



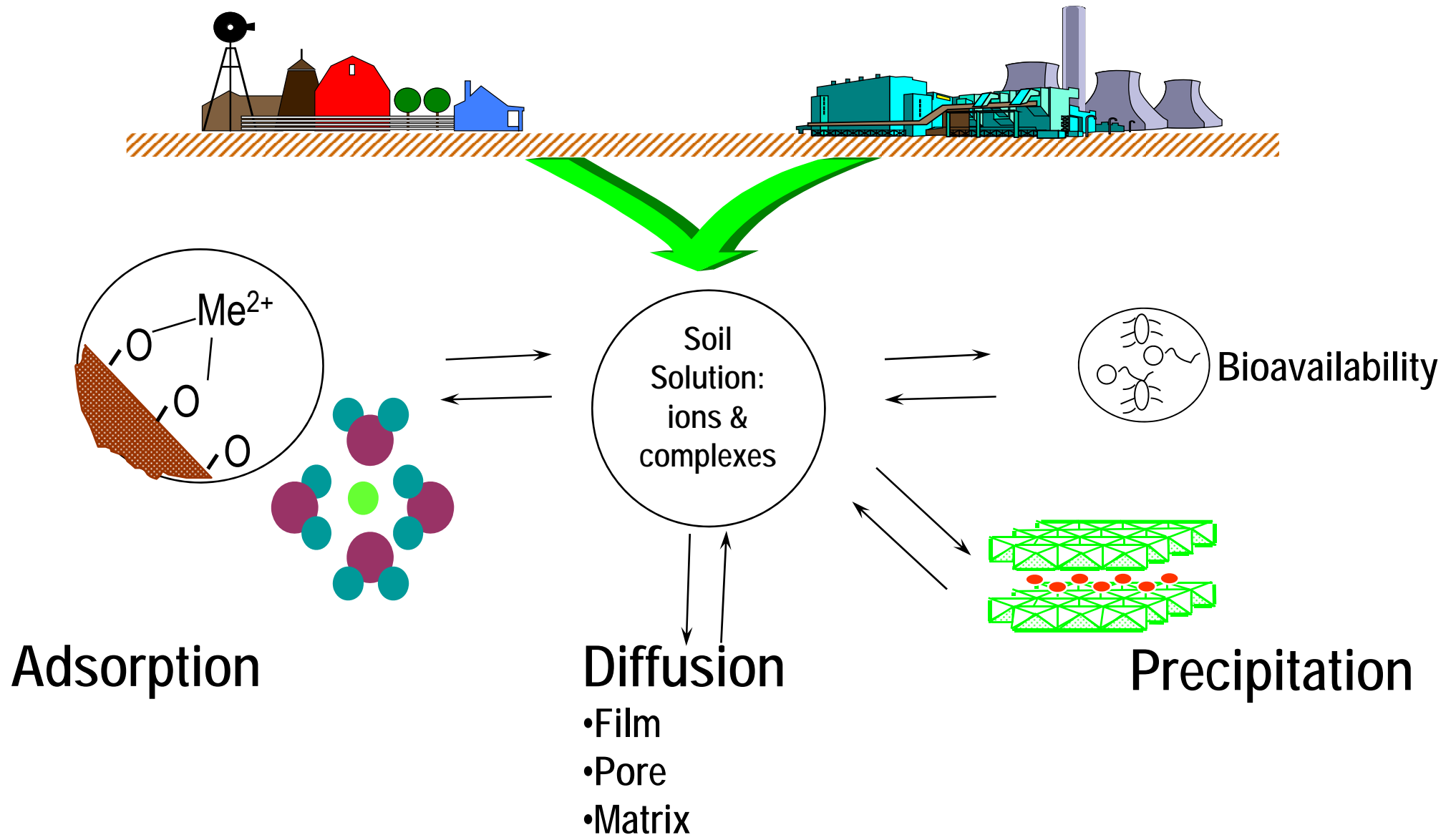
Wir schaffen Wissen – heute für morgen

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



- 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

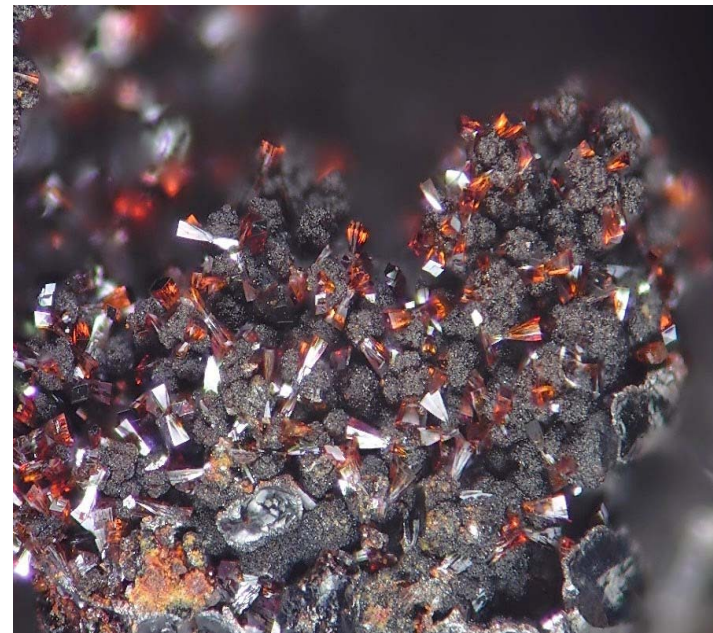
Structure/chemical formula unclear



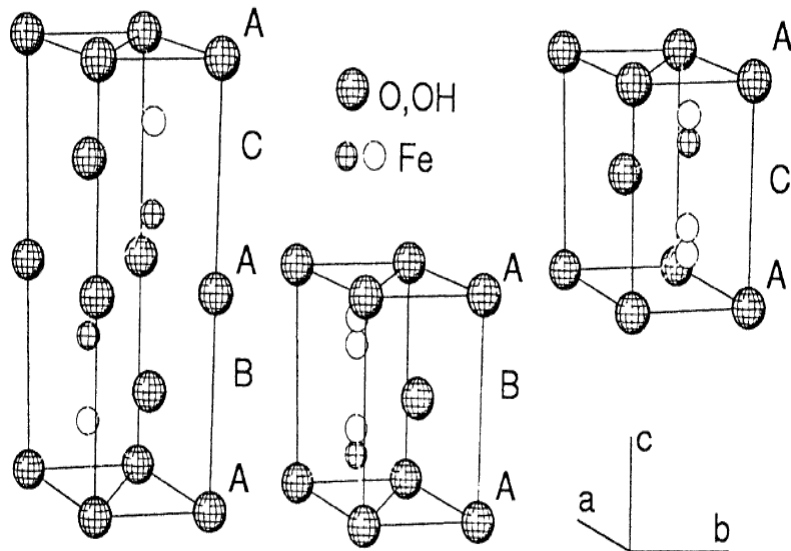
Lepidocrocite

Orthorhombic crystal structure

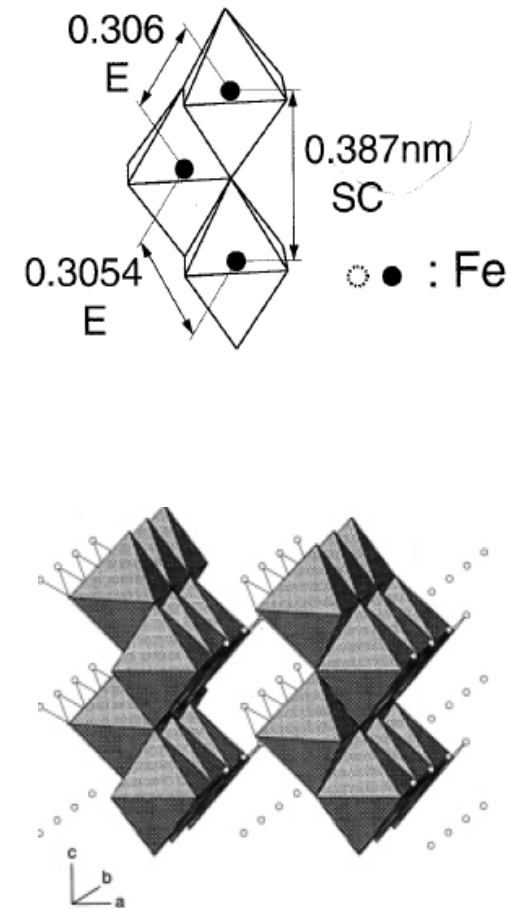
Well-crystalized



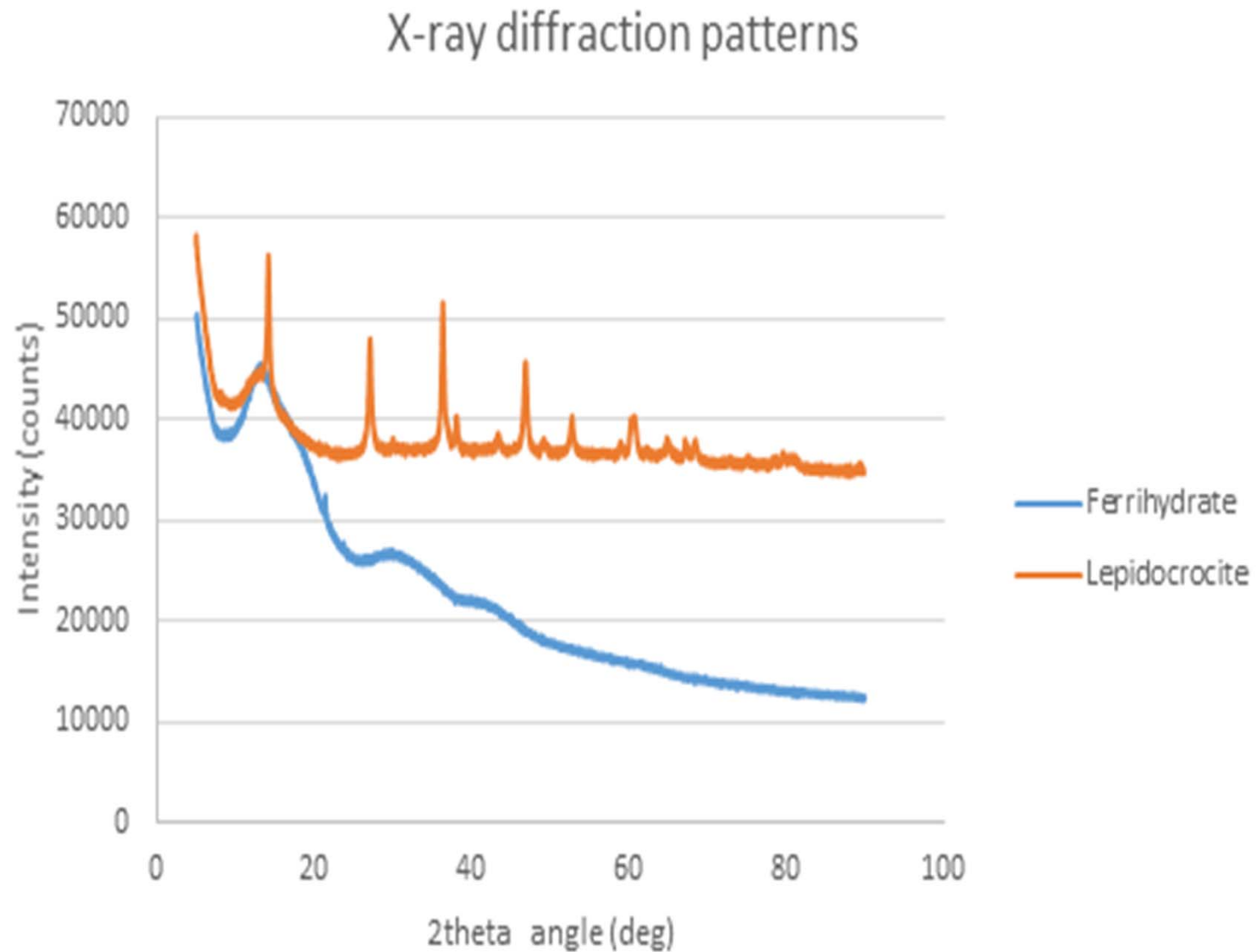
Ferrihydrite $\text{Fe}_5\text{O}_8\text{H} \cdot 4\text{H}_2\text{O}(\?)$



Lepidocrocite ($\gamma\text{-FeOOH}$)



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



cod by the curvature coupling of stretching loss to the reaction coordinate (2.6–2.8), i.e., a bifurcation of reaction paths for stretched reactants must occur, presumably near minimum energy of the transition state. The internal branching fraction for the nonadiabatic pathway is quite substantial, $\alpha_1^0/(\alpha_1^0 + \alpha_1^1) \sim 0.5$ from Fig. 3 (where α_1^0 and α_1^1 are the pair cross sections for the (0,0) and (1,0) last pairs from the stretch-excited reactants, respectively), indicating a facile process. Theory predicts a strong Coriolis coupling between stretching and bending modes (20, 27); this is nonadiabatic transition could then be initiated and facilitated by the transitional nature of bending motions of the CD, moiety during source of the reaction.

