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PSI

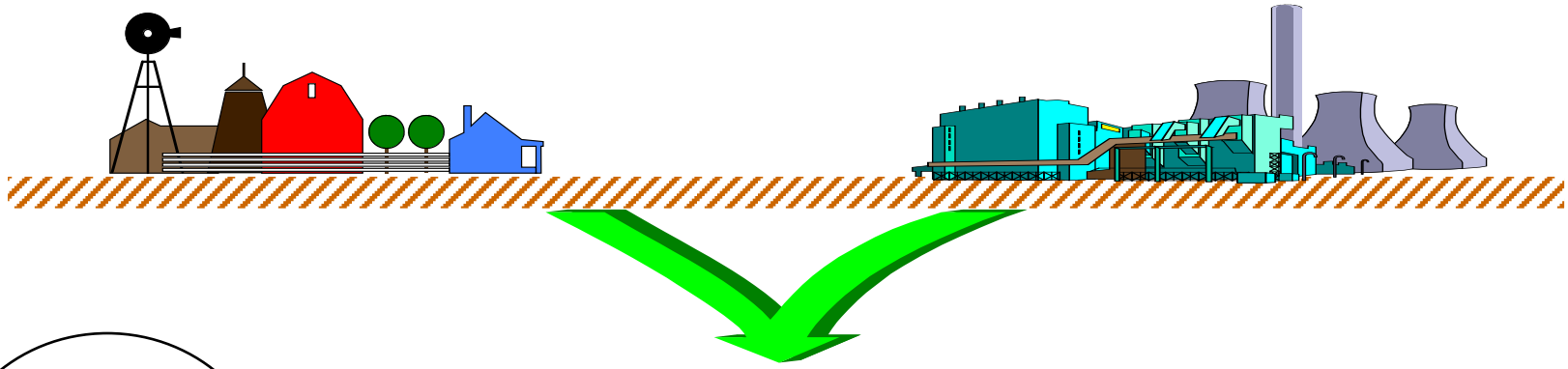
Wir schaffen Wissen – heute für morgen

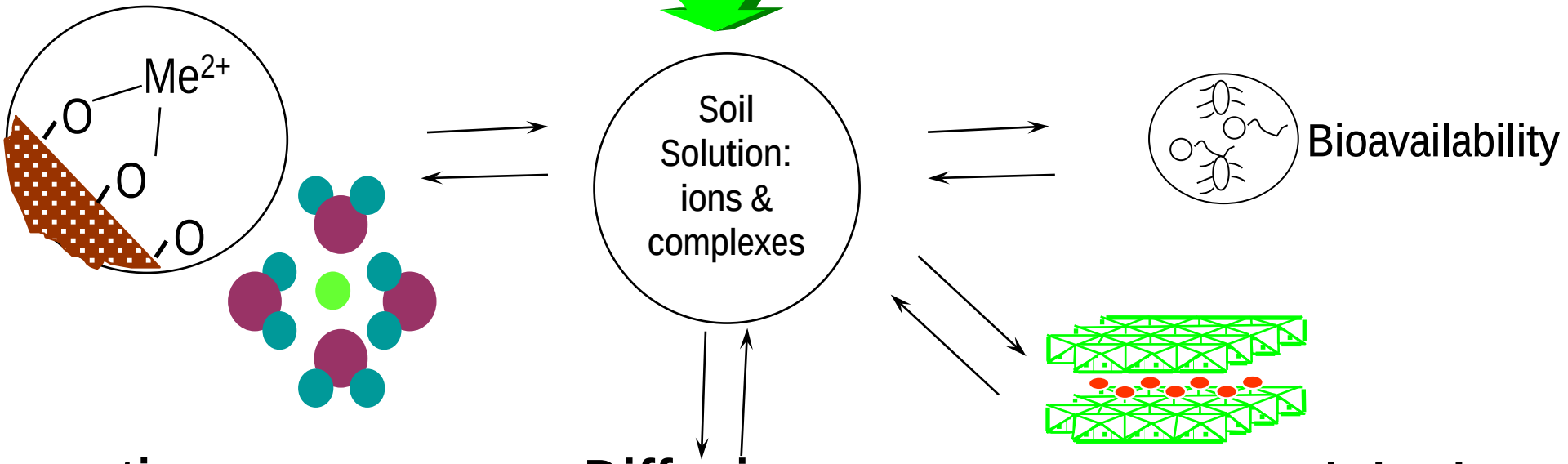
Introduction to EXAFS practical – scientific problem to be analysed

Camelia Borca
Paul Scherrer Institute

Introduction of Metals into Soil Environments:

Primary minerals, Agriculture, Industry, Sewage sludge, etc





Adsorption

Diffusion

- Film
- Pore
- Matrix

Precipitation

Iron (hydr)oxides

- Iron (Fe) - abundant in earth crust, mostly as iron (hydr)oxides
- 16 different (hydr)oxides, mostly formed as weathering products
- Often nano-sized crystals with high surface area – most reactive sorbents for contaminants in the environment

We will look at the structure of:

Ferrihydrite

Very common iron hydroxide

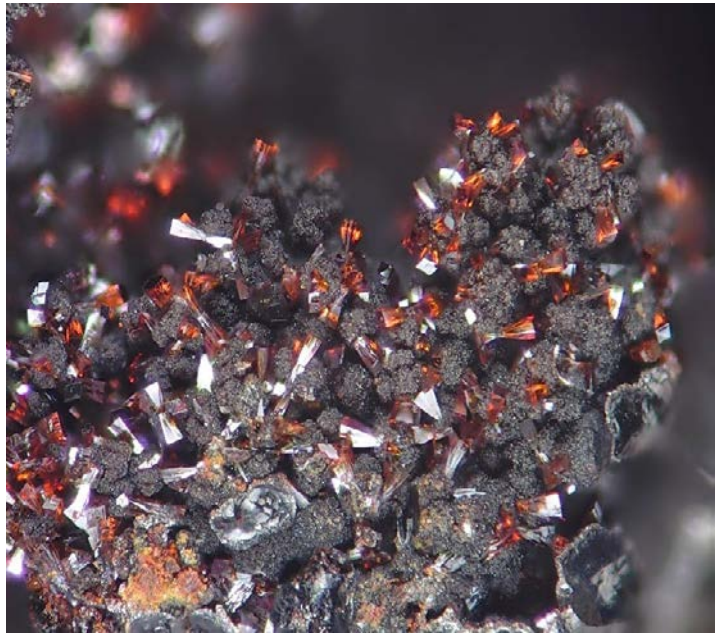
Poorly ordered

Structure/chemical formula unclear

Lepidocrocite

Orthorhombic crystal structure

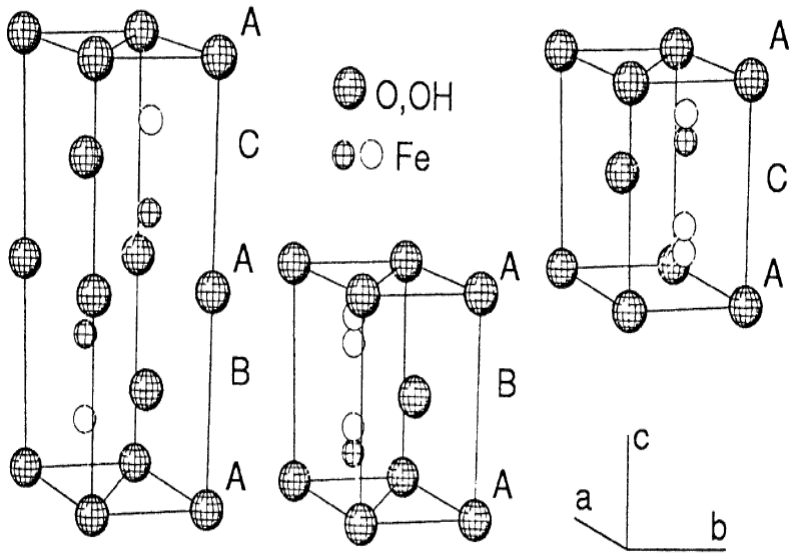
Well-crystalized



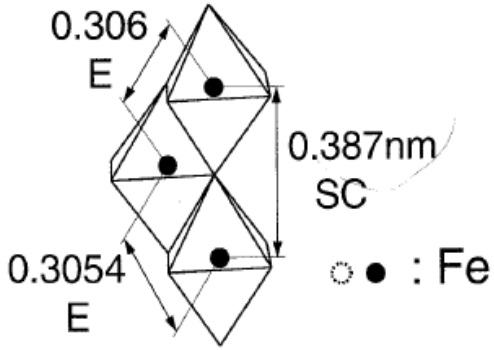
Webmineral.com

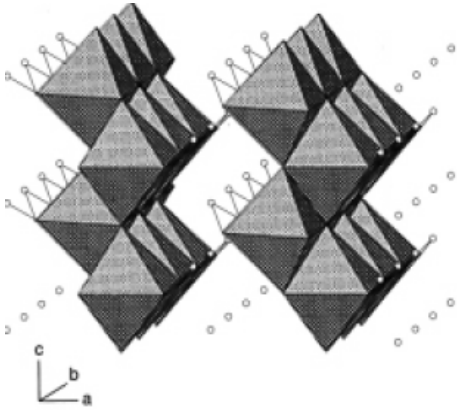
Structures of Ferrihydrite and Lepidocrocite

Ferrihydrite $Fe_5O_8H•4H_2O(?)$



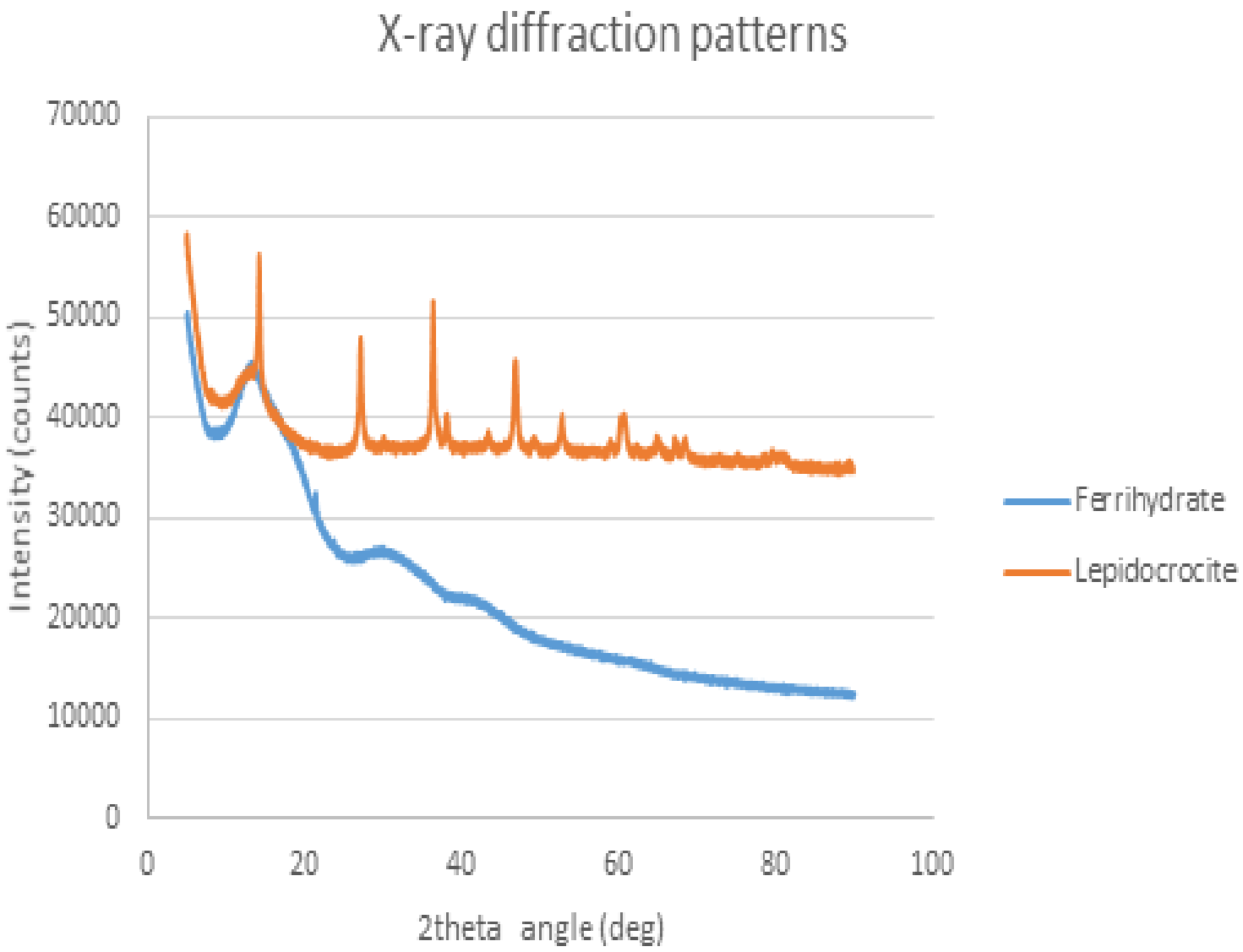
Lepidocrocite (γ-FeOOH)





(Cornell, 2003)

But…. Do we know the structure? …. XRD



The debate is still ongoing

The Structure of Ferrihydrite, a Nanocrystalline Material

F. Marc Michel, Lars Ehm, Sytle M. Antao, Peter L. Lee, Peter J. Chupas, Gang Liu, Daniel R. Strongin, Martin A. A. Schoonen, Brian L. Phillips, John B. Parise

Despite the ubiquity of ferrihydrite in natural sediments and its importance as an industrial sorbent, the nanocrystallinity of this iron oxyhydroxide has hampered accurate structure determination by traditional methods that rely on long-range order. We uncovered the atomic arrangement by real-space modeling of the pair distribution function (PDF) derived from direct Fourier transformation of the total x-ray scattering. The PDF for ferrihydrite synthesized with the use of different routes is consistent with a single phase (hexagonal space group $P6_3mc$; $a \approx 5.95$ angstroms, $c \approx 9.06$ angstroms). In its ideal form, this structure contains 20% tetrahedrally and 80% octahedrally coordinated iron and has a basic structural motif closely related to the Baker-Figgis δ-Keggin cluster.

Size-Driven Structural and Thermodynamic Complexity in Iron Oxides

Alexandra Navrotsky, Lena Mazeina, Juraj Majzlan

Iron oxides occur ubiquitously in environmental, geological, planetary, and technological settings. They exist in a rich variety of structures and hydration states. They are commonly fine-grained (nanophase) and poorly crystalline. This review summarizes recently measured thermodynamic data on their formation and surface energies. These data are essential for calculating the thermodynamic stability fields of the various iron oxide and oxyhydroxide phases and understanding their occurrence in natural and anthropogenic environments. The competition between surface enthalpy and the energetics of phase transformation leads to the general conclusion that polymorphs metastable as micrometer-sized or larger crystals can often be stabilized at the nanoscale. Such size-driven crossovers in stability help to explain the occurrence of different iron oxides in nature.

$S°$ (J mol^{-1} K^{-1})	$\Delta S_f°$ (J mol^{-1} K^{-1})	$\Delta G_f°$ (kJ mol^{-1})	$\Delta H_s°$ (J m^{-2})	ΔH_s (J m^{-2})
87.4 ± 0.2 (31)	−274.5 ± 0.3 (31)	−744.4 ± 1.3 (31)	0.75 ± 0.16 (13)	1.9 ± 0.3 (18)
93.0 ± 0.2 (17)	−268.9 ± 0.3 (17)	−731.4 ± 2.0 −717.8 ± 6.6 (15)	0.57 ± 0.10 (4)	0.71 ± 0.13 (4)
59.7 ± 0.2 (17)	−237.9 ± 0.2 (17)	−490.6 ± 1.5	0.60 ± 0.10 (12)	0.91 ± 0.09 (18)
65.1 ± 0.2 (17)	−232.5 ± 0.2 (17)	−482.7 ± 3.1	0.40 ± 0.16 (10)	0.62 ± 0.14 (10)
53.8 ± 3.3 (32)	−246.2 ± 3.3 (32)	−481.7 ± 1.9 −483.1 ± 1.3 (13) −711.0 ± 2.0 (15)	0.34 ± 0.04 (11)	0.44 ± 0.04 (11)

CRYSTAL GROWTH

Aqueous formation and manipulation of the iron-oxo Keggin ion

Omid Sadeghi, Lev N. Zakharov, May Nyman*

There is emerging evidence that growth of synthetic and natural phases occurs by the aggregation of prenucleation clusters, rather than classical atom-by-atom growth. Ferrihydrite, an iron oxyhydroxide mineral, is the common form of Fe^{3+} in soils and is also in the ferritin protein. We isolated a 10 angstrom discrete iron-oxo cluster (known as the Keggin ion, Fe_{13}) that has the same structural features as ferrihydrite. The stabilization and manipulation of this highly reactive polyanion in water is controlled exclusively by its counterions. Upon dissolution of Fe_{13} in water with precipitation of its protecting Bi^{3+}-counterions, it rapidly aggregates to ~22 angstrom spherical ferrihydrite nanoparticles. Fe_{13} may therefore also be a prenucleation cluster for ferrihydrite formation in natural systems, including by microbial and cellular processes.

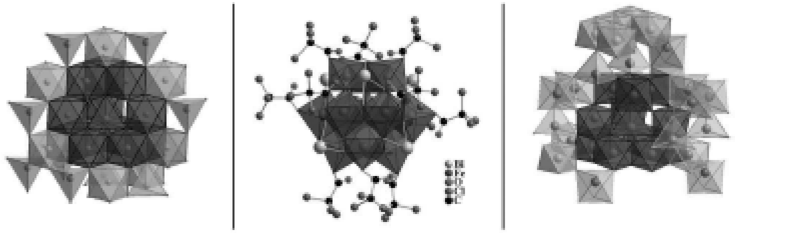
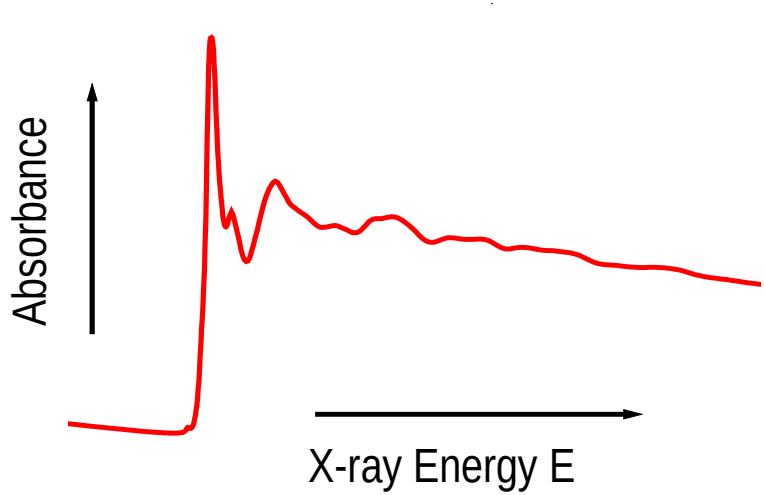


Fig. 1. The iron Keggin ion. Views of the iron Keggin ion in different structures. **(Left)** Magnetite, emphasizing the ε-Keggin isomer building unit (red polyhedra). The four trimers of edge-sharing octahedra are likewise connected together by edge-sharing. **(Middle)** Bi_6-α-Fe_{13}. In the α-isomer, the four trimers are linked together by corner-sharing. **(Right)** A view of ferrihydrite, structure determined from pair distribution function (5). The red polyhedra emphasize the δ-Fe_{13} building block. In the δ-isomer, three of the trimers are edge-sharing, and the fourth is corner-linked.

