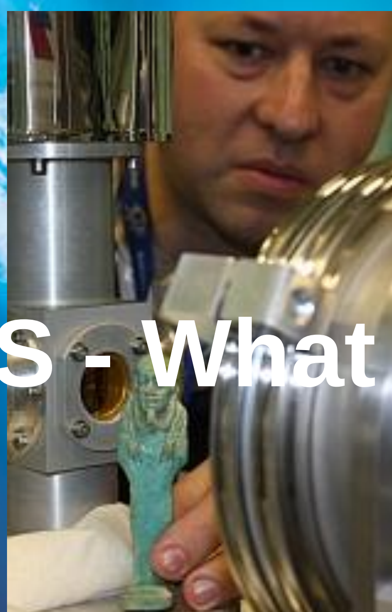


XAFS - What is it and why use it?

Chris Glover

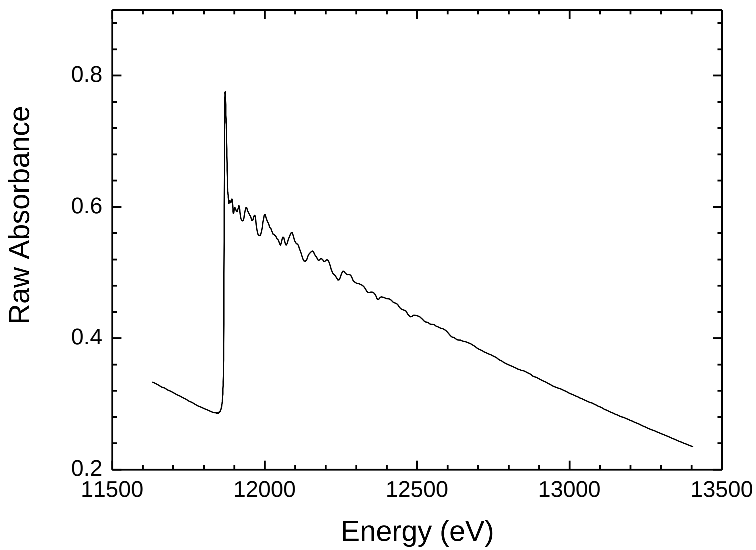
AS Conservation Workshop 2010

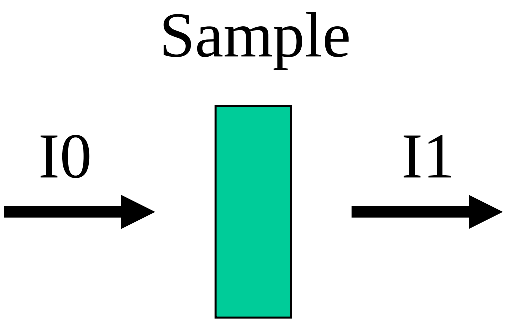
Sorry – I have to bore you first

$$\chi(k) = \sum_i \frac{S_0^{\,2} N_i}{k R_i^{\,2}} F_i(k) \exp(-2k^2\sigma_i^{\,2}) \exp\left(\frac{-2R_i}{\lambda}\right) \sin[2kR_i + \delta_i(k)]$$

What are these weird acronyms?

X-ray Absorption Fine-Structure is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge.

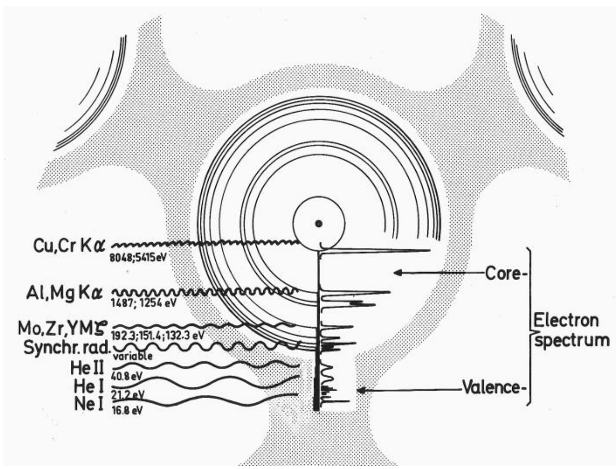


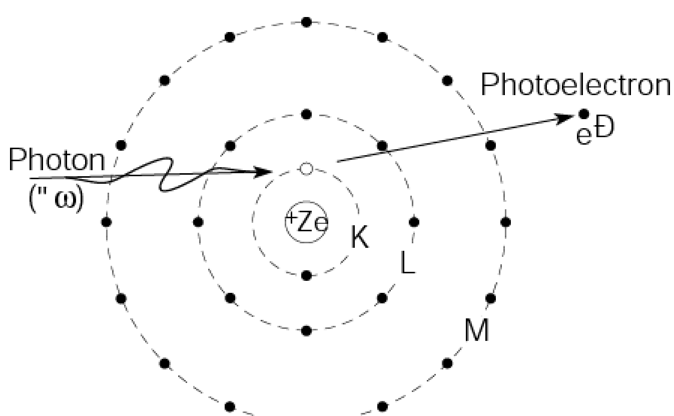


XAS	X-Ray Absorption Spectroscopy
XAFS	X-Ray Absorption Fine Structure Spectroscopy
EXAFS	Extended X-Ray Absorption Fine Structure Spectroscopy
XANES	X-Ray Absorption Near Edge Spectroscopy