References and Notes
1. C. H. Hsu, *Acc. Chem. Res.* **5**, 161 (1972).
2. R. N. Zurek, *Science* **279**, 1075 (1998).
3. F. F. Crim, *Acc. Chem. Res.* **32**, 877 (1999).
4. K. Liu, *J. Chem. Phys.* **125**, 112307 (2006).
5. Y. Yan, S. H. Hsu, A. N. Zurek, F. F. Crim, *J. Chem. Phys.* **116**, 10744 (2002).
6. S. Yan, R. J. Hilday, F. F. Crim, *J. Chem. Phys.* **119**, 4555 (2003).
7. S. Yan, R. J. Hilday, F. F. Crim, *J. Chem. Phys.* **119**, 998 (2003).
8. R. J. Hilday, C. H. Hsu, C. J. Anzures, F. F. Crim, *J. Chem. Phys.* **125**, 10101 (2006).
9. M. R. Simpson, T. P. Radtke, S. A. Kariak, L. J. Lee, R. N. Zurek, *J. Phys. Chem.* **100**, 7938 (1996).

The Structure of Ferrihydrite, a Nanocrystalline Material

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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 $P6_3/mc$; $a = 5.35$ Å, $c = 9.06$ Å). In its ideal form, this structure contains 20% tetrahedrally and 80% octahedrally coordinated iron and has a basic structure. Real-space fitting indicates structural second-order effects such as internal

Ferrihydrite is ubiquitous in surface environments (1, 2) and is used in industrial applications (3, 4). It occurs in pristine soils as the precursor to hematite as a result of acid mine drainage. Because of its extremely high surface reactivity, ferrihydrite plays a substantial

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 pre-nucleation 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 ferrihydrite protein. We isolated a 10 Å 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 Å spherical ferrihydrite nanoparticles. Fe_{13} may therefore also be a pre-nucleation cluster for ferrihydrite formation in natural systems, including by microbial and cellular processes.

Iron oxides and oxyhydroxides are ubiquitous in the environment and serve vital roles in interrelated phenomena of contaminant transport, pH control of surface and ground water, and microbial activity (1–4). Relevant phases include hematite, magnetite, goethite, and ferrihydrite. The structure of ferrihydrite,

the most common iron oxyhydroxide in soil and in the core of the ferrihydrite protein, is constructed to the Al₁₃ Keggin cluster (5). The ferrihydrite structure has been highly debated (6–8), but the general framework contains linked and fused iron-oxyhydroxide Keggin units. The Keggin ion or molecule is a metal-oxo structural motif in natural and synthetic materials (9). Even before the proposed structure of ferrihydrite, an iron Keggin cluster (henceforth referred to as Fe_{13}) was presumed to be synthetically attainable—analogue to

the Al₁₃-Keggin cluster ($Al_3O_4(Al_9O_{18})(H_2O)_4$)₄⁷⁻, which was first crystallized and structurally characterized over 50 years ago (10).

The identified nonclassical growth behavior of iron oxides in both nature (3) and the laboratory (2)—defined by the aggregation of pre-nucleation clusters rather than atom-by-atom growth—supports the existence of a discrete Fe_{13} ion as a precursor to ferrihydrite and magnetite (Fig. 1). However, the higher reactivity (acidity) of Fe^{3+} -bound H_2O as compared with Al^{3+} -bound H_2O in the Al₁₃ Keggin ion has thus far thwarted all synthetic efforts to capture a discrete Fe_{13} ion from water. Instead, iron oxyhydroxide nanoparticles and precipitates are obtained, bypassing the intermediate discrete cluster state. The closest species to Fe_{13} reported thus far is $[Fe_3O_4(Fe_9O_{18})(OCH_3)_4]^{7-}$ (11). Although possessing the Keggin structure, this cluster was synthesized in anhydrous conditions and is surface-passivated entirely with nonaqueous ligands. It is neither a truly precursor for iron oxide nucleation, nor provides identification of the aqueous ligands and net charge of Fe_{13} derived from water.