X-ray Absorption Spectroscopy (XAS):

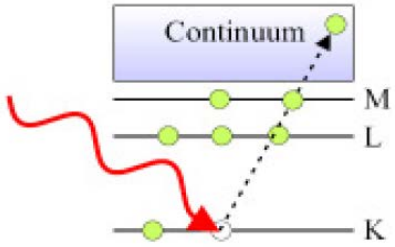
- ✓ Detailled chemical und structural information (oxidation state, coordination numbers, bond distances, system disorder)
  - Solution species
  - Crystaline and amorphous solids
  - Surface complexes
- ✓ in-situ, non destructiv
- ✓ minimal sample preparation
- ✓ high selectivity/sensitivity (few ppm)



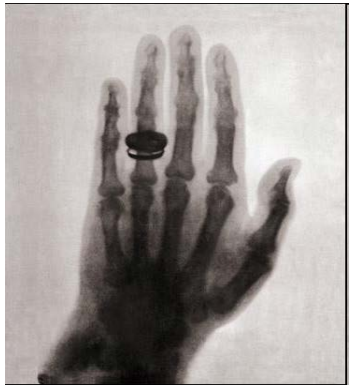
X-ray absorption spectroscopy

Visible light
λ ~ 0.5 µm
E ~ 2 eV

valence
electrons

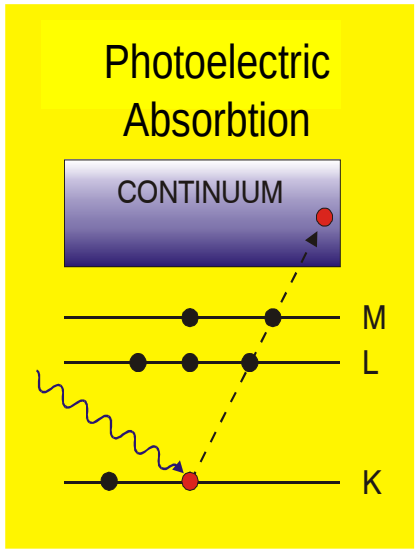


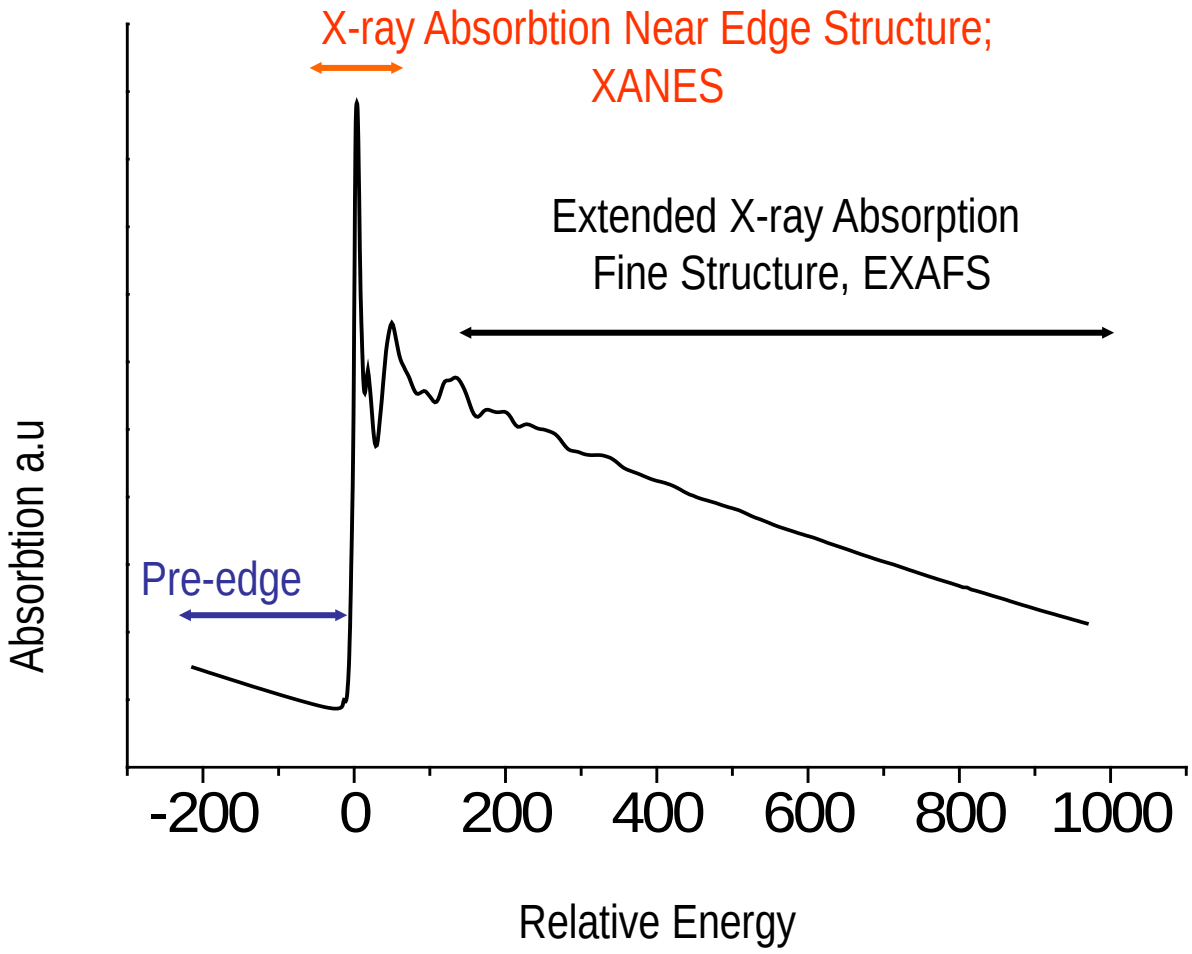
X-ray light
λ ~ 1 Å (=0.1 nm)
E ~ 10 keV



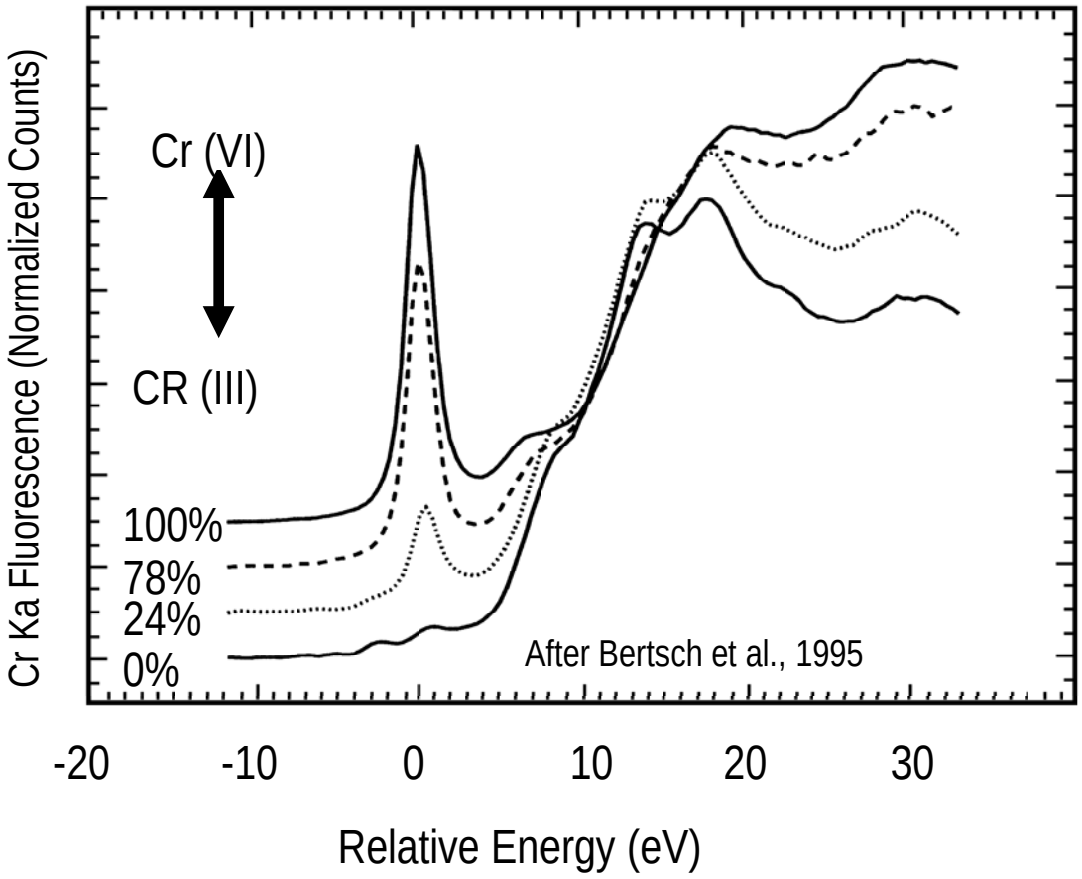
core
electrons

Main Principle





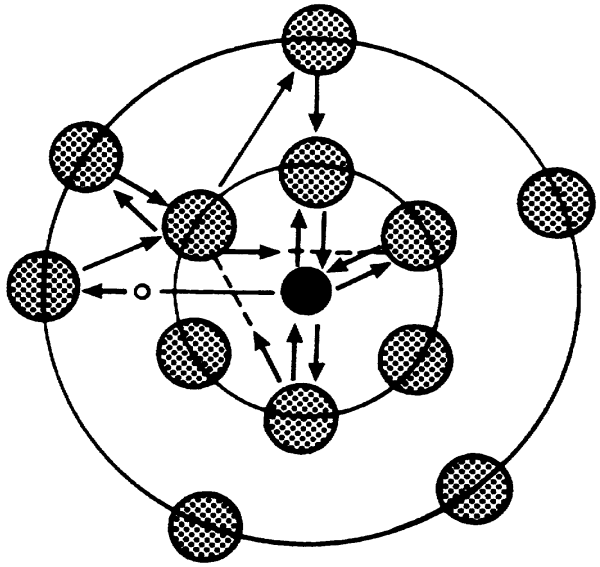
Pre-edge



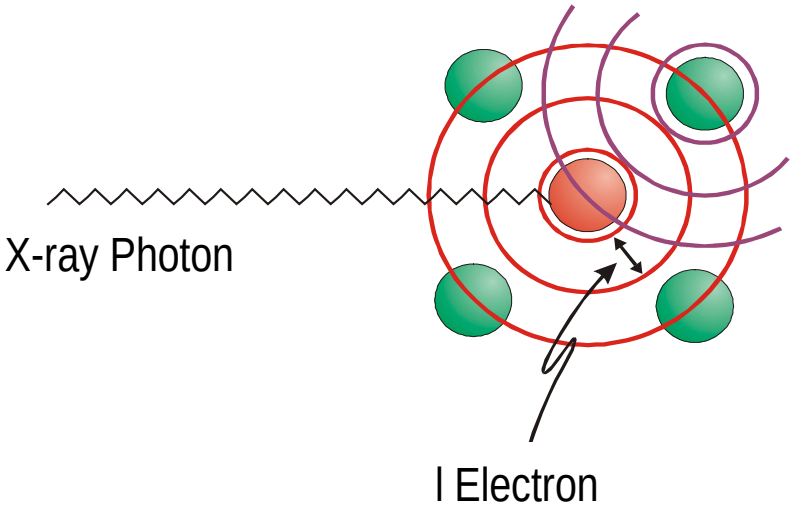
- E < Eb
- transition of e^- from ground state (e.g., 1s, 2s) to empty or partly filled, excited states (nd orbital)
  - selection rules for e^- transitions
- speciation of Cr(VI) and Cr(III)
  - Cr(VI)
    - toxic and mobil
  - Cr(III)
    - hardly toxic
    - sorbed or incorporated into mineral phases

XANES

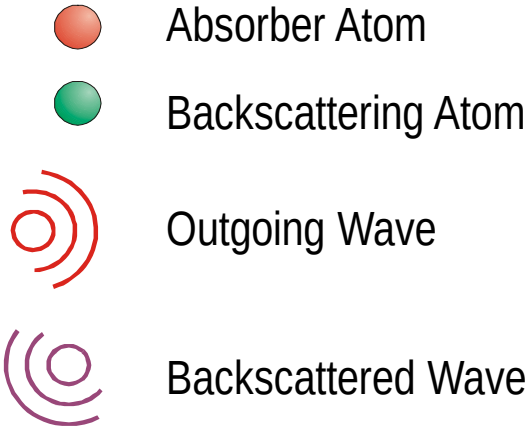
- E ~ Eb
- Multiple scattering of photoelectron
- Very intense and complicate resonance features: finger-printing and theoretial calculations
- Energy of absorption edge depends on oxidation state
  - Chemical shift of 1-3 eV for each withdrawing e^-



EXAFS



- E>Eb
- 50 - 1000 eV above absorption edge
- simplified illustration: constructive & destructive frequencies from the outgoing photoelectron



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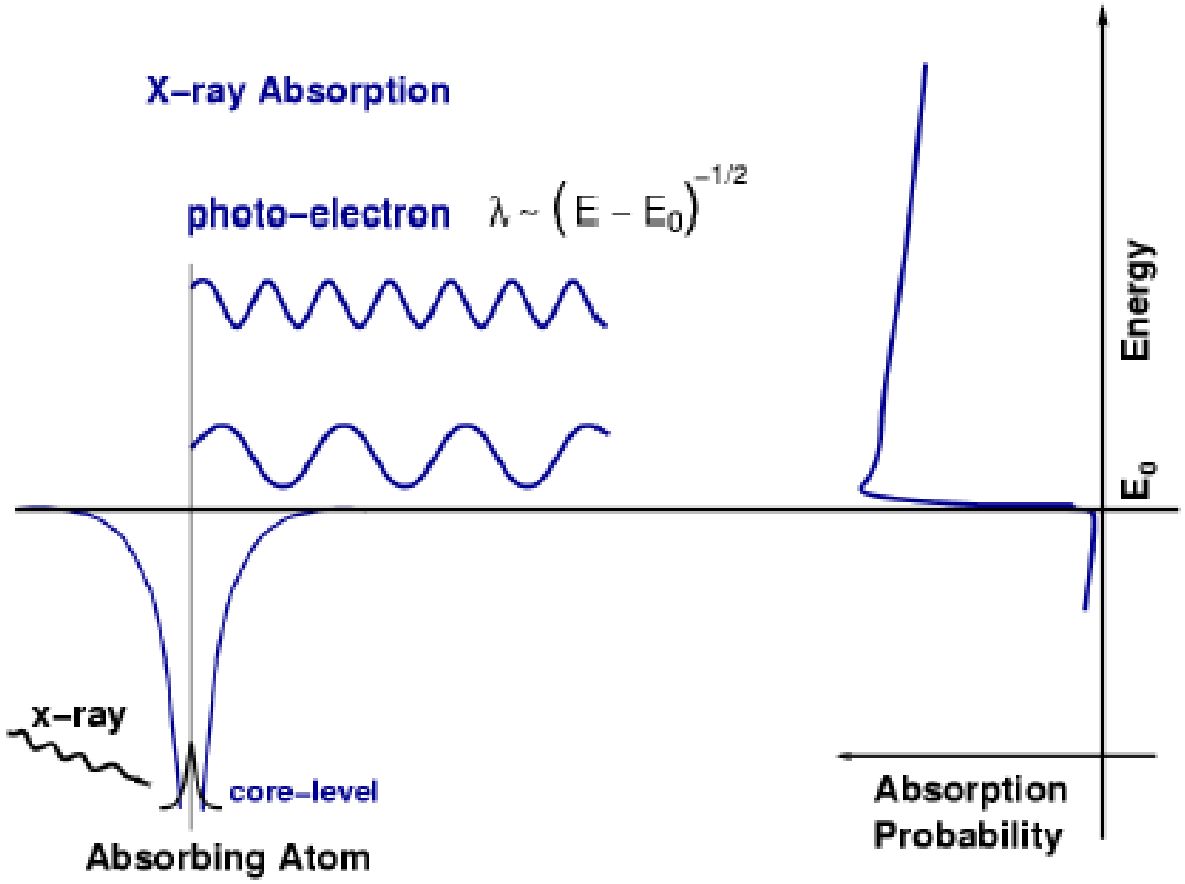
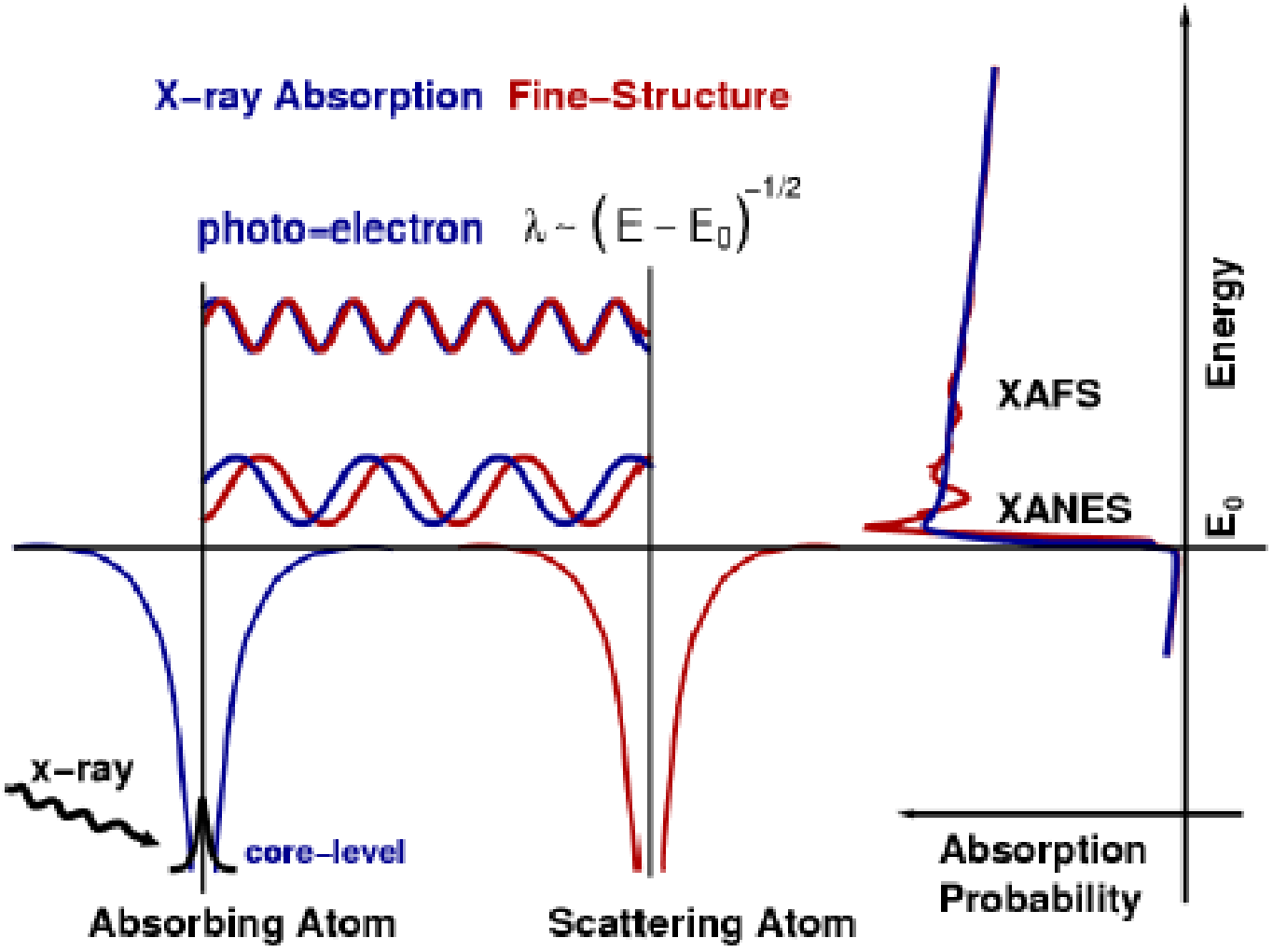
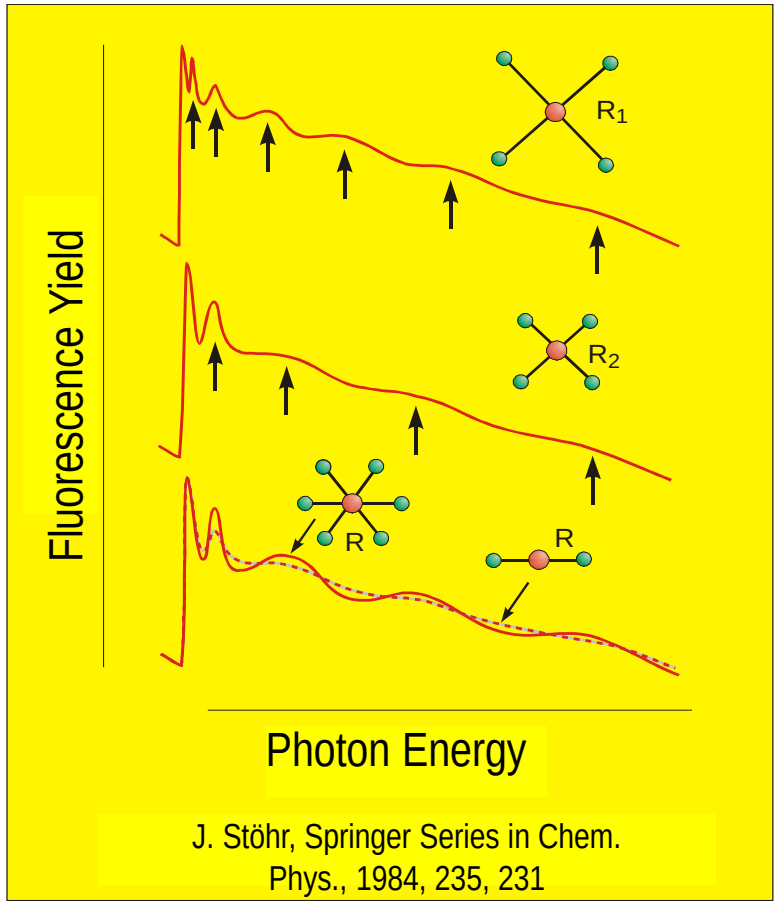
Free atom