A local probe - create a core hole

Incident X-ray to matter (gas, liquid or solid) of sufficient energy to remove bound core (localised) electron. By virtue of the different binding energies, we have element specificity.



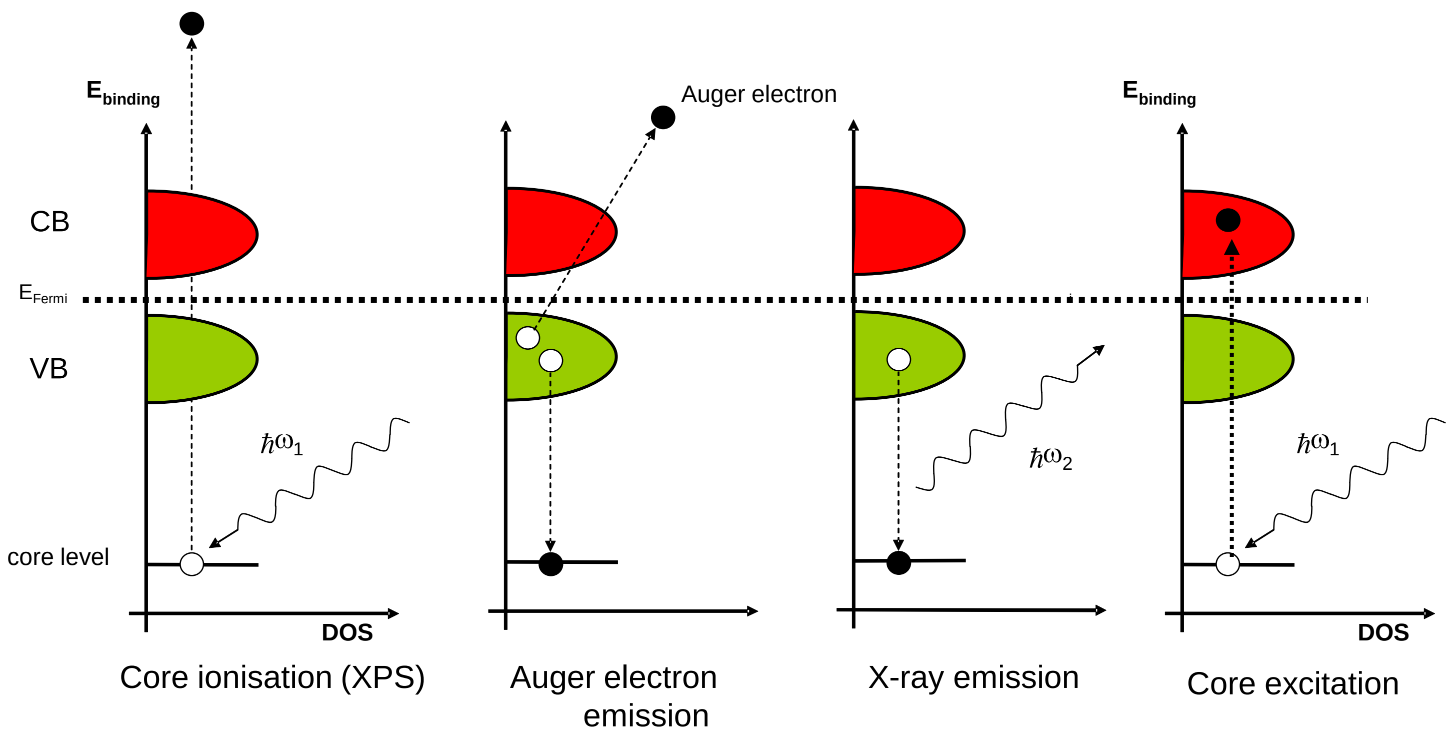


Element	Z	K_{abs}-edge (eV)	L_{abs}-edge (eV)
Be	4	112	—
C	6	284	—
N	7	410	—
O	8	543	—
Al	13	1,560	73
Si	14	1,839	99
S	16	2,472	163
Ca	20	4,039	346
Ti	22	4,966	454
V	23	5,465	512
Cr	24	5,989	574
Fe	26	7,112	707
Ni	28	8,333	853
Cu	29	8,979	933
Se	34	12,658	1,434
Mo	42	20,000	2,520
Sn	50	29,200	3,929
Xe	54	34,561	4,782
Pt	78	78,395	11,564
Au	79	80,725	11,919