Here, we present strategies to stabilize and crystallize the discrete Fe_{13} Keggin ion from water and redissolve it in water, both as unassociated and aggregated forms. Because Fe_{13} is a very highly charged polyanion, contrary to the analogous Al₁₃ polycation, we chose likewise highly charged counteranions (Bi^{3+})

of iron as a nutrient. They have many commercial applications: pigments, catalysts, medical devices, sensors, and recording media. Nanotechnology increasingly makes use of iron oxide nanoparticles and thin films.

Iron oxides exist in a few dozen varieties of polymorphs (1). Anhydrous iron oxides include hematite (α - Fe_2O_3), magnetite (γ - Fe_2O_3), and the less common δ - and β - Fe_2O_3 , Fe_3O_4 (mag-

netite), and Fe_3O_4 (wüstite) contain both ferrous and ferric iron. Magnetite and magnetite, both spinels, can form a continuous solid solution. The oxyhydroxides, nominally $Fe(OH)_3$, include goethite, lepidocrocite, akaganeite, and several other polymorphs. They often contain excess water. More hydrated forms such as ferrihydrite, nominally $Fe(OH)_3$, have even more variable water content. Hydrated phases containing both ferrous and ferric iron include the green rusts, layered hydroxides with different anions in the interlayer. A further complication is that many iron oxides, both in nature and in the laboratory, are exceedingly fine-grained (nanophase) and therefore hard to characterize.

This complexity has meant that until recently, knowledge of the structural details, thermodynamics, and reactivity of iron oxides has been lacking. One could not understand or predict which phases form under what conditions, which polymorphs are stable and which metastable, and

S^0 (J mol ⁻¹ K ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (J mol ⁻¹)	ΔH^0 (J mol ⁻¹)
87.4 ± 0.2 (3)	-274.5 ± 0.3 (3)	-744.4 ± 1.3 (3)	0.75 ± 0.16 (13)	1.9 ± 0.3 (18)
93.0 ± 0.2 (17)	-268.9 ± 0.3 (17)	-731.4 ± 2.0	0.57 ± 0.10 (4)	0.71 ± 0.13 (8)
		-717.8 ± 6.6 (15)		
59.7 ± 0.2 (17)	-237.9 ± 0.2 (17)	-490.6 ± 1.5	0.60 ± 0.10 (12)	0.91 ± 0.09 (8)
65.1 ± 0.2 (17)	-232.5 ± 0.2 (17)	-482.7 ± 3.1	0.40 ± 0.16 (10)	0.62 ± 0.14 (8)
53.8 ± 3.3 (3)	-246.2 ± 3.3 (3)	-481.7 ± 1.9	0.34 ± 0.04 (11)	0.44 ± 0.04 (8)
		-483.1 ± 1.3 (13)		
		-711.0 ± 2.0 (15)		

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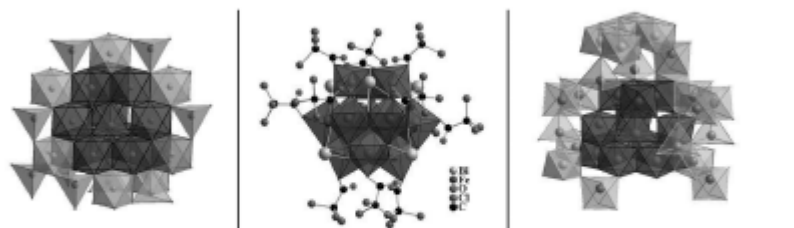
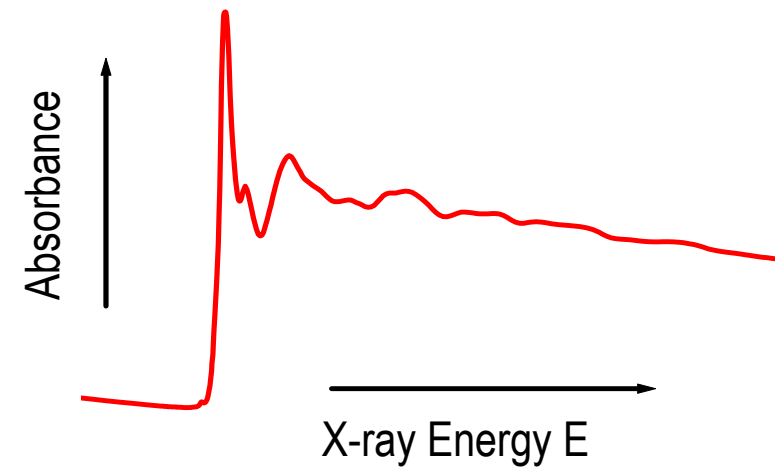