Cluster of atoms



EXAFS

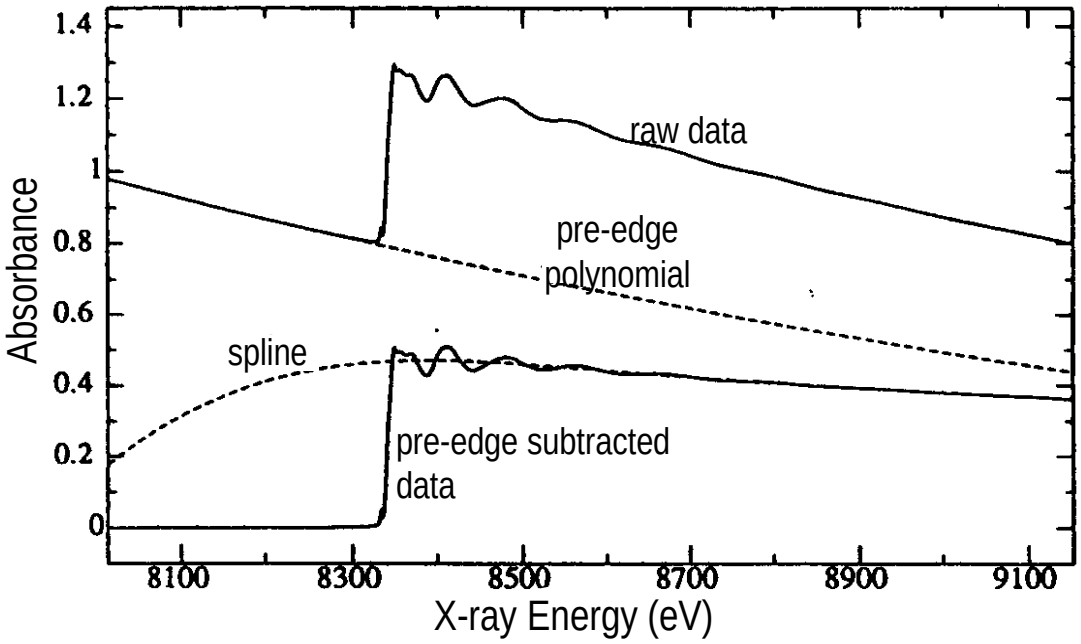


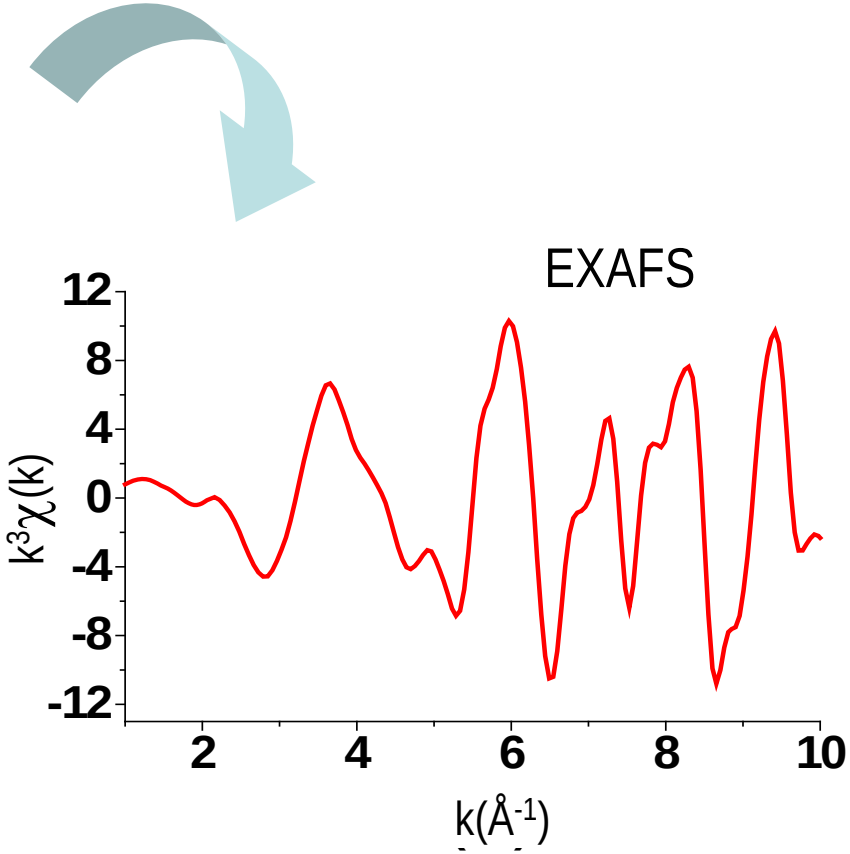
J. Stöhr, Springer Series in Chem. Phys., 1984, 235, 231

- Interference pattern (EXAFS)
  - Frequency correlated to bond distance
  - Amplitude correlated to coordination number and identity

$$\chi(k) = \Sigma\, a(k)\, \sin[2kR+\alpha(k)]$$

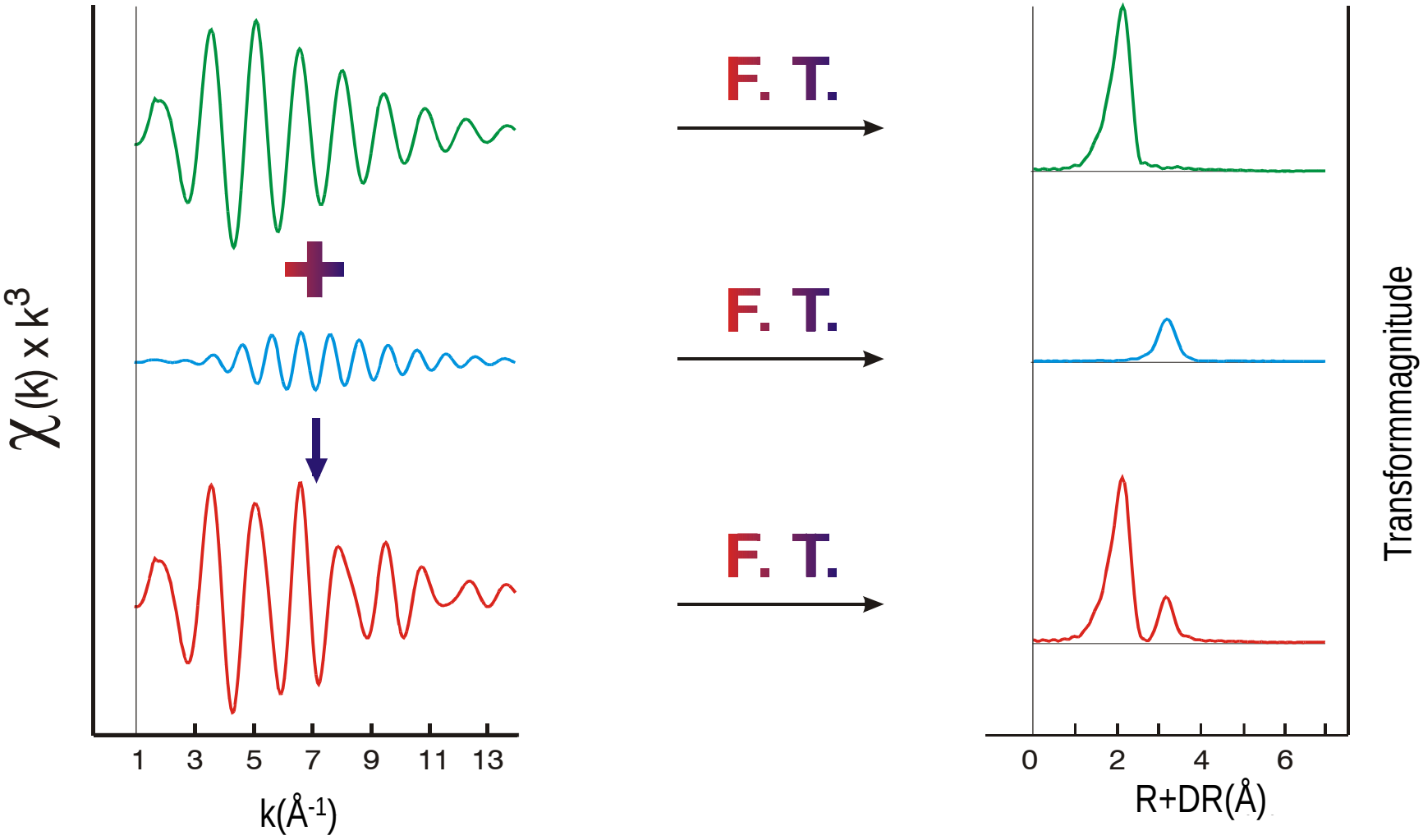
Data Analysis





- extraction of EXAFS
  - pre-edge & spline, normalization
  - convertion to wave vector $k^2 = 2m\,(E-E_0) / \hbar^2$
  - normally weighted by k^3

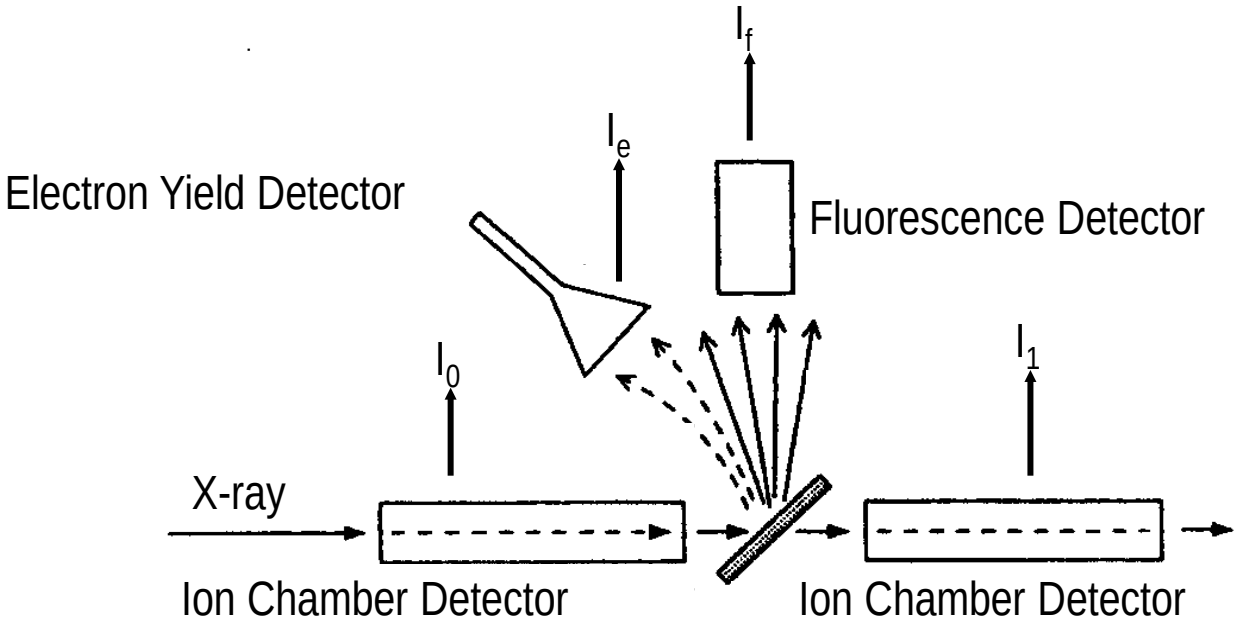
Fourier Transformation

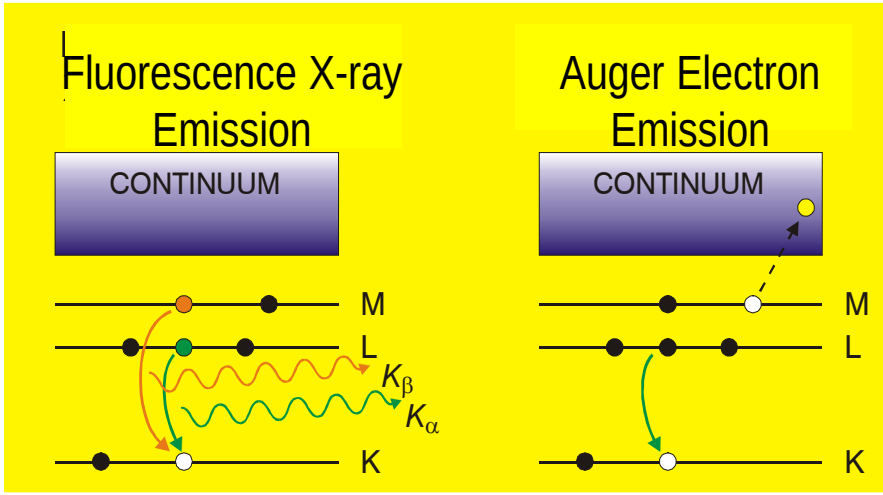


$$\chi(k) = \Sigma\, a(k)\, \sin[2kR + \alpha(k)]$$

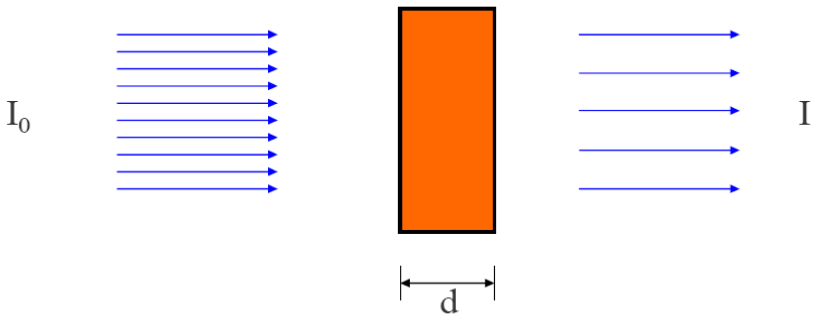
Experimental set-up

- Transmission
  - $A = mx = \ln(I_0/I_1)$
  - concentrated samples
- Fluorescence
  - $A = mx = I_f/I_0$
  - dilute samples
- Electron-yield
  - $A = mx = I_e/I_0$
  - surface sensitive

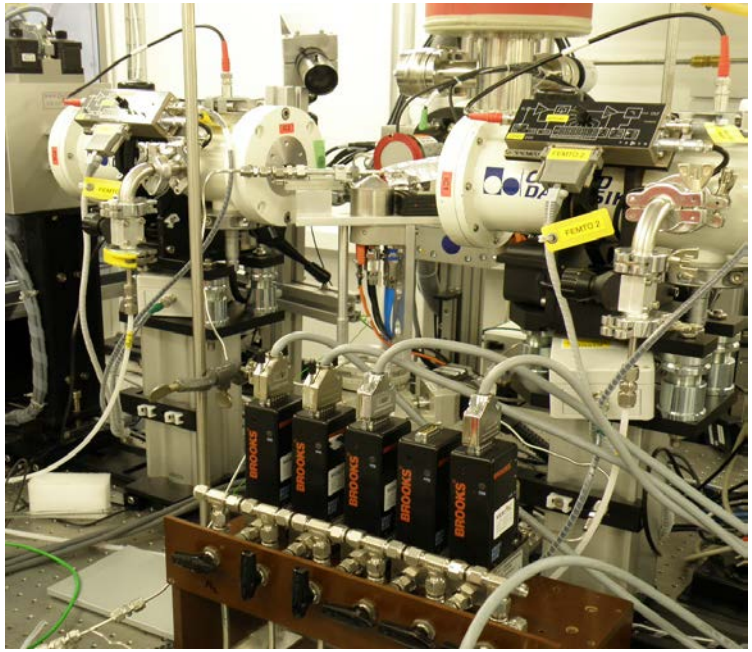




XAFS: measurement of the X-ray absorption coefficient (μ)



Lambert Beer's Law: $I = I_0 \cdot e^{-\mu d}$



μ depends strongly on x-ray energy E and atomic number Z, and on the density ρ and Atomic mass A:

$$\mu \approx \frac{\rho Z^4}{A E^3}$$

What do you measure?