The fate of the core hole…

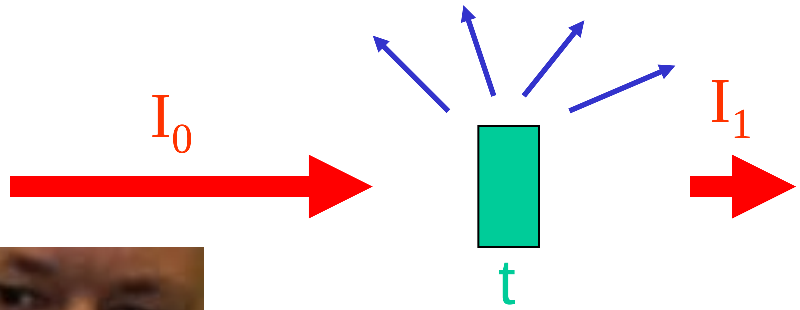
A core hole is energetically unstable, and is filled by a higher lying electron on the order of fs (10^{-15} sec). This results in an Auger electron decay or emission of an X-ray with characteristic energy. It is possible measure the actual absorption of a sample, or to detect these events *proportional* to the absorption.

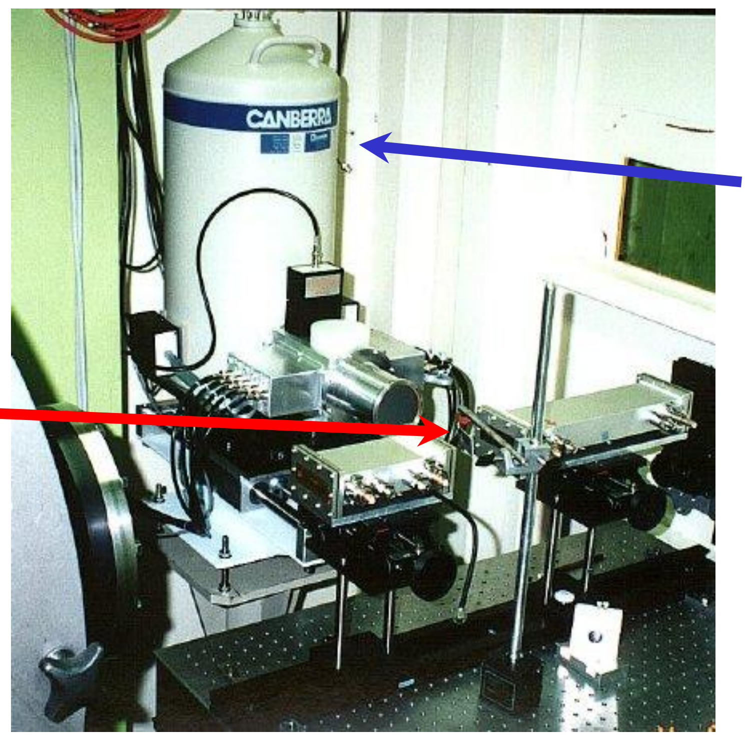
$$E_{\mathrm{kin}} = \hbar\omega - E_B - \phi$$