Fig. 1. The iron Keggin ion. Views of the iron Keggin ion in different structures. (Left) Magnetite, $(Fe^{1/3})(Fe^{2/3})_{13}O_4$ emphasizing the e Keggin building unit (red polyhedra). The four trimers of edge-sharing octahedra are likewise connected together by edge-sharing. (Middle) $Bi_3+(FeO)_{13}O_4(OH)_{10}(O_2CCH_3)_4]^{7-}$. $Bi_3+(FeO)_{13}$ in the a 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 $8-Fe_{13}$ building block. In the δ isomer, three of the trimers are edge-sharing, and the fourth is corner-linked.

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



X-ray absorption spectroscopy

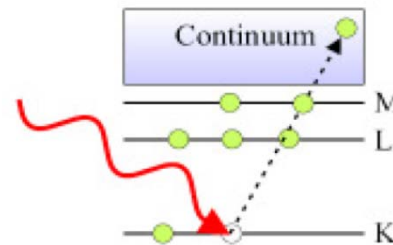
Visible light
 $\lambda \sim 0.5 \mu\text{m}$
 $E \sim 2 \text{ eV}$



X-ray light
 $\lambda \sim 1 \text{ \AA} (=0.1 \text{ nm})$
 $E \sim 10 \text{ keV}$



valence
electrons

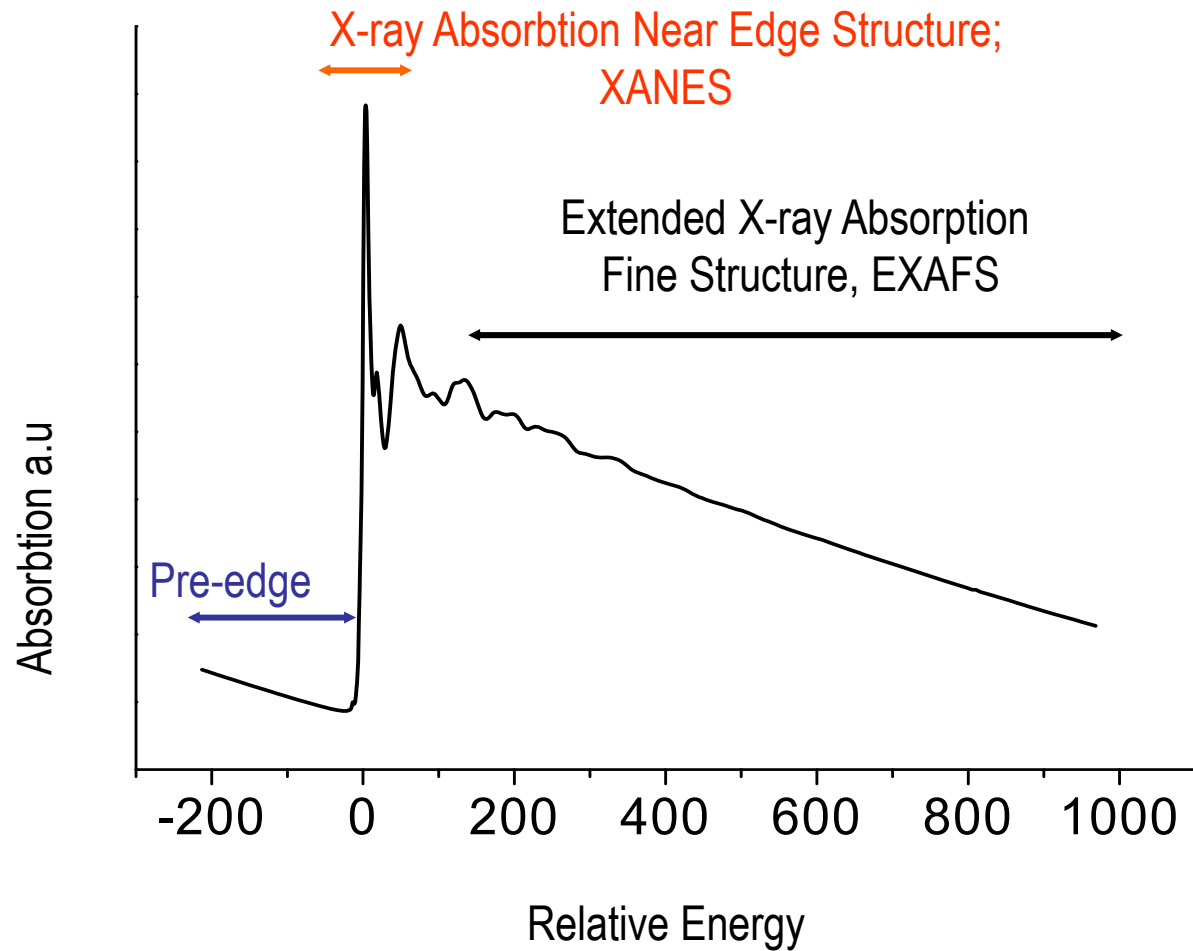
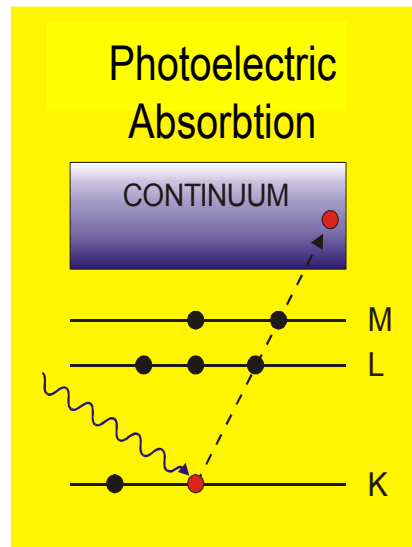