- Absorption as function of energy

Need a Synchrotron…

SLS

Diamond

Soleil

ESRF

and many more…

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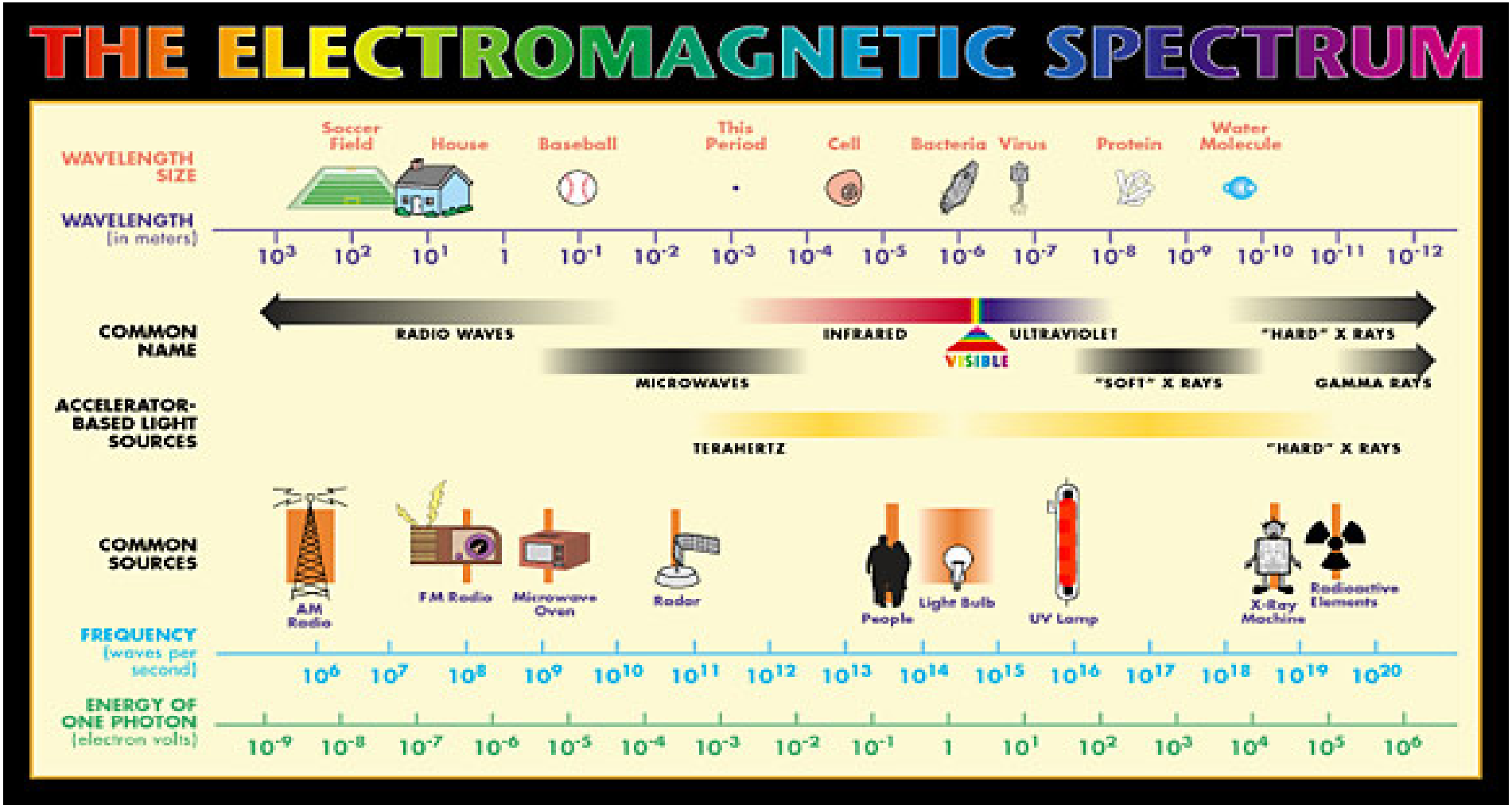
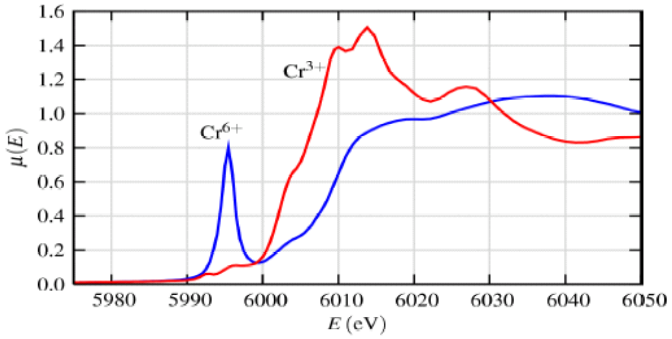
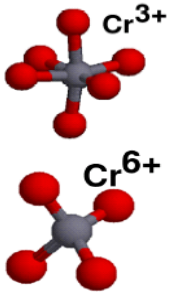
Synchrotrons produce bright light

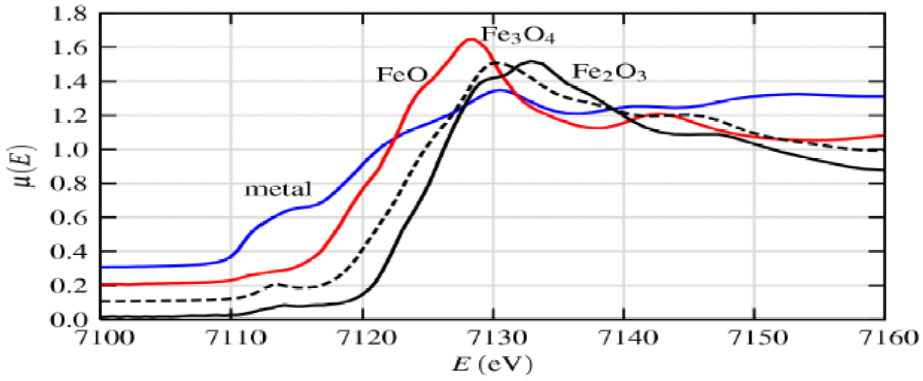


Summary so far:

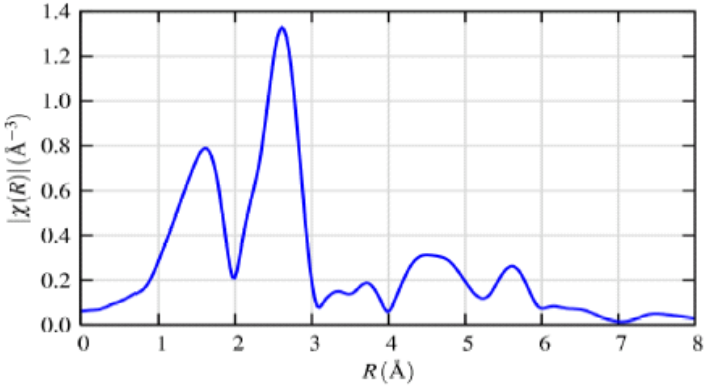




Pre-edge:
- localized electronic states
- coordination chemistry

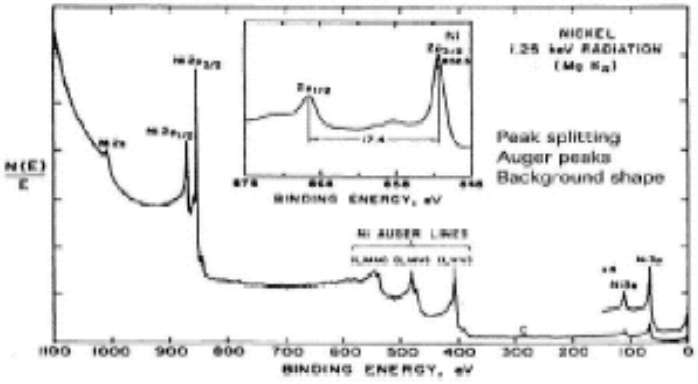


XANES: (DOS)
- oxidation state
- band structure
- multiple scattering



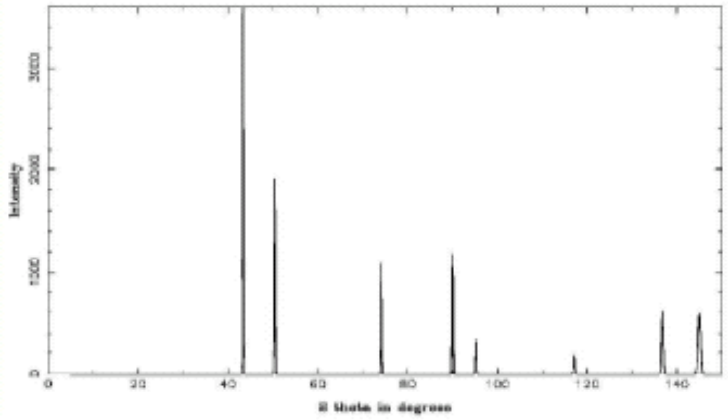
EXAFS:
- Identity of nearest neighbors
- Bond distances
- Coordination numbers
- Amount of disorder

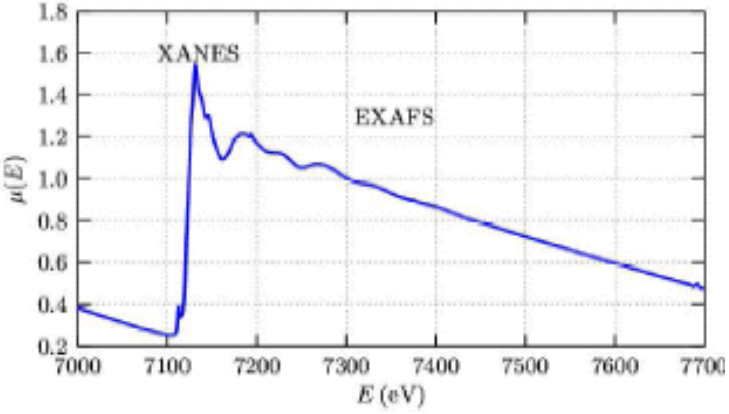
Comparison: XPS, XRD, XAS



- electronic information
- surface sensitive
- In-situ application difficult
- UHV needed

- structural information
- bulk technique
- In-situ
- long range order

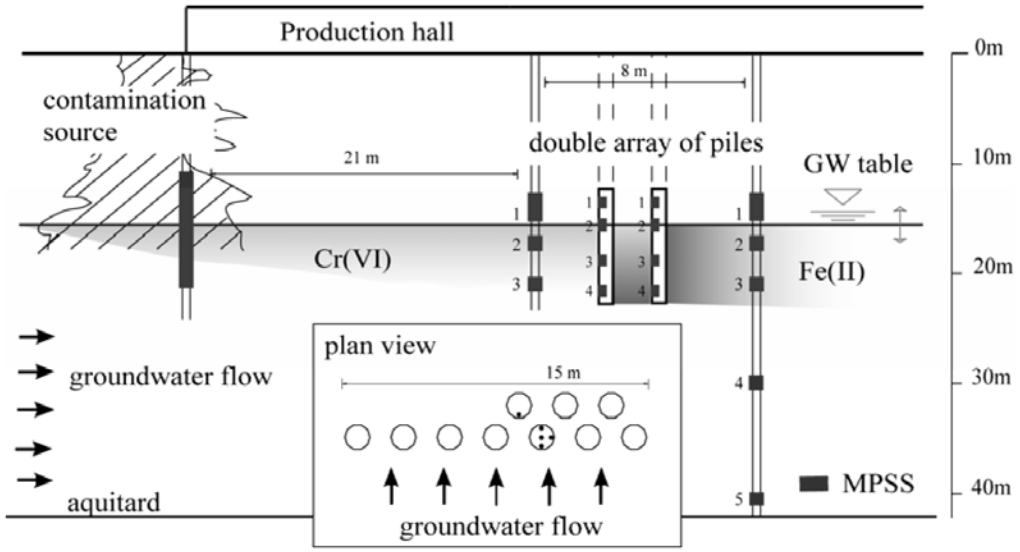




- electronic and structural information
- bulk and surface sensitive
- amorphous materials
- In-situ
- synchrotron needed

Example: Fe-oxides as contaminant sorbent

Wood impregnation in Willisau



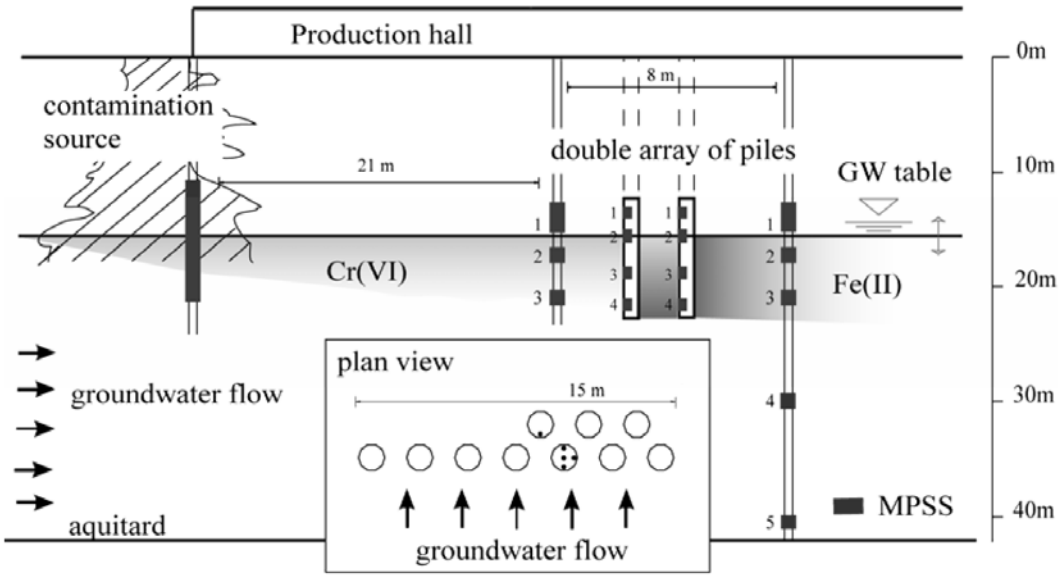
E_H=150 mV
$[SO_4^{2-}]$=30 mg/L
$[NO_3^-]$=11 mg/L
pH = 7

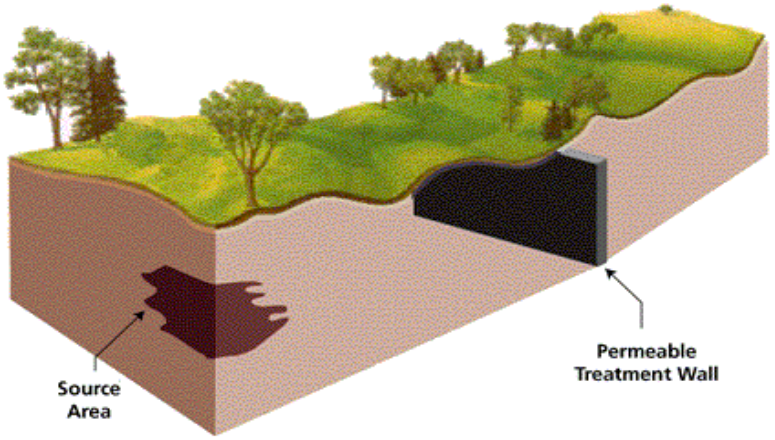
- Contaminants Cr(VI), Cu
- ~1 t Cr at a depth of 3-12 m
- Groundwater protection zone ([Cr(VI)]max = 0.01 mg/L)

Permeable reactive barrier

24
Cr
52.00

Permeable Reactive Barrier (PRB): couple the oxidation of Fe(0) with the reduction of Cr(VI)

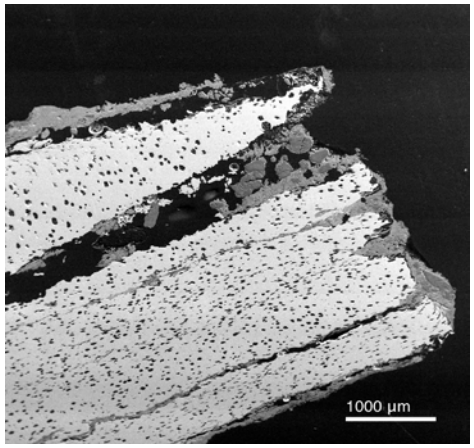


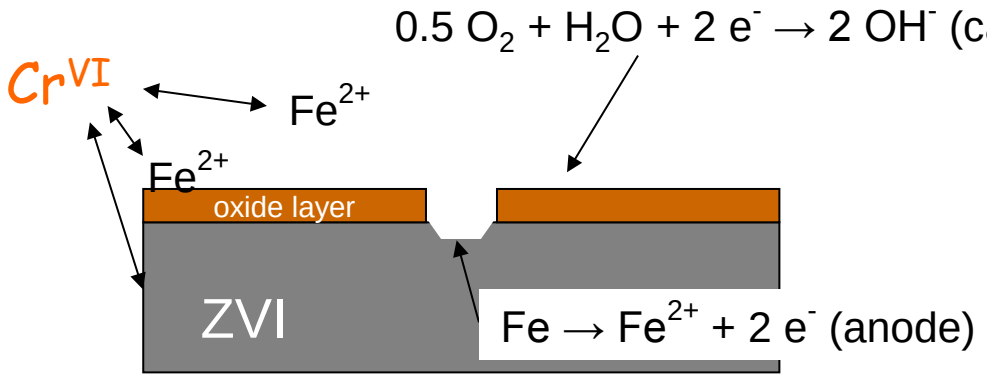


- Contaminants Cr(VI), Cu
- ~1 t Cr at a depth of 3-12 m
- Groundwater protection zone ([Cr(VI)]max = 0.01 mg/L)

$$Fe^0 + Cr^{VI}O_4^{2-} + 8H^+ \leftrightarrow Fe^{3+} + Cr^{3+} + 4H_2O$$

Permeable reactive barrier





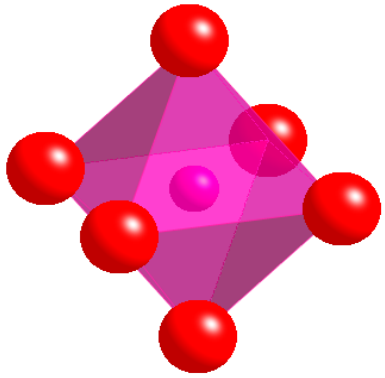
$$3Fe^{2+} + HCrO_4^- + 8H_2O = Fe_3Cr(OH)_{12}(s) + 5H^+$$

- homogeneous redox reaction (Buerge & Hug, 1997) → Molecular Cr/Fe ratio: 1/3 Hansel et al., 2003
- heterogeneous redox reaction (Buerge & Hug, 1999) → >1/3 (Cr clusters) Grolimund et al., 1999
- ZVI-Cr^{VI}-direct reaction (Liu et al., 2008) → ?

