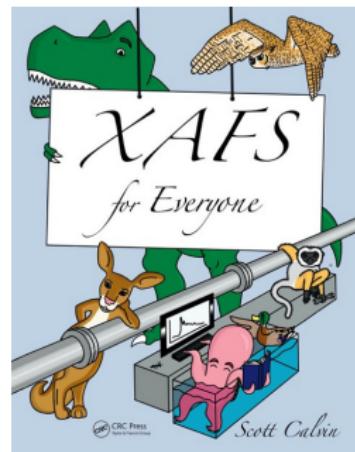
About synchrotron science

↪ <http://www.lightsources.org/>

About X-ray Absorption Spectroscopy

↪ <http://www.xrayabsorption.org/>

↪ XAFS for Everyone by Scott Calvin



Information about XAS

☞ <http://xrayabsorption.org/Tutorials>

The screenshot shows a Mozilla Firefox browser window displaying the IXAS (The International X-ray Absorption Society) website. The URL in the address bar is <https://xrayabsorption.org/tutorials/>. The page title is "IXAS: The International X-ray Absorption Society". The main navigation menu includes "IXAS", "Conferences", "Resources", "Data & Software", and "People". A "Tutorials" section is highlighted. Below it, a sub-section titled "Tutorials" contains text about X-ray absorption and related spectroscopies, mentioning external websites like <https://xafs.xrayabsorption.org/tutorials.html>. It also notes that many tutorial resources are available online. A list of external links follows, including "XAFS Tutorials" from Grant Bunker, "XAS Overview" from Iztok Arcon, "X-ray Spectroscopy mini Courses" from Jim Penner-Hahn, and "XAS Education" from Bruce Ravel. Another section lists "Some slides from oral presentations hosted here (PDF format except where noted)" with links to Matt Newville's XAFS overview, XAFS Fundamentals, EXAFS Processing by Shelly Kelly, and EXAFS Data Analysis by Shelly Kelly. To the right, there is a "NEWS AND EVENTS" calendar for May 2020, a "RELATED SITES" section with links to XAFS2021 Conference, IUCr XAFS Commission, and the IXAS website, and a "SITE ACCESS" sidebar with links to Log In, Entries feed, Comments feed, and WordPress.org.

Tutorials - IXAS: The International X-ray Absorption Society - Mozilla Firefox

IXAS: The International X-ray Absorption Society

Search

Tutorials

Tutorials on X-ray absorption and related spectroscopies. See also <https://xafs.xrayabsorption.org/tutorials.html>.

There are many tutorial resources available on-line. Many of these may be from Training Workshops and Short Courses and so may change over time. A partial list of external websites with introductory and tutorial pages on XAFS

- XAFS Tutorials from Grant Bunker, Illinois Institute of Technology
- XAS Overview from Iztok Arcon, University of Nova Gorica, Jozef Stefan Institute, Slovenia
- X-ray Spectroscopy mini Courses from Jim Penner-Hahn, University of Michigan.
- XAS Education from Bruce Ravel, National Institute of Standards and Technology. See also: <https://speakerdeck.com/bruceravel>

Some slides from oral presentations hosted here (PDF format except where noted):

- XAFS Overview from Matt Newville, University of Chicago. Slides from an overview of XAFS.
- Fundamentals of XAFS from Matt Newville, University of Chicago. A longer (~40 page) writeup of notes and discussion of the basics of XAFS.
- Basics of EXAFS Processing from Shelly Kelly, UOP. Introducing the basics of processing $\chi(k)$ data in Athena.
- Basics of EXAFS Data Analysis from Shelly Kelly, UOP. Introducing the basics of modeling EXAFS

<https://xrayabsorption.org/feed/> in Artemis

May 2020

M	T	W	T	F	S	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	31

RELATED SITES:

- XAFS2021 Conference
- IUCr XAFS Commission
- [xafs.xrayabsorption.org](https://xrayabsorption.org)

SITE ACCESS

Log In

Entries feed

Comments feed

WordPress.org

Free* XAS software

☞ <http://bruceravel.github.io/demeter/>

The screenshot shows a Mozilla Firefox browser window displaying the Demeter XAS Data Processing and Analysis website. The address bar shows the URL: <http://bruceravel.github.io/demeter/>. The page content includes:

- About**, **Windows**, **Mac**, **Screenshots**, **Docs**, **Source code**, **Old releases** buttons.
- About Demeter** section: Describes Demeter as a comprehensive system for processing and analyzing X-ray Absorption Spectroscopy data.
- Demeter Is:** A bulleted list detailing its features:
 - currently at version 0.9.26
 - available for **Linux**, **Windows**, and **Macintosh**
 - a set of **perl** modules and related files
 - a programming tool -- it is the thing from which applications are built
 - free software**, freely available from a **git server**
 - actively developed and maintained
 - in use by its author and users for real data analysis problems
 - a front end to **Feff**, **Larch**, and **lfeffit** (and, soon, **Fefft**)
 - the code base for **Athena** and **Artemis**
 - named for the **Greek goddess of the harvest**
- Windows download:** A red button with a download icon and the text "Version 0.9.26".
- Source code:** A red button with a GitHub icon and the text "View On GitHub".
- Demeter © 2006-2018
Bruce Ravel** footer text.
- To ask questions or report bugs :** A link to "Use the **lfeffit Mailing List**".
- To cite Demeter in a publication, use:** A citation: *B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, Journal of Synchrotron Radiation 12, 537-541 (2005) doi:10.1107/S0909049505012719*
- The new WebAtoms:** reborn and updated!
- Windows Installer & Updater** section: A link to "Download the 64 bit Installer package and double-click to install the Demeter system".
- Have a question?** A red button with a question mark icon.
- Found a bug?** A red button with a bug icon.
- lfeffit Mailing List** link.
- The lfeffit Mailing List** is the best place to ask questions about the software and about XAFS. Please use the mailing list rather than contacting the author of Demeter directly.

* Free of cost, freely available source code, freely redistributable

Introduction to X-ray Absorption Spectroscopy