What do we measure? $I_1 = I_0 \, e^{-\mu t}$

Which requires a continuous source of X-rays…. synchrotron





Fluorescence mode

Measure characteristic X-ray from core hole decay

Proportional to EXAFS

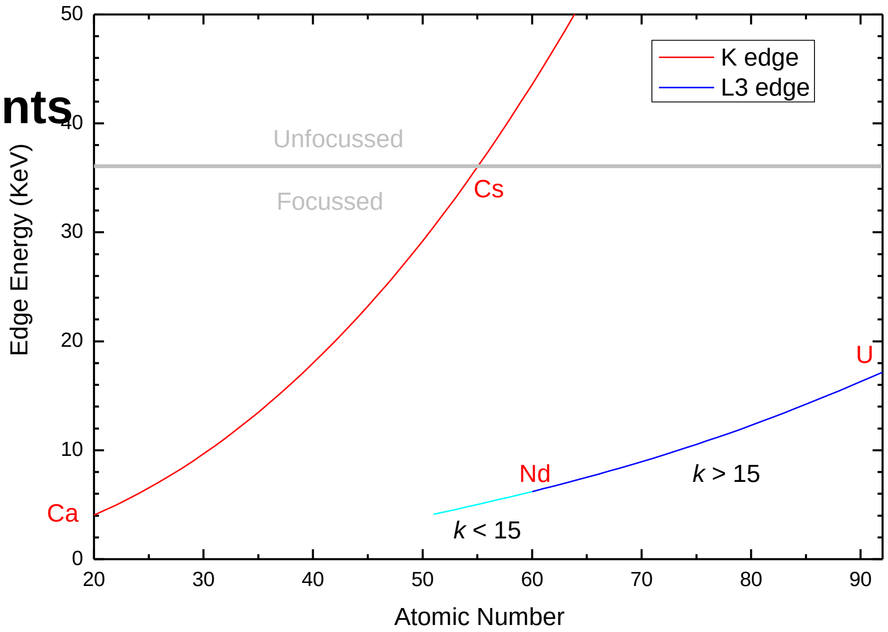
Count rate limited

Needs dilute or thin samples ppm… ppb?

May require corrections

Why do we use XAFS?

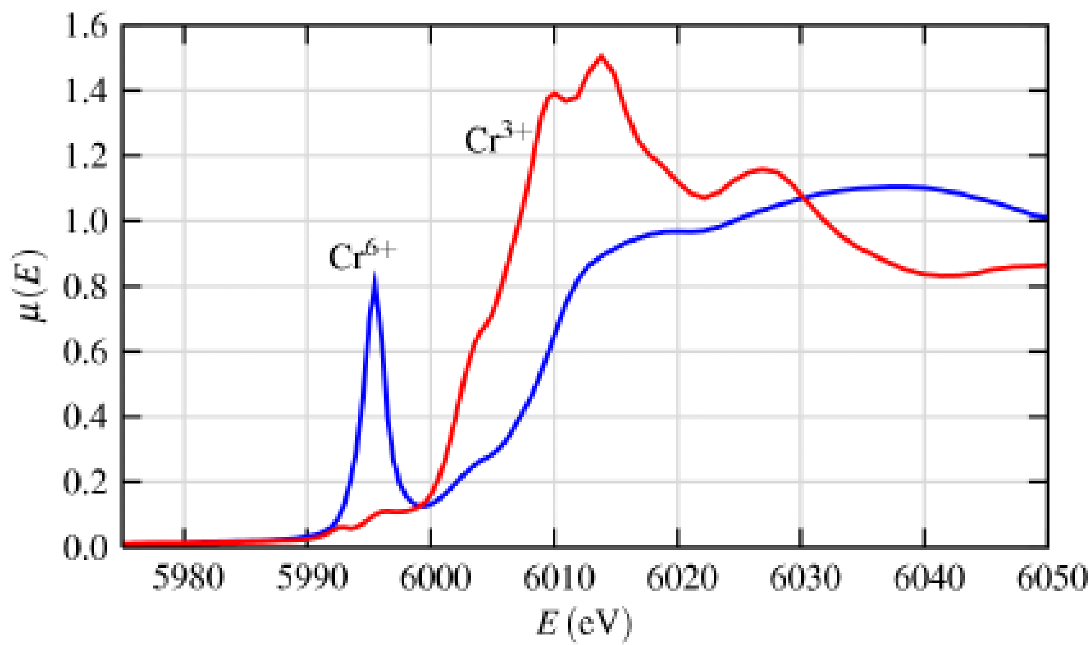
- Element specific (via core hole binding energy)
- Structural and chemical information
- Works at low concentrations (ie part monolayer and < ppm)
- Local atomic coordination and chemical state
- Applies to any element
- Generally minimal sample requirements
- crystals, amorphous, liquids, gases
- Relatively easy to measure
- ~ Z > 20 with 'HARD' X-rays

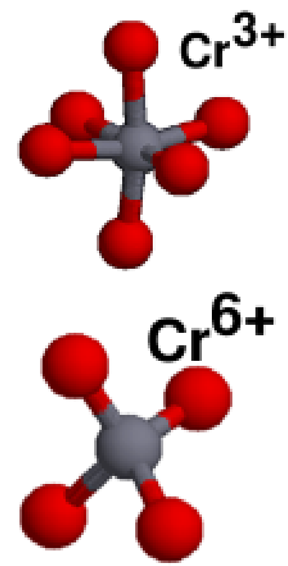


XANES – Oxidization state and coordination chemistry

The XANES of Cr $^{3+}$ and Cr $^{6+}$ show a dramatic dependence on oxidation state and coordination chemistry.