Local structure ↔ Mechanism

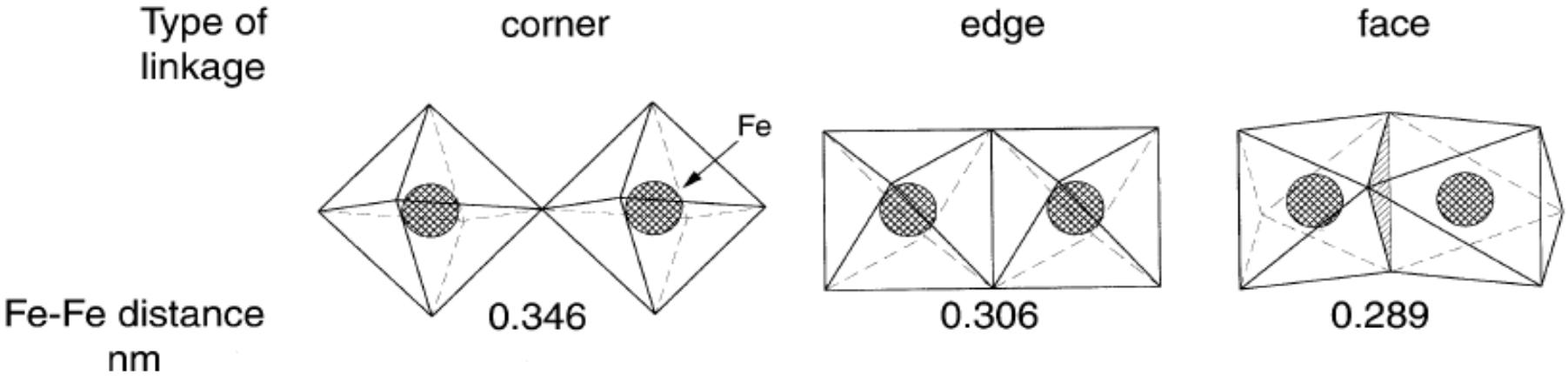
Hitchhiker's guide to molecular structure

The basic structural unit
of Fe^{III} and oxides:

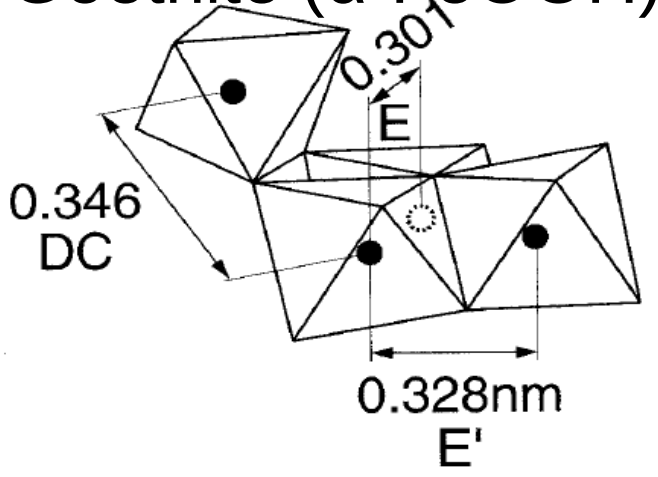


FeO_6 octahedron
(also: $CrO_3(OH)_3$ $FeO_3(OH)_3$)

Local structure



Goethite (α-FeOOH)



- interatomic distances
- 3D-arrangement

Why study local (~5Å) structure ?

Nucleation, growth, aggregation of mineral phases

Sorption complexes

Important properties e.g. color
(α-Cr_2O_3 – α-Al_2O_3:Cr^{3+})

Relation to molecular Fe/Cr
(-> mechanism)

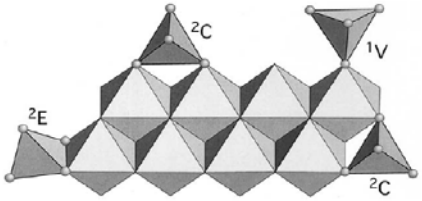
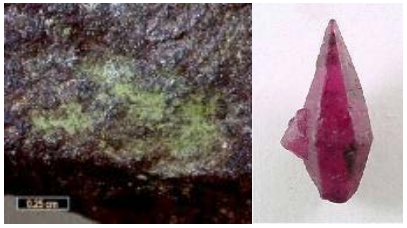
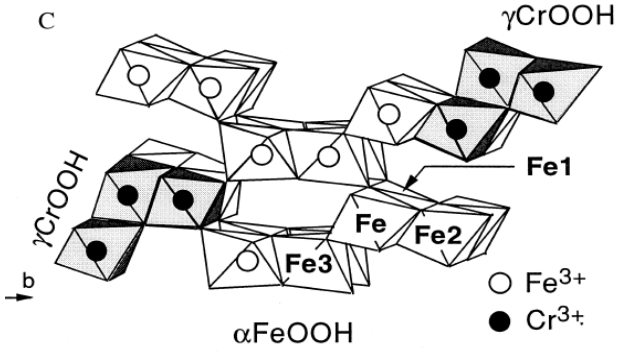


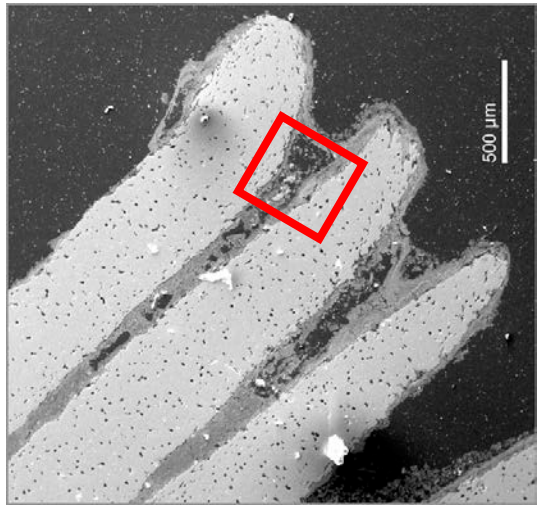
Fig. 1. Possible surface complexes of AsO_4 tetrahedra on goethite.

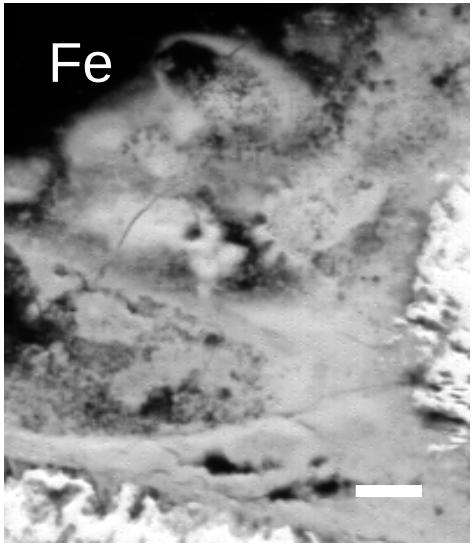
Sherman & Randall, GCA, 67 (2003), 4223.

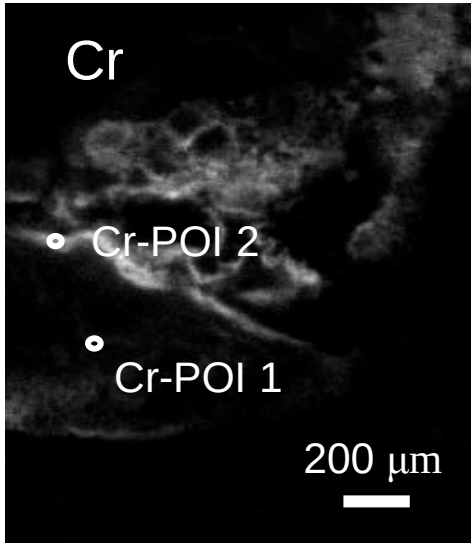


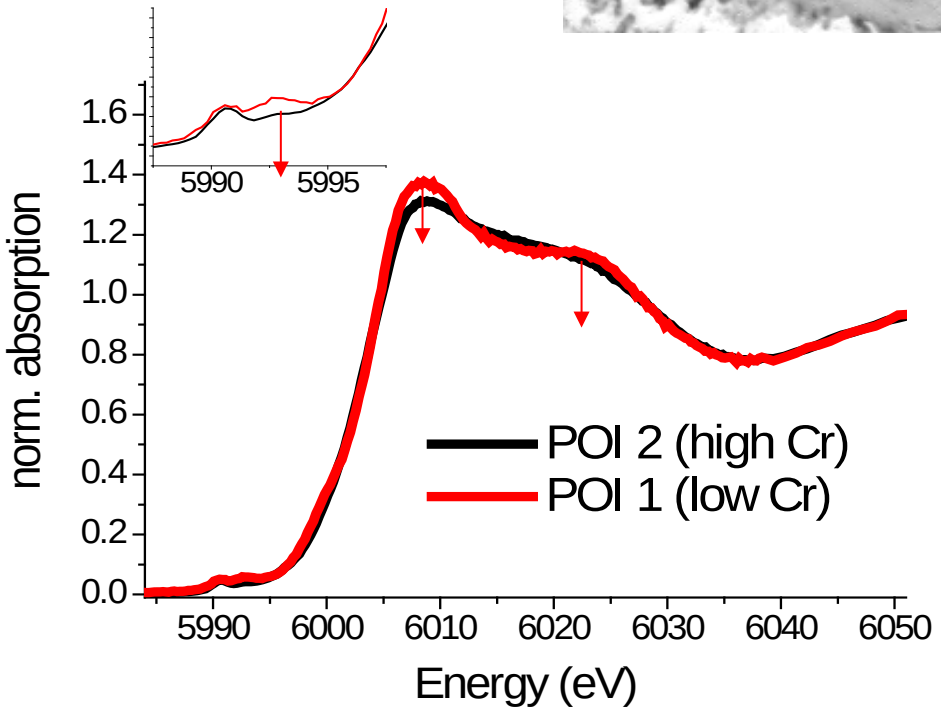


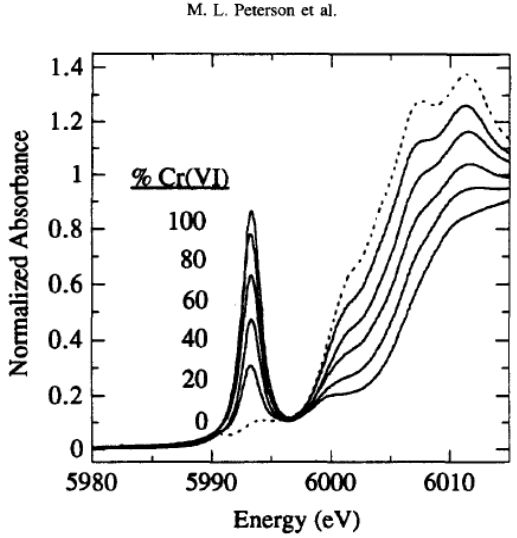
Permeable reactive barrier











Peterson et al., *GCA* 61: 3399, 1997.

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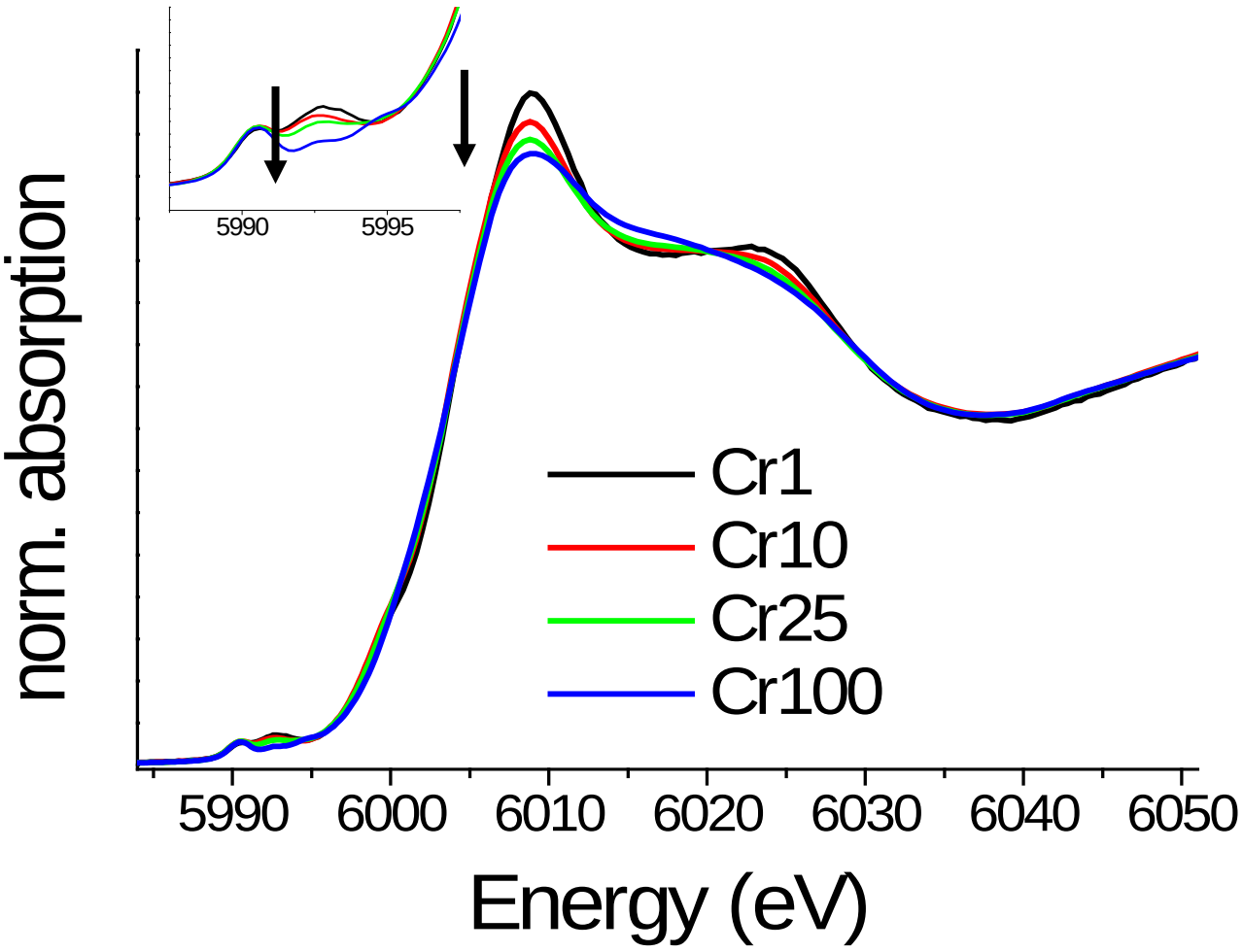
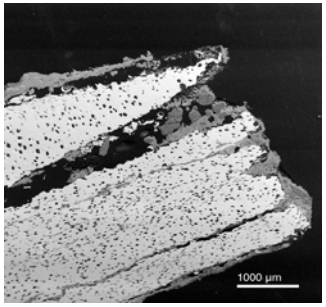
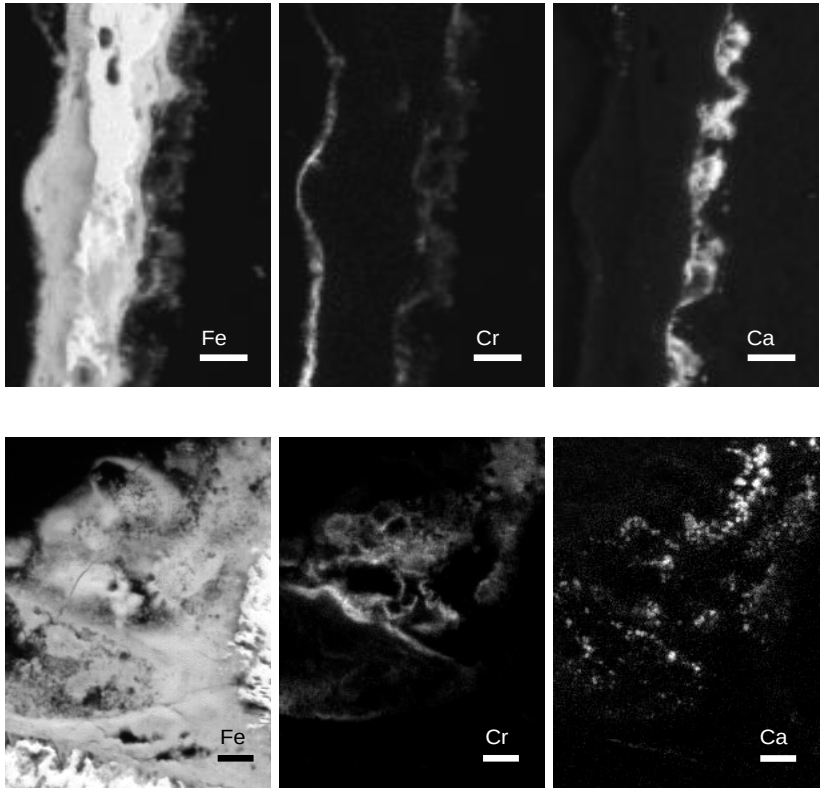
XANES