core
electrons

Energy
↑



Main Principle



Pre-edge

- $E < E_b$
- 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)

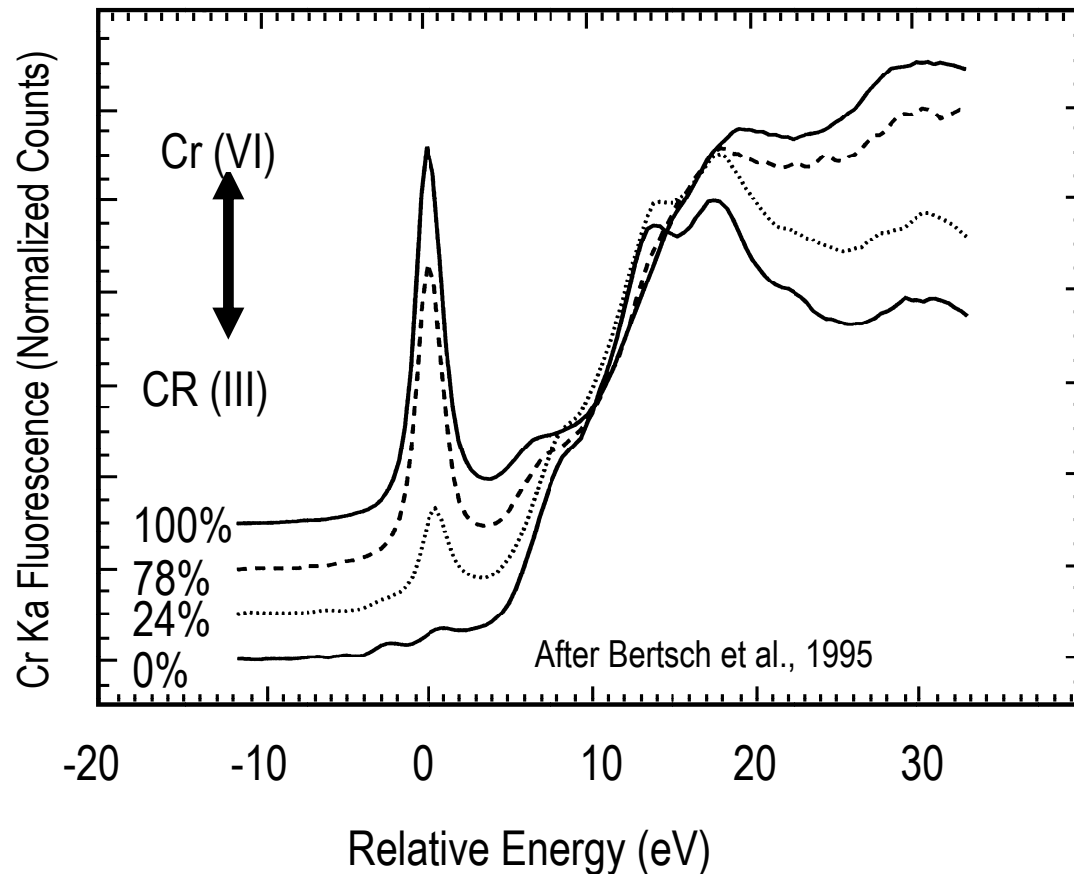
- Cr(VI)