For ions with partially filled d **shells, the** p-d **hybridization changes dramatically as *regular octahedra* distort - large for *tetrahedral* coordination.**





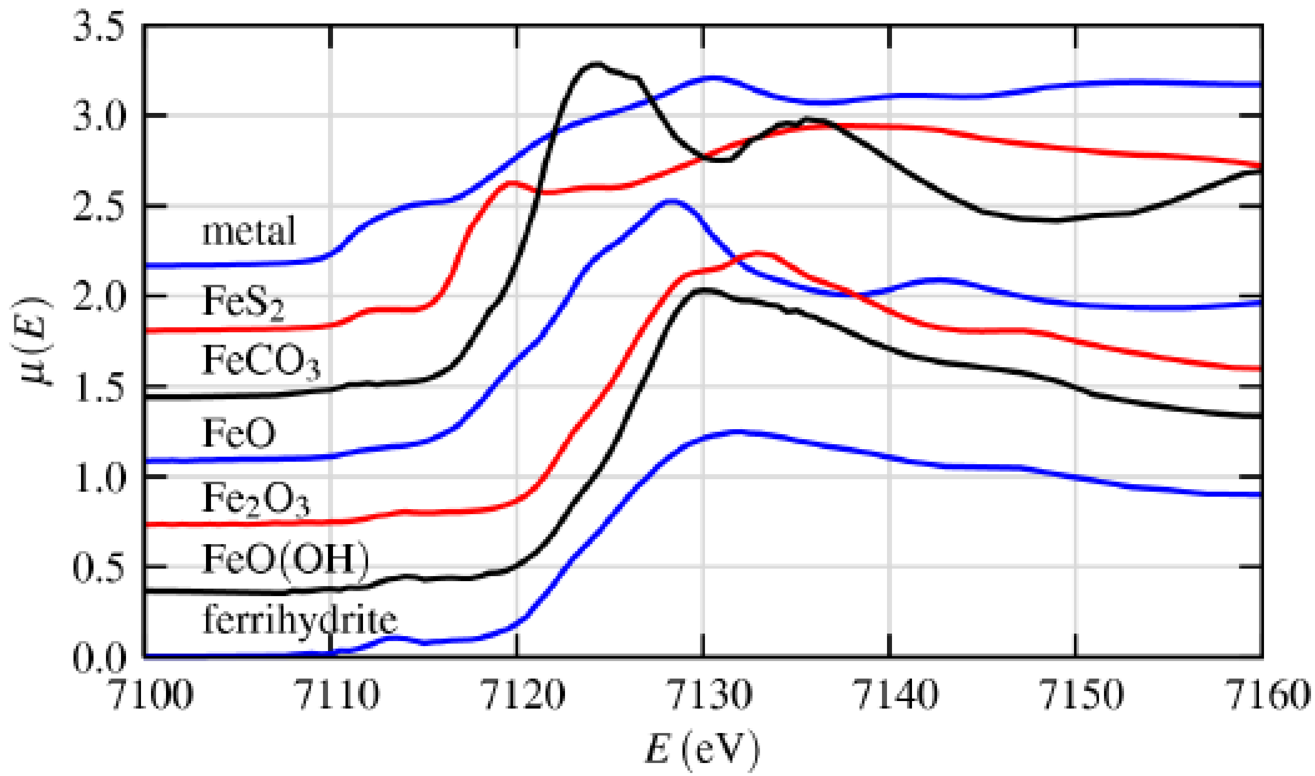
Borrowed from M. Newville

Chemical shifts and oxidation state

XANES can be used as a fingerprint of phases and oxidization states

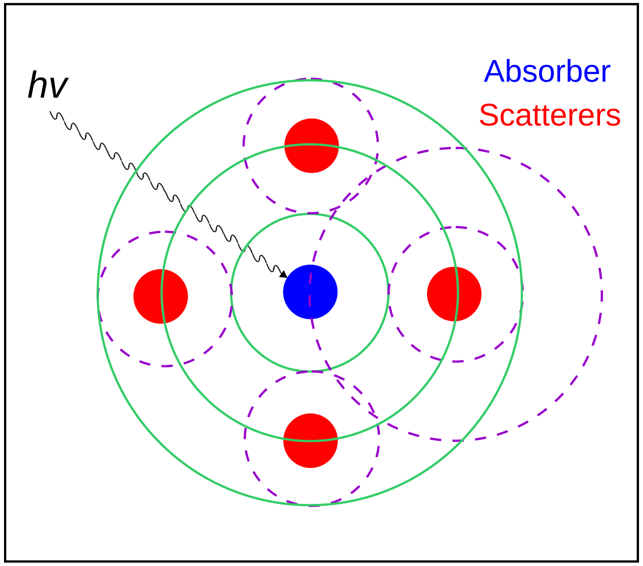
Analysis can be simple linear combinations of spectra, or fully calculated (rare)

Calculations are mostly qualitative, and can be described in terms of: coordination chemistry, molecular orbitals, band-structure or multiple scattering