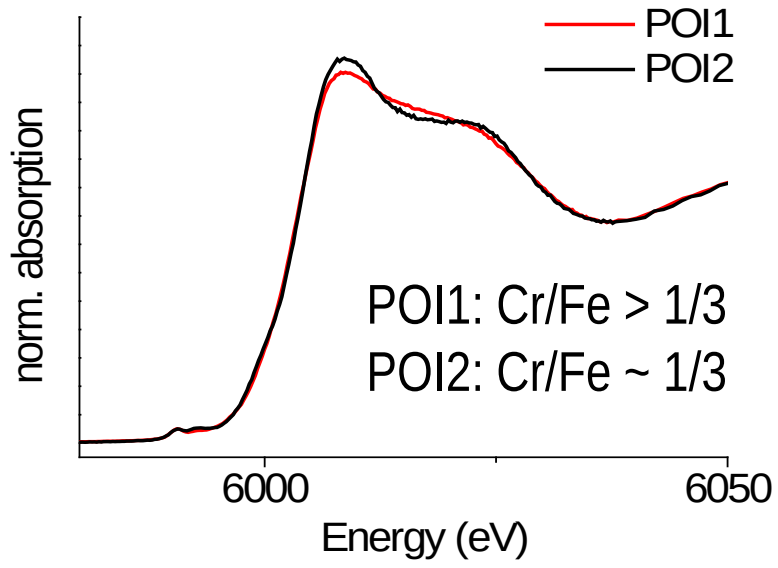


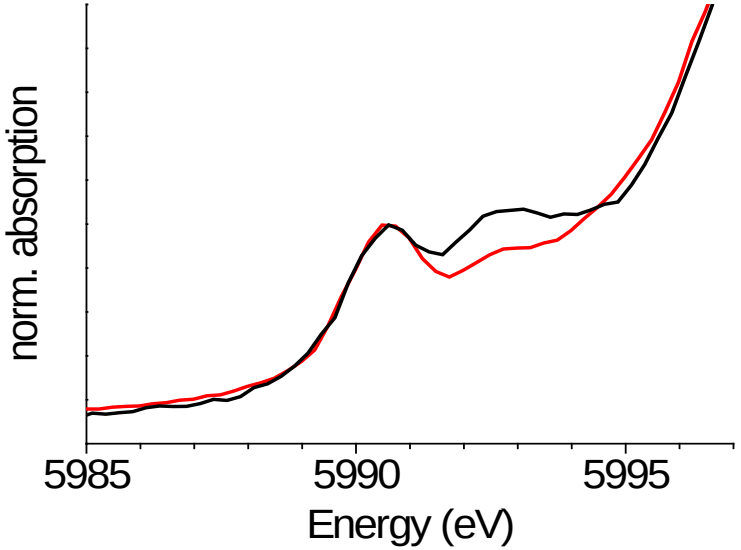
Back to the beginning: Permeable Reactive Barrier



Cr/Fe < 1/10







homogeneous & heterogeneous redox reactions

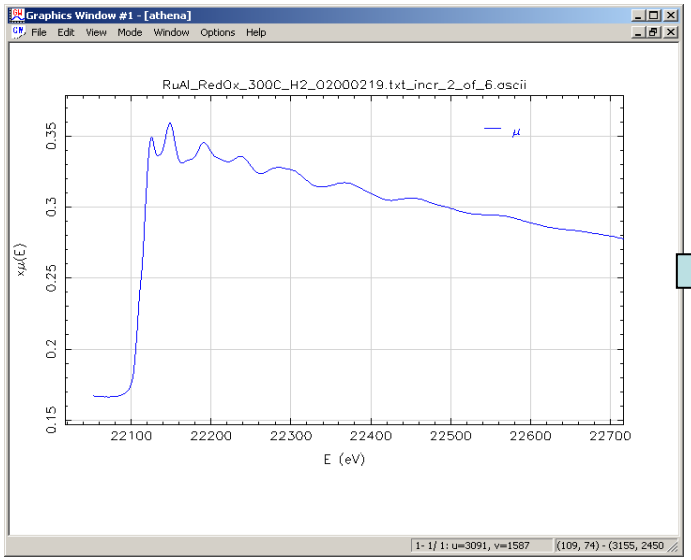
B. Flury, J. Frommer, U. Eggenberger, U. Mäder, M. Nachtegaal, R. Kretzschmar. *Environ. Sci. Tech.* 43, 6786-6792

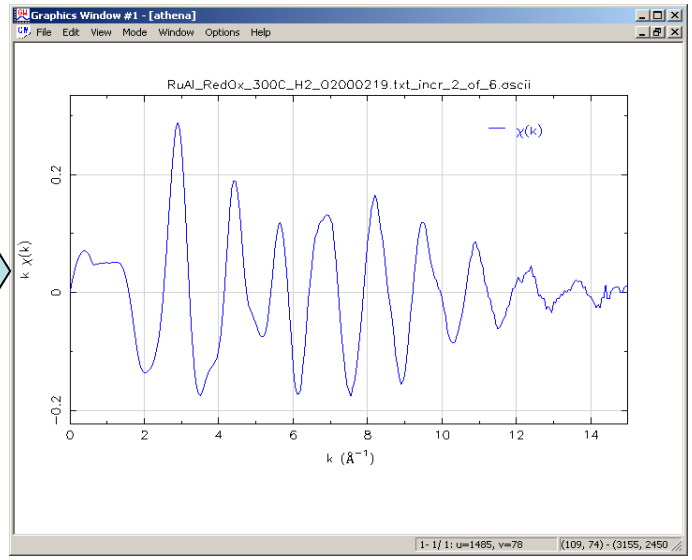
Tomorrow's goals:

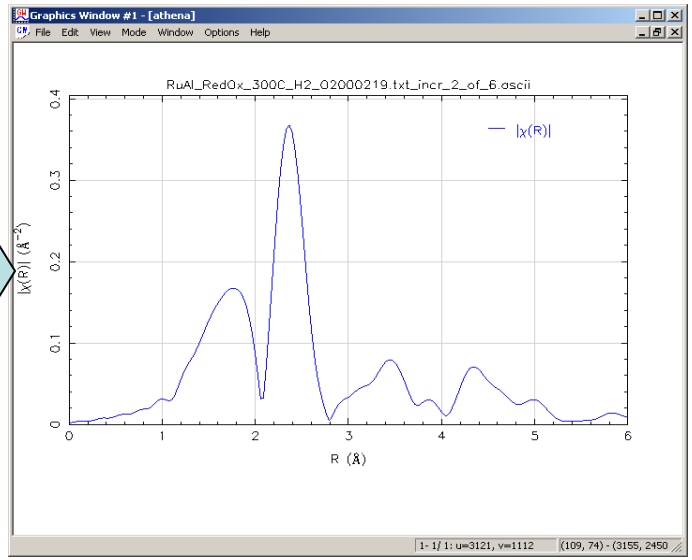
Basic data reduction steps of

- compare data that is measured in different modes (trans. / fluo.) and correct for different absorbances

- extract the EXAFS signal (chi(k)) and the Fourier-transformed EXAFS signal
  - look at radial distribution function, and fit the first shell neighbour

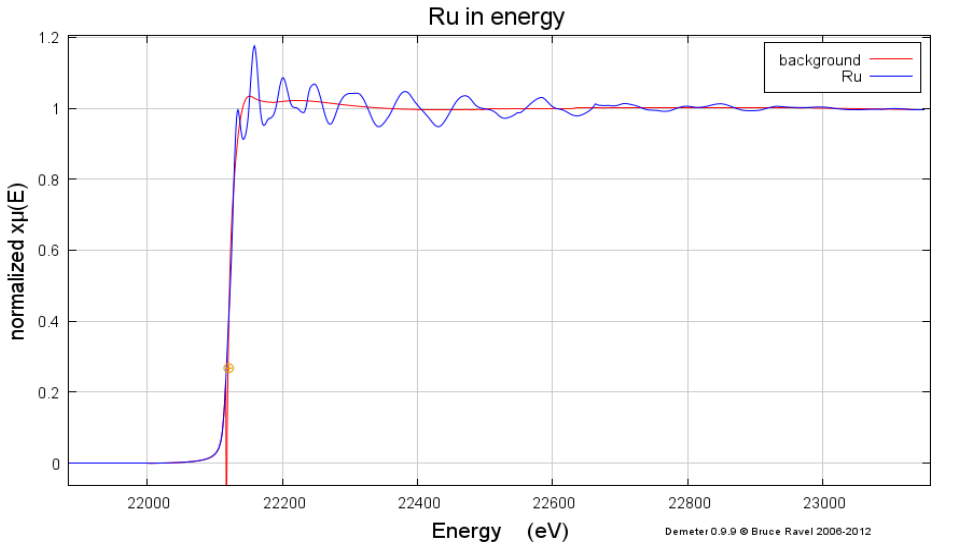


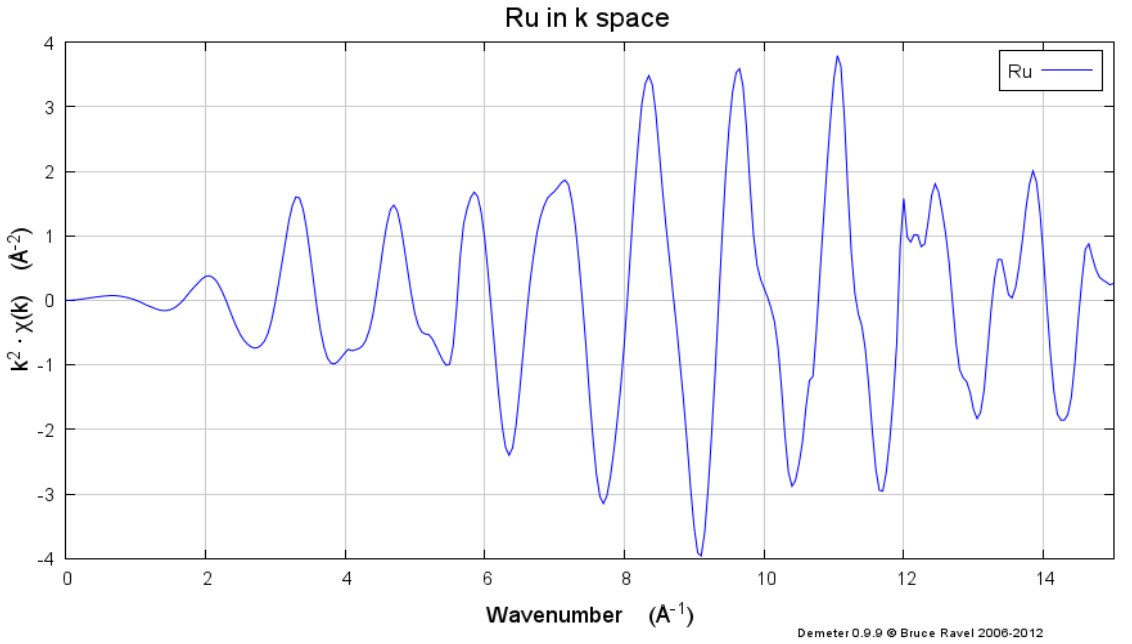




Excellent tutorial of Demeter (by Bruce Ravel): http://www.diamond.ac.uk/Beamlines/Spectroscopy/Techniques/XAS.html

Extraction of the EXAFS signal – chi(k)





1. Extract EXAFS signal

- Subtract smooth background

Normalized oscillatory part of absorption coefficient

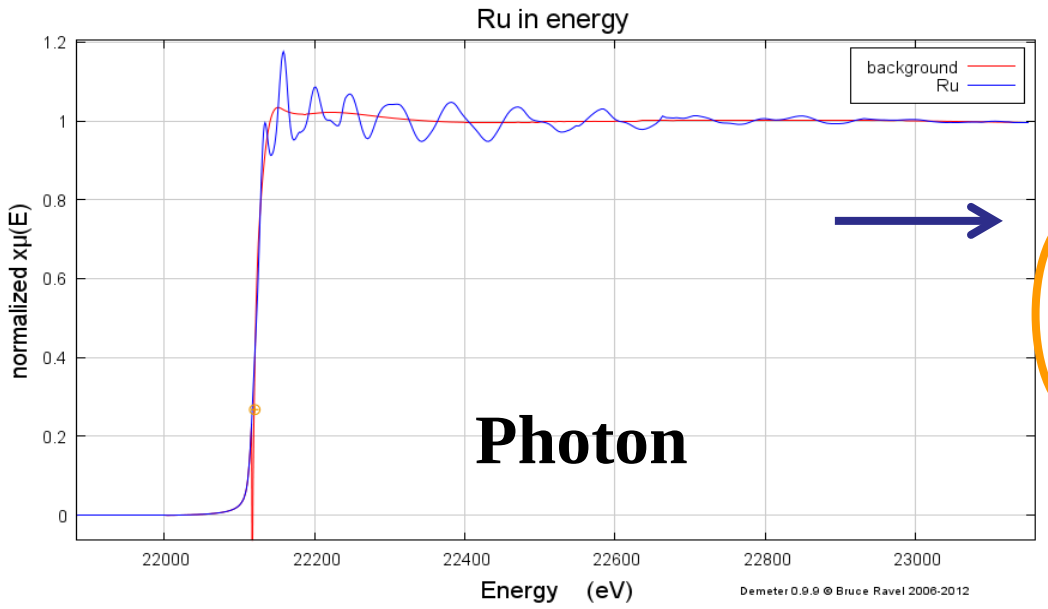
Measured Absorption coefficient

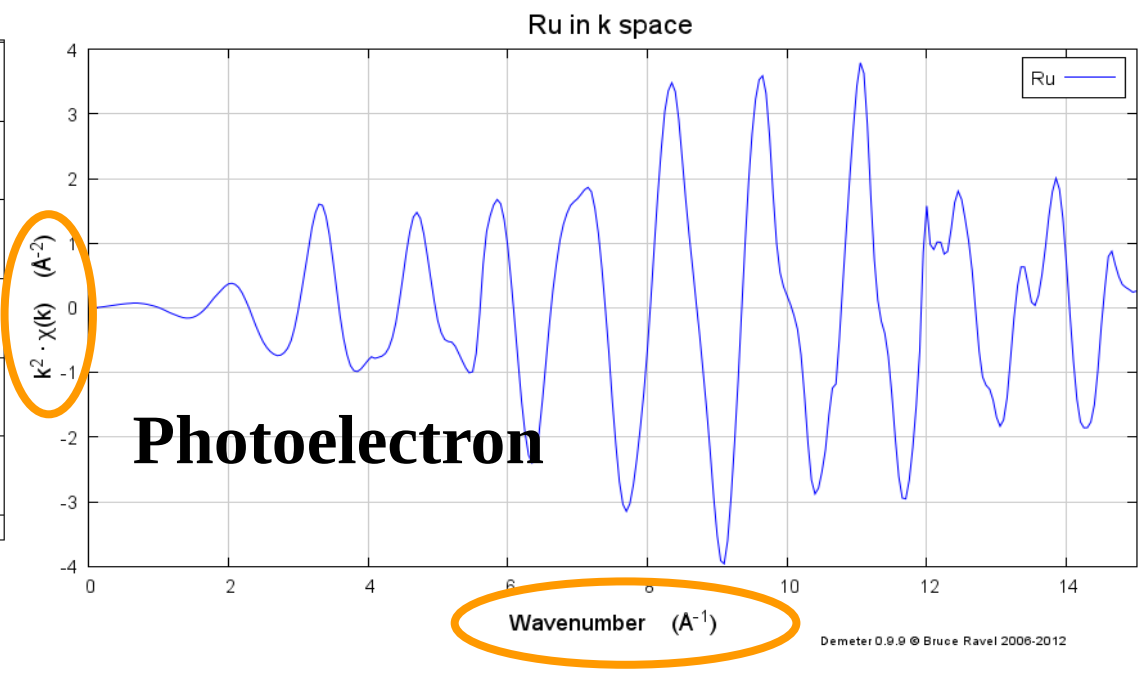
Bkg: Absorption coefficient without contribution from neighboring atoms (Calculated)

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)} \sim \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}$$

Evaluated at the Edge step (E_0)

Extraction of the EXAFS signal – chi(k)





2. Transformation from E-space to k-space

- Scattering of photoelectron on neighboring atoms

- Unit of k-space: inverse Angstroms
- „stretch“ the x-axis
- amplify signal at high energies (k-weight)

Mass of electron

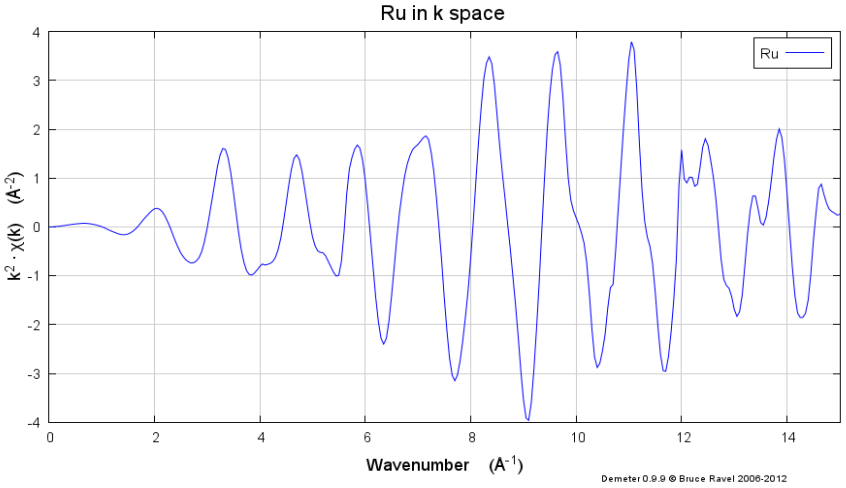
Edge Energy

$$k^2 = \frac{2m_e(E-E_0)}{\hbar^2} \sim \frac{\Delta E}{3.81}$$

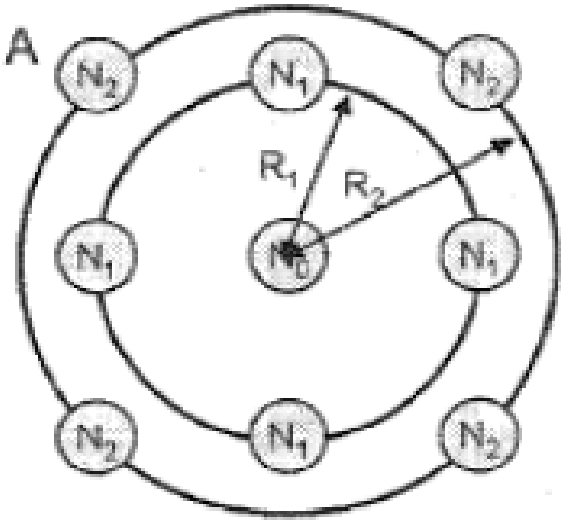
Plank's constant

Conversion of chi(k) to the pseudo radial distribution function (RDF)

To understand and visualize the geometric structure of our sample we need to Fourier transform the EXAFS signal from inverse distance into the distance domain



?