Borrowed from M. Newville

The EXAFS process

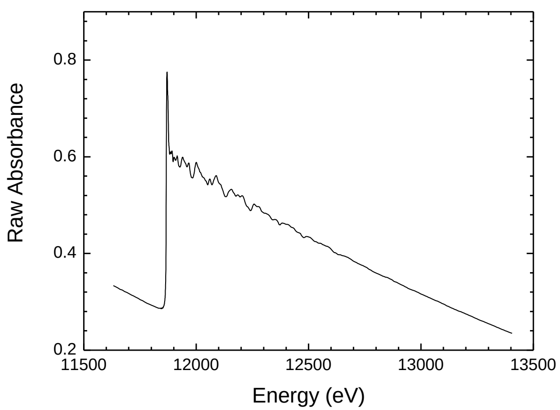


We consider the ejected photoelectron as a spherical de Broglie wave with wavenumber, *k*, and momentum, *p,* emanating from the ionised core

$$k = \frac{\sqrt{2m_e(E - E_0)}}{\hbar} \qquad \frac{p^2}{2m} = h\nu - E_0$$

Depending on the electron wavelength (number), and the atomic surroundings of the absorbing atom, the outgoing wave will scatter from nearby atoms and interfere with the originating wave. We know that in XAS we observe the final state – such interference effects the final state and thus modulates the measured absorption coefficient. Thus, the EXAFS carries information concerning the *local atomic environment* surrounding the absorbing atom.

It is a straightforward process to extract the ‘wiggles’ to obtain structural information.



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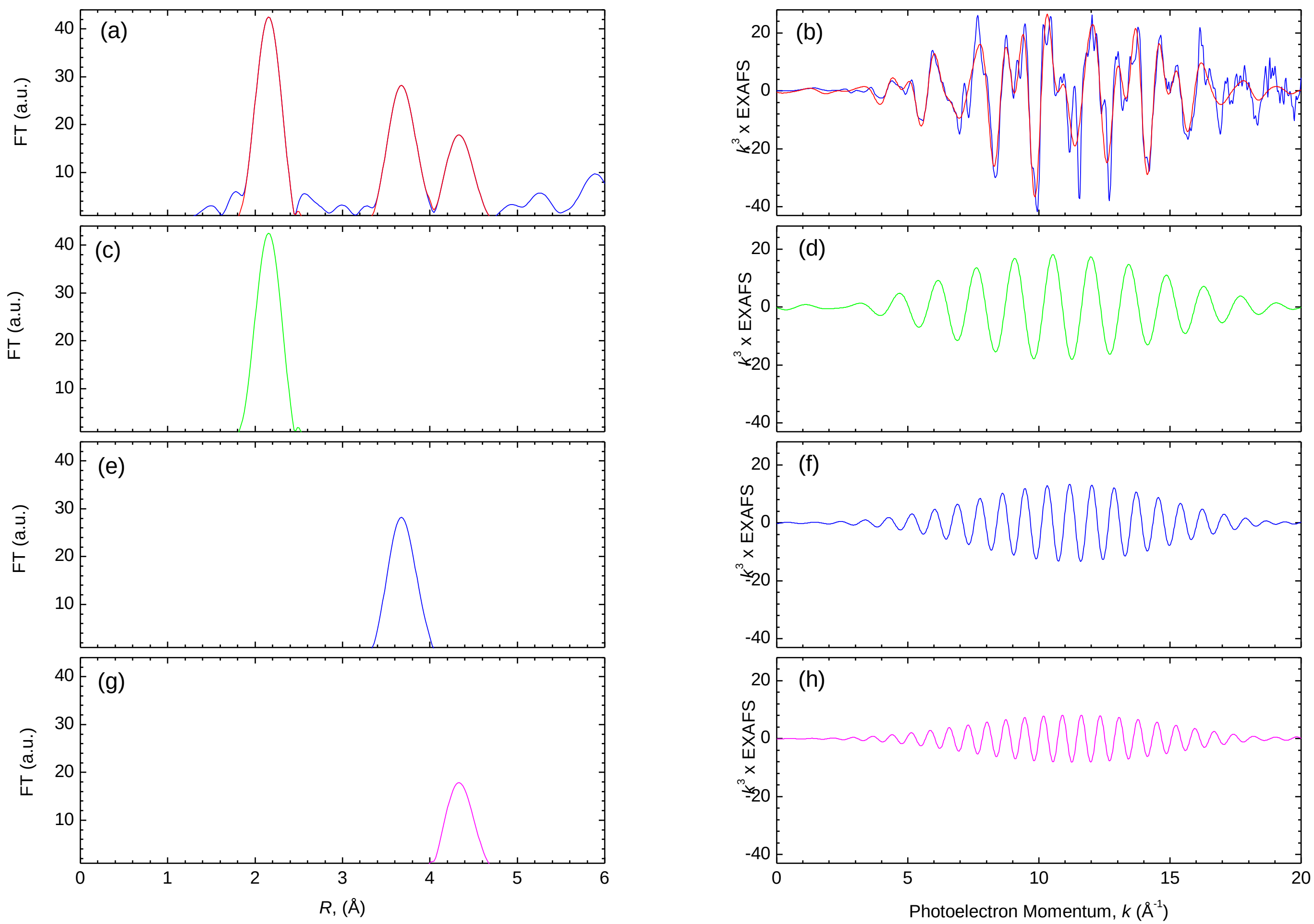
EXAFS RDF

Note that EXAFS requires only *local* order. Works equally well for crystalline or amorphous (or liquid) matter. The weight of the higher shells determines the 'crystalline' perfection.



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Example: Saving the Vasa

The 17th century Swedish warship *Vasa* sank on its maiden journey in 1628 in Stockholm Harbour.

It was recovered in 1961 (after 333 years 'at sea' – anoxic), 'preserved' and is currently on display in the 'Vasa Museum' in Sweden.

Initially the oaken timbers were in good condition, but high acidity and a rapid spread of sulfate salts and elemental sulfur were observed.

The problems faced by the Vasa are common to many resurrected wrecks.

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Example: Saving the Vasa

S K edge X-ray absorption spectroscopy as a function of depth in the timber revealed:

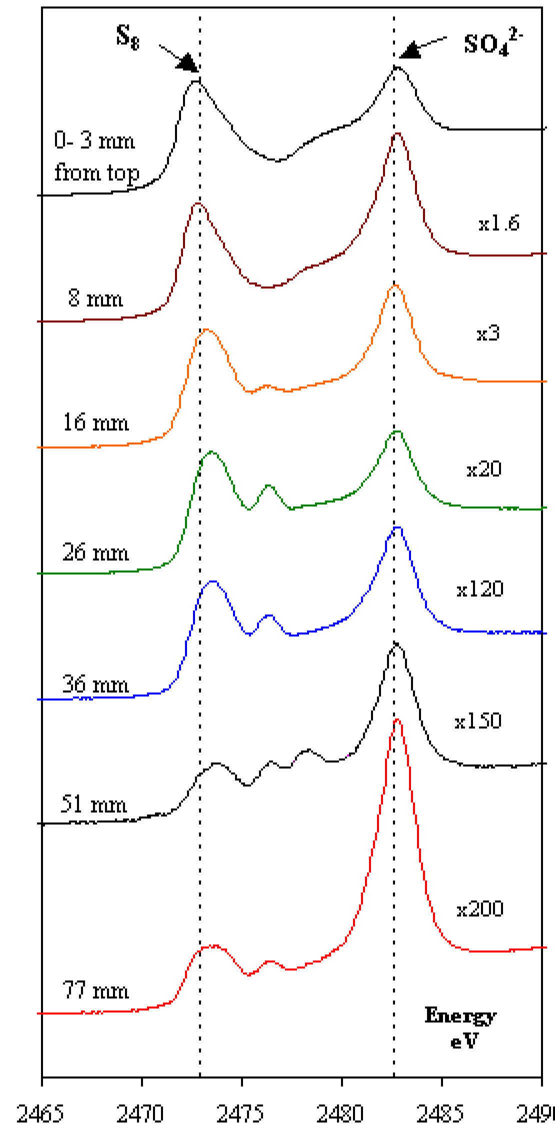
unexpectedly large amounts of embedded elemental sulfur (0.2-4 mass%)

sulfate and, in minor amounts, several sulfur compounds of intermediate oxidation states

In humid (O containing) museum atmospheres:

$$S + O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

Acidic wood hydrolysis is a severe threat to the continued preservation of the Vasa



Sandström, M. *et al* Nature **415**, 893-897 (2002)

Example: Rocky Flats, Denver, USA

For 40 yrs, Rocky Flats Nuclear Weapons Plant primary manufacturing facility for U.S. nuclear weapons arsenal.

Materials: machined plutonium and uranium; waste from toxic metals (eg beryllium); hazardous solvents, degreasers, and other chemicals.

Long series of leaks, accidents etc. Closed abruptly in 1989 by the EPA and FBI

DOE estimated cleanup would take 70 years at > $37 B.

Hypothesis that plutonium soluble in surface and ground water, accounting for increasing concentrations at measurement sites – disagreed with scientific 'evidence' – developed public mistrust.