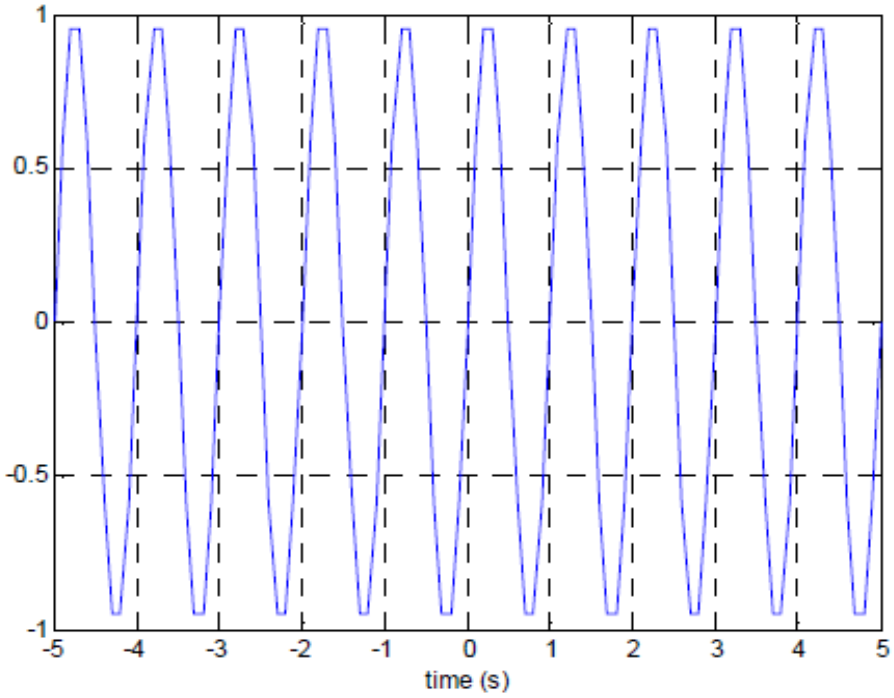


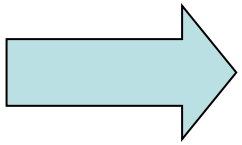
N_0 X-ray absorbing atom
N_1 1st neighboring scatterer (shell)
N_2 2nd neighboring scatterer (shell)

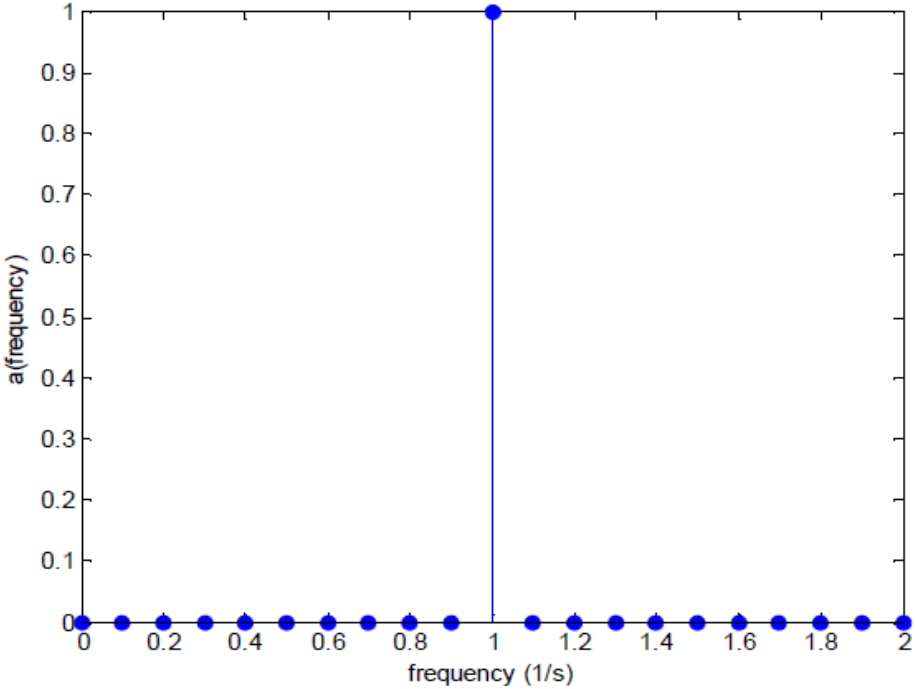
R_x distance between absorber and scatterer

Fourier transformation crash course

- FT transforms data from one dimension into its reciprocal one
- example: transformation from the time into the frequency domain







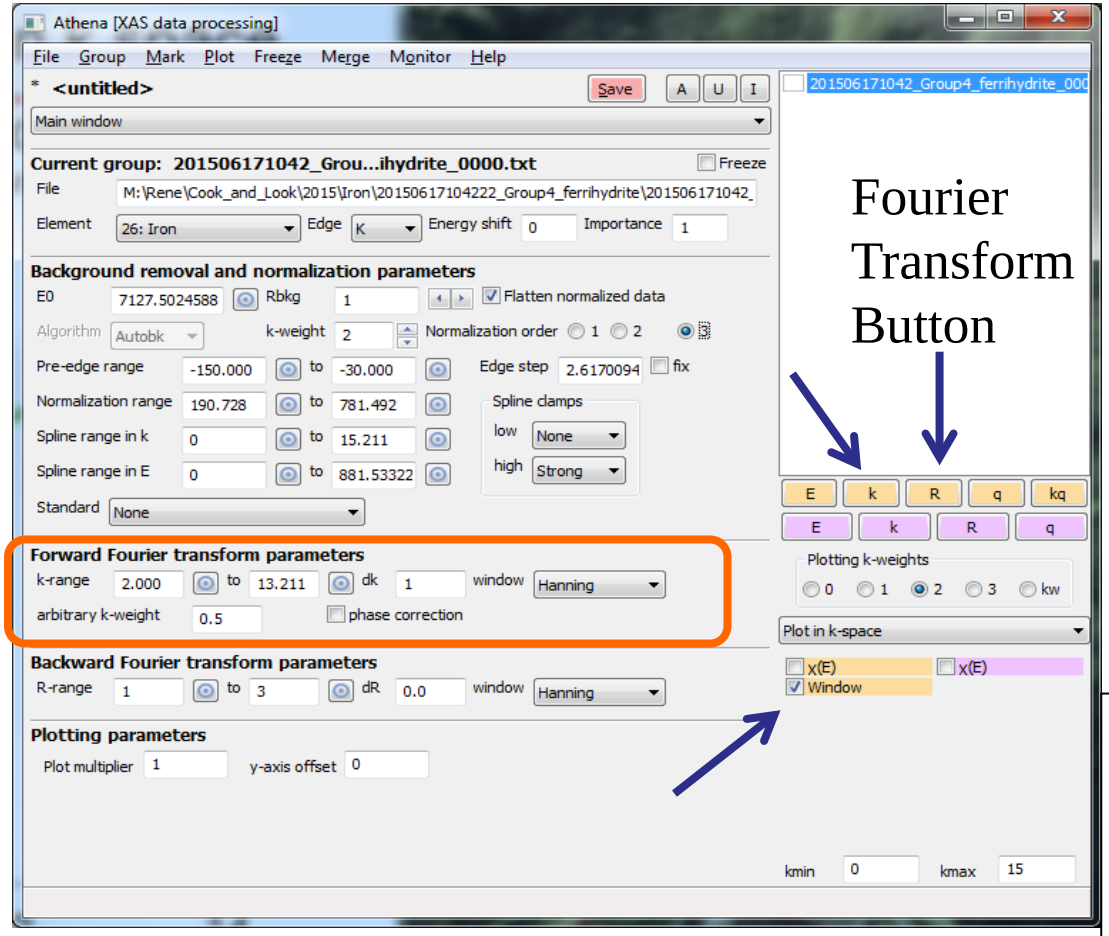
Wave function with period length of 1 s

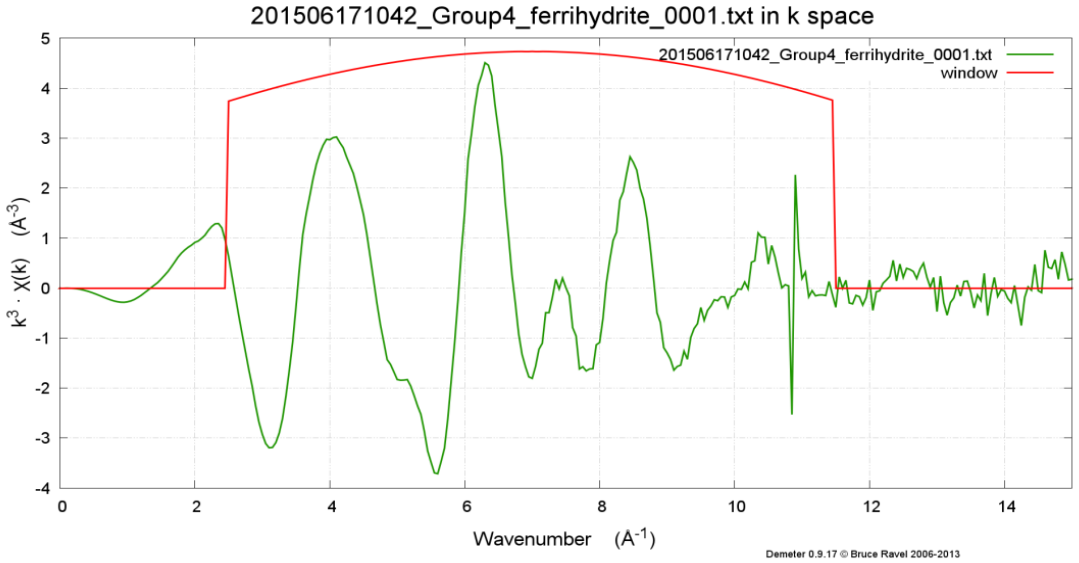
Frequency of 1 Hz

Conversion of chi(k) to the pseudo radial distribution function (RDF)

Define k-range for Fourier transformation

Lower limit: 2-3 $Å^{-1}$; upper limit: as far as reasonable (consider signal to noise)

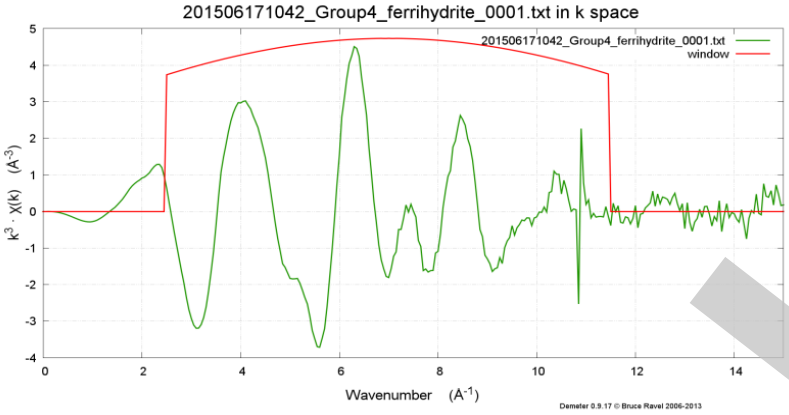




Recover the distance of scattering atoms from the frequency of the scattered wave

→ Fourier transform the EXAFS function (from $Å^{-1}$ to Å)

Conversion of chi(k) to the pseudo radial distribution function (RDF)



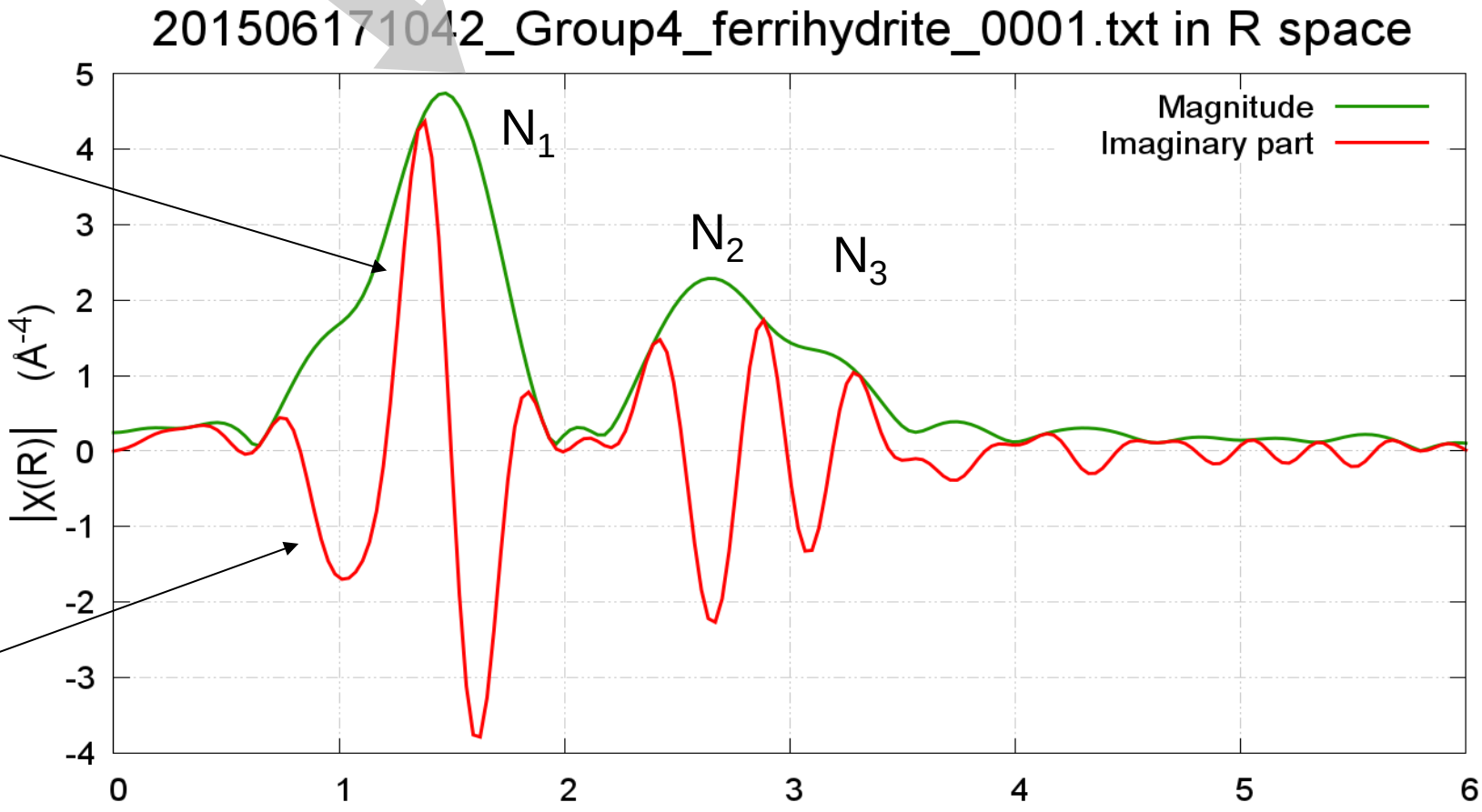
Fourier transformed of the EXAFS signal

Remember: FT creates a complex function

➔ always show magnitude AND real or imaginary part

magnitude

Imag part



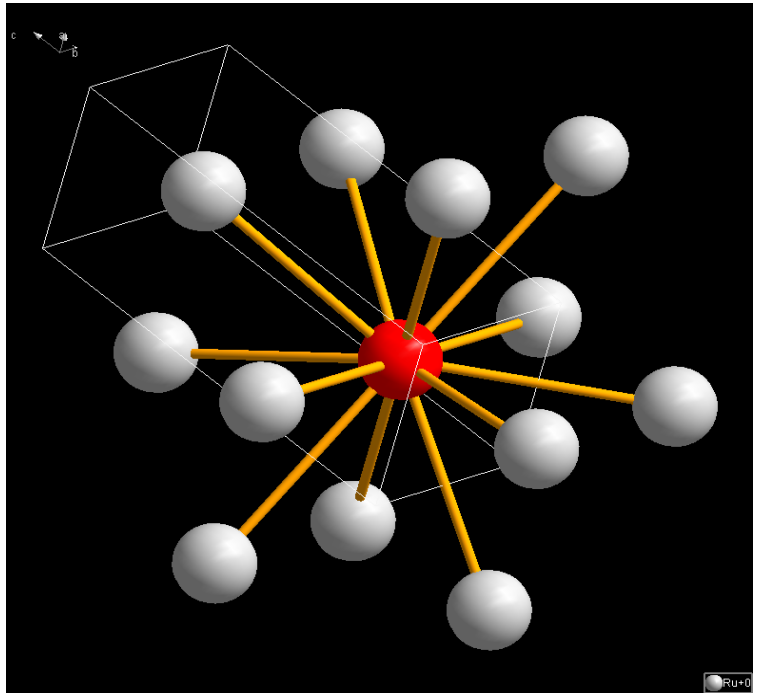
Part 2: Fitting of EXAFS data

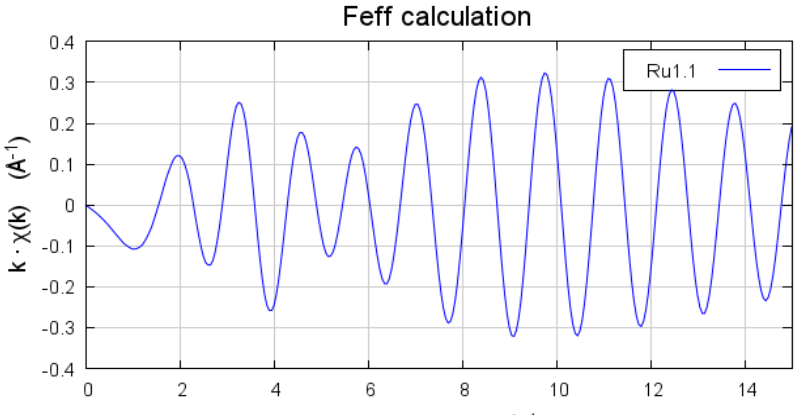
The pseudo RDF created in the previous step is now analyzed by fitting with a set of model structures

➔ Create a model of the assumed structure

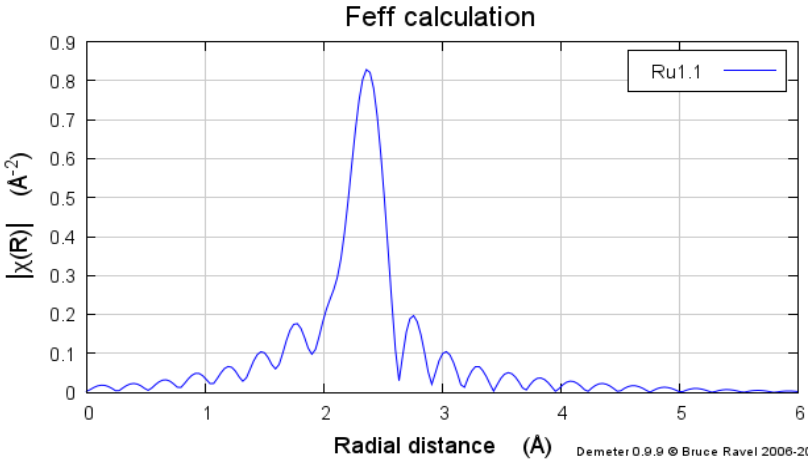
➔ Calculate the EXAFS function of this theoretical structure (ATOMS @ ifeffit)

➔ Fit the model to the data, extract structural parameters





Calculated scattered wave



Corresponding RDF

Part 2: Fitting of EXAFS data

What information can we extract from a fit?

EXAFS function

$$\chi(k) = \sum_i \frac{N_i F_i(k) S_0^2}{kR_i^2} e^{\frac{-2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin\left(2kR_i + \phi_i(k)\right)$$

Sum of damped sine functions with a pre-factor

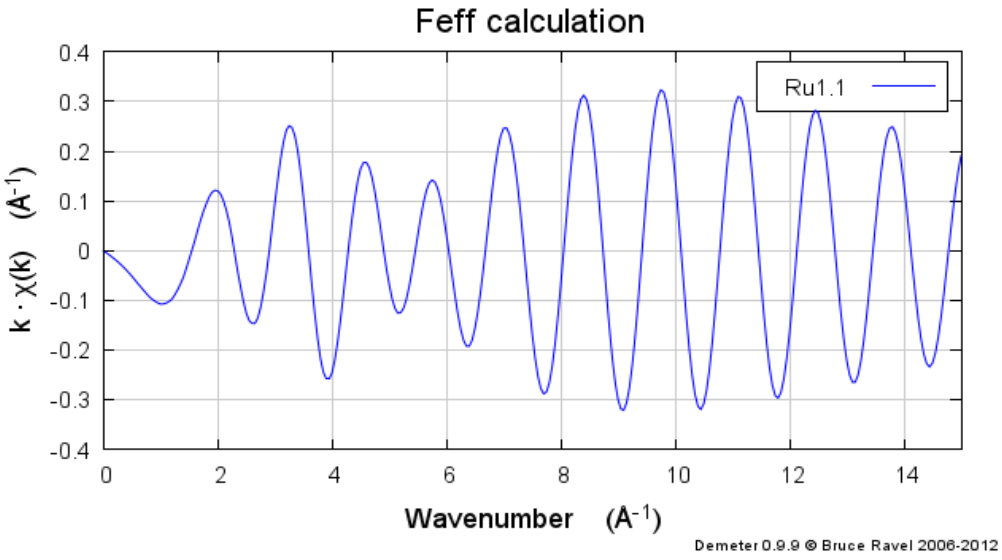
Structural Parameters:

N: coordination number → amplitude

R: radial distance → frequency

σ^2: pseudo Debye waller factor → damping

Theoretical first Ru-Ru shell of metallic ruthenium

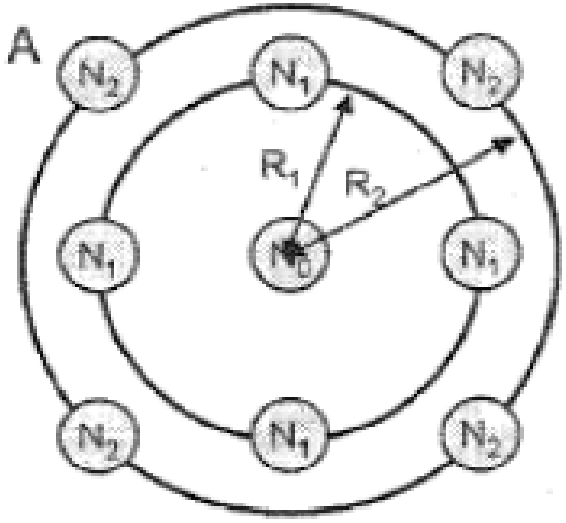


Calculate EXAFS signal of model compound! → FEFF

Part 3: Understanding the fit results

Reminder: what‘s a coordination shell?

Every shell of atoms has a specific distance from the absorber and a specific coordination number



From fitting of EXAFS data information about

- the distance R of each shell from the absorbing atom

- the number of atoms in each shell (coordination number) is obtained.

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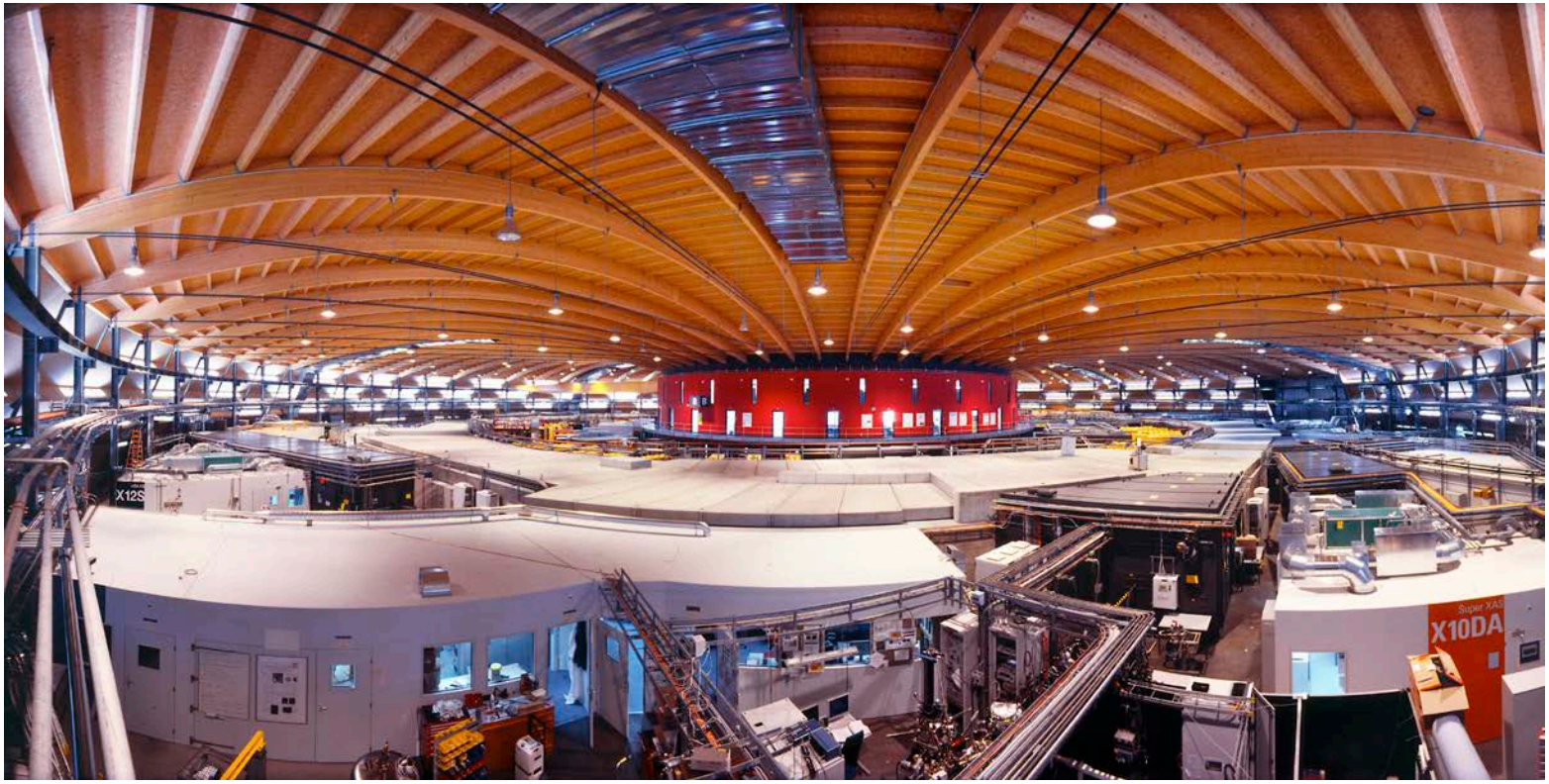
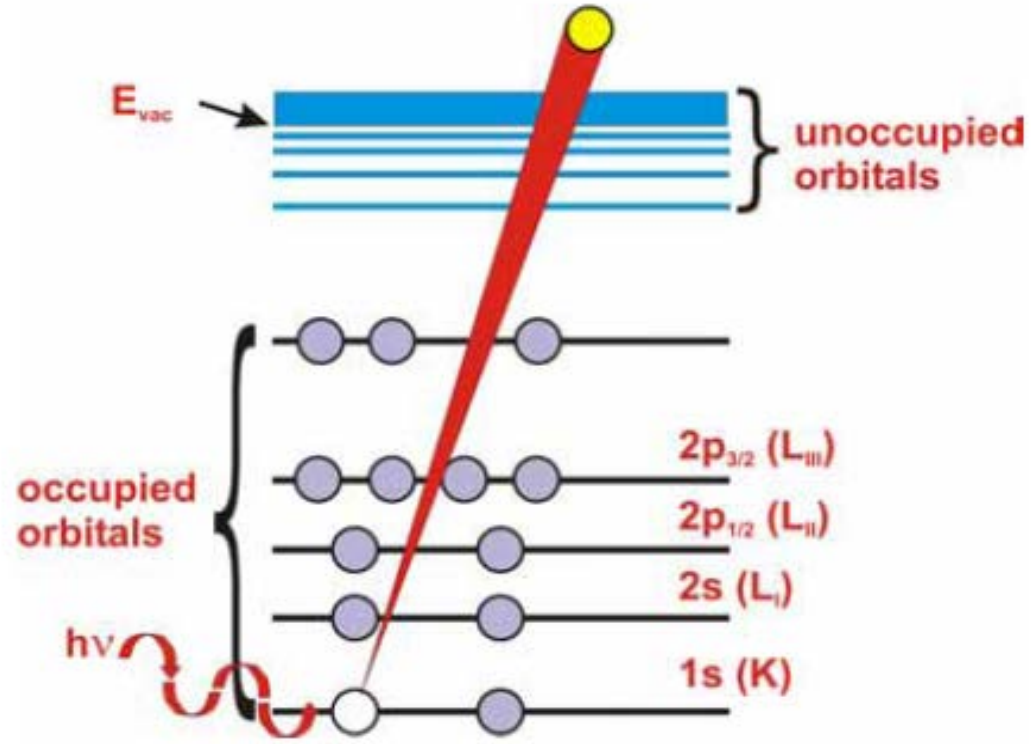
XAS at the Swiss Light Source

Beamline	Energy Range (keV)	Spot Size (μm)	K-Edges	Absorption	Fluorescence	Electron yield	Speciality
PHOENIX	0.8 - 8	2 x 2	Na - Co	x	x	x	**Energy Range Variable Pola-rization**
MicroXAS	5 - 23	1 x 1	Ti - Mo	x	x		**Femto Diffraction radioactive samples**
SuperXAS	6 - 40	5 x 10	Cr - La	x	x		**Absorption, Fluorescence, Quick, Chemical environmnets**
Pollux	0.2 - 1.2	0.04 x 0.04	C - Mg	X	(X)		**Nano focus, STXM, absorption spectroscopy, phase contrast**
nanoXAs	0.2 - 1.2	0.04 x 0.04	C - Mg	??	??	X	**Combine AFM with STXM**



Thank you for your attention! Questions?

The basic concept of XAFS

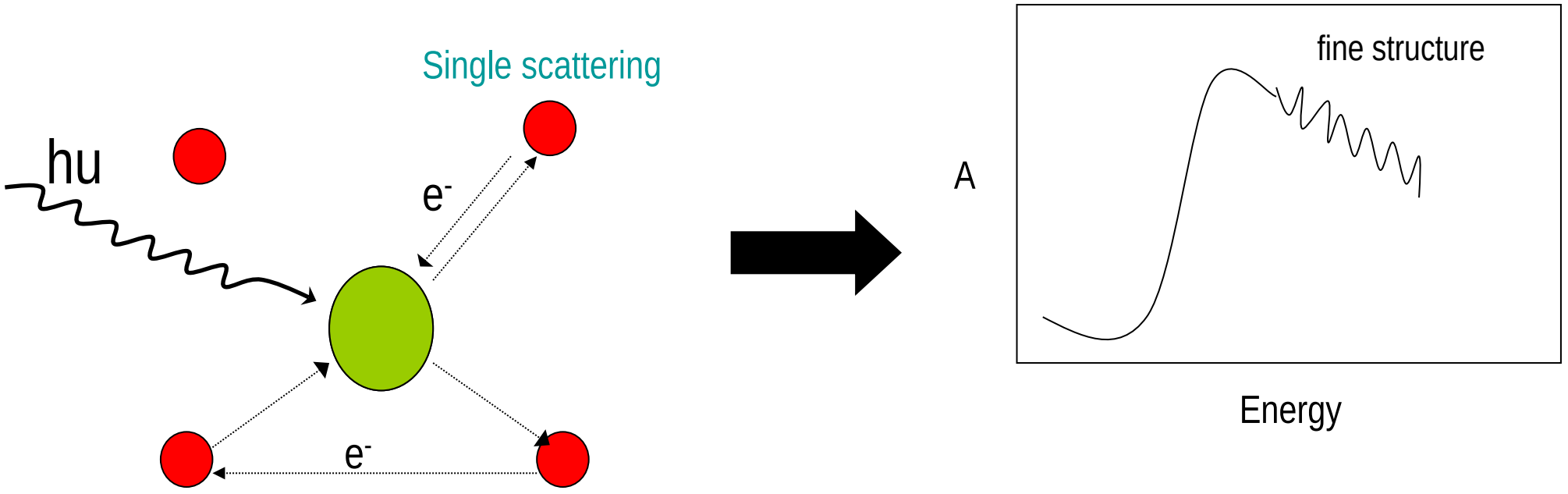


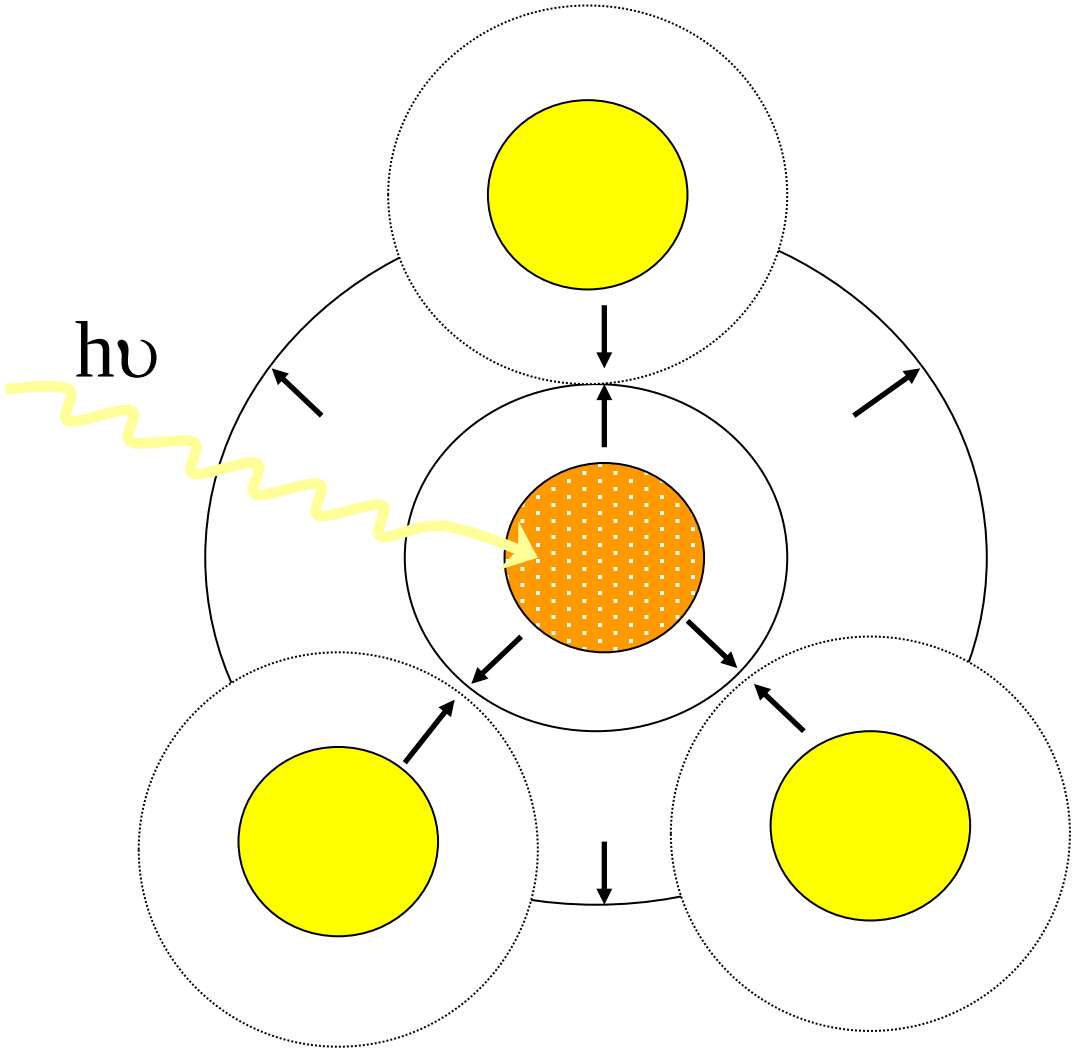
X-rays (light with wavelength 0.06- 12 Å or energy 1-200 keV) are absorbed by all matter through the photo-electric effect:

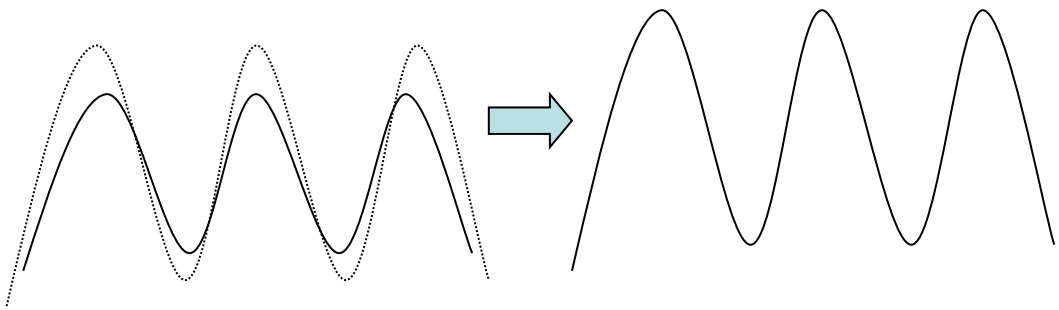
An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core level electron (K, L, or M shell) which is subsequently ejected from the atom. Any excess energy from the X-ray is given to the ejected photo-electron.

Cook and Look 2015

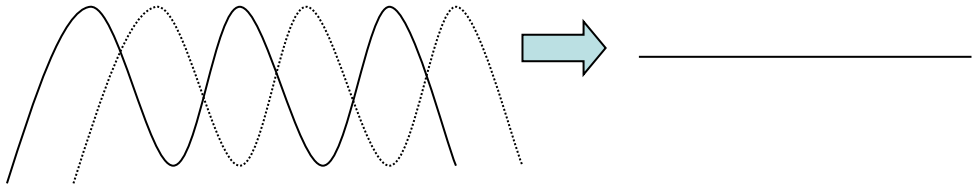
Electrons have a particle and wave nature. The photoelectron wave propagates away from the central atom (absorber), and it may scatter off neighboring atoms and finally return to its point of origin.







In phase



Out of phase

The consequence of these scattering phenomena and wave interactions is that the intensity of X-ray absorption oscillate with a dependence on the structural environment of the absorber. Mathematically modeling these oscillations provides precise local structural information.