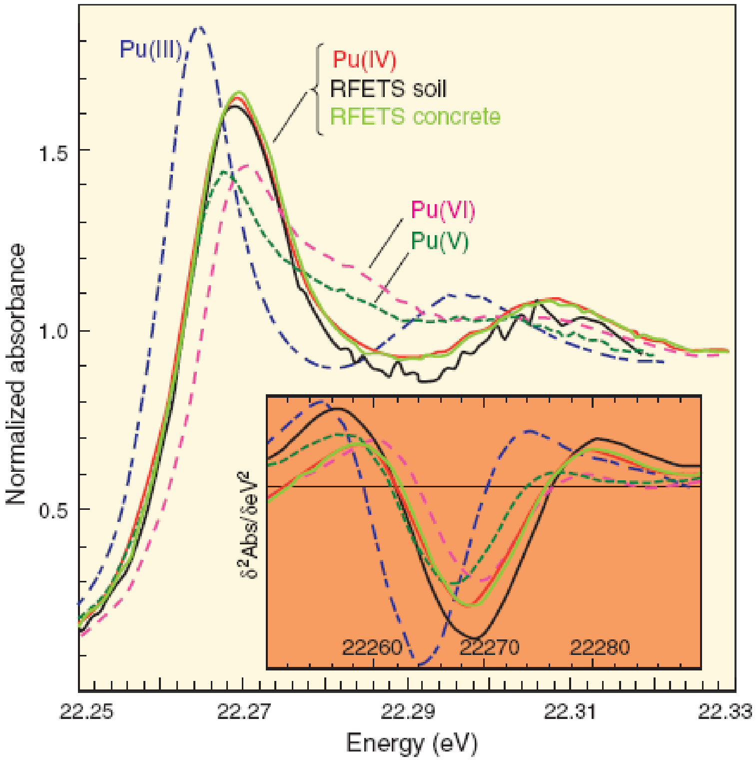
$Pu(OH)_4$ or PuO_2 have limited solubility; tend to adhere to particles. Particle transport?

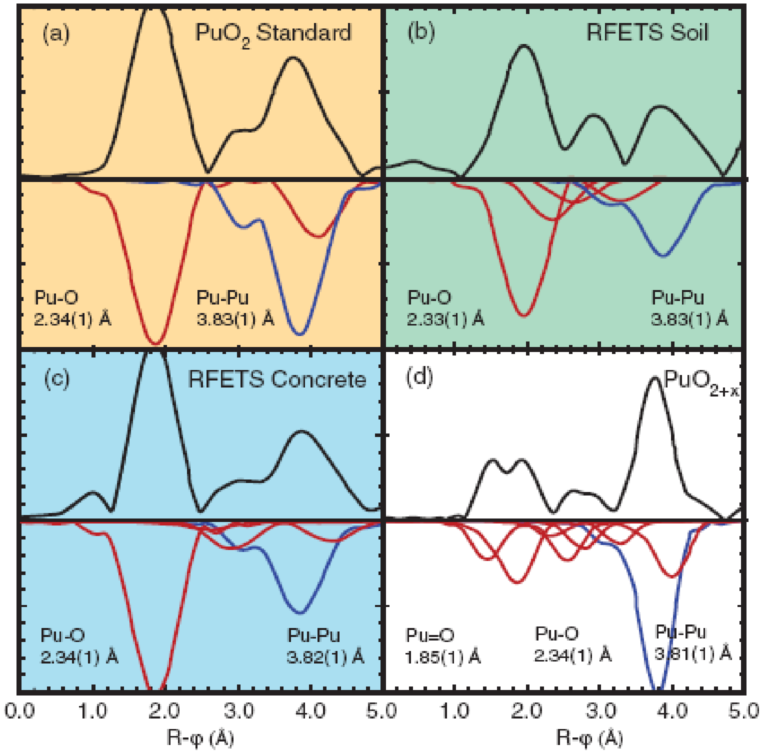
In 1969 spontaneous combustion in a glovebox in Building 776 started a fire that spread through the filter plenum.

It is estimated that 5,000 gallons of oil containing 86 grams of plutonium leaked into the soil from

Example: Rocky Flats, Denver, USA.

XAFS and EXAFS applied to Pu contaminated soils to determine chemical form and oxidation state





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Example: Rocky Flats, Denver, USA.

XAS studies showed that at Rocky Flats, Pt and Am form insoluble oxides and colloids that adhere to small soil and mineral particles., migrating by wind and surface-water resuspension and sedimentation processes

This understanding showed that soluble transport models were not appropriate and led to the development and application of erosion and sediment transport models

An independent contractor, the Kaiser-Hill Co., and the DOE undertook a massive effort to devise a subsequent plan, which brought the figure down to $7 billion over 10 years.

That plan was completed in December of 2005, 1 year ahead of schedule.

Ref: Actinide Research Quarterly, 2006, LANL.

References for further information

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES, in *Chemical Analysis* 92, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.

Basic Principles and Applications of EXAFS, Chapter 10 in *Handbook of Synchrotron Radiation*, pp 995–1014. E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland, 1983

International XAS Society: www.i-x-s.org

Ifeffit software: cars9.uchicago.edu/ifeffit

Your local XAFS practitioner or beamline scientist

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