- toxic and mobil

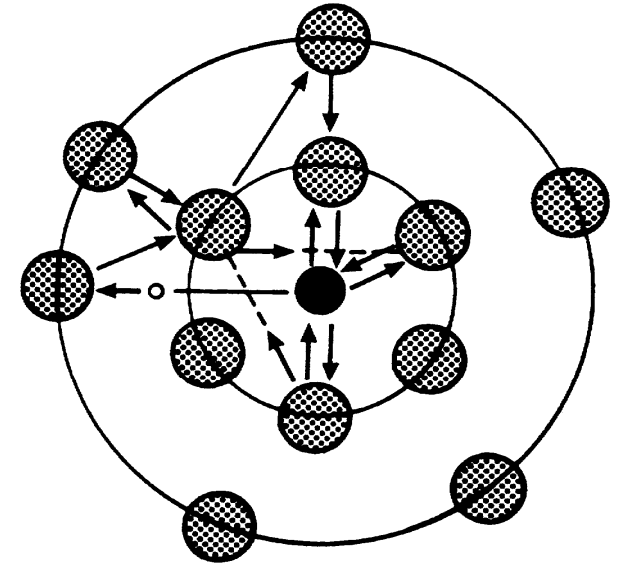
- Cr(III)

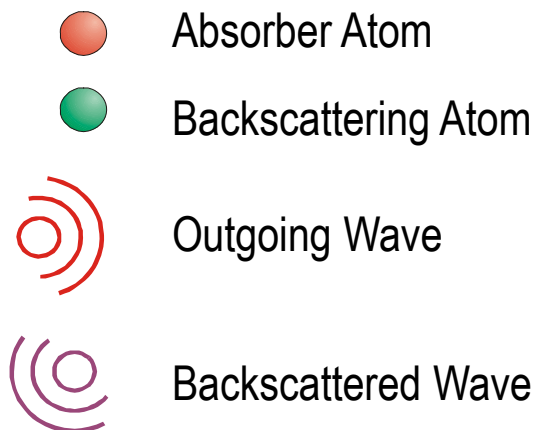
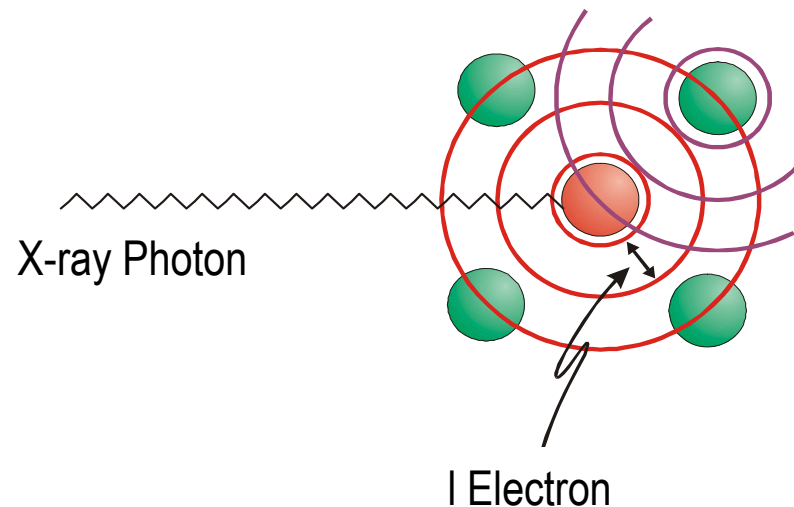
- hardly toxic

- sorbed or incorporated into mineral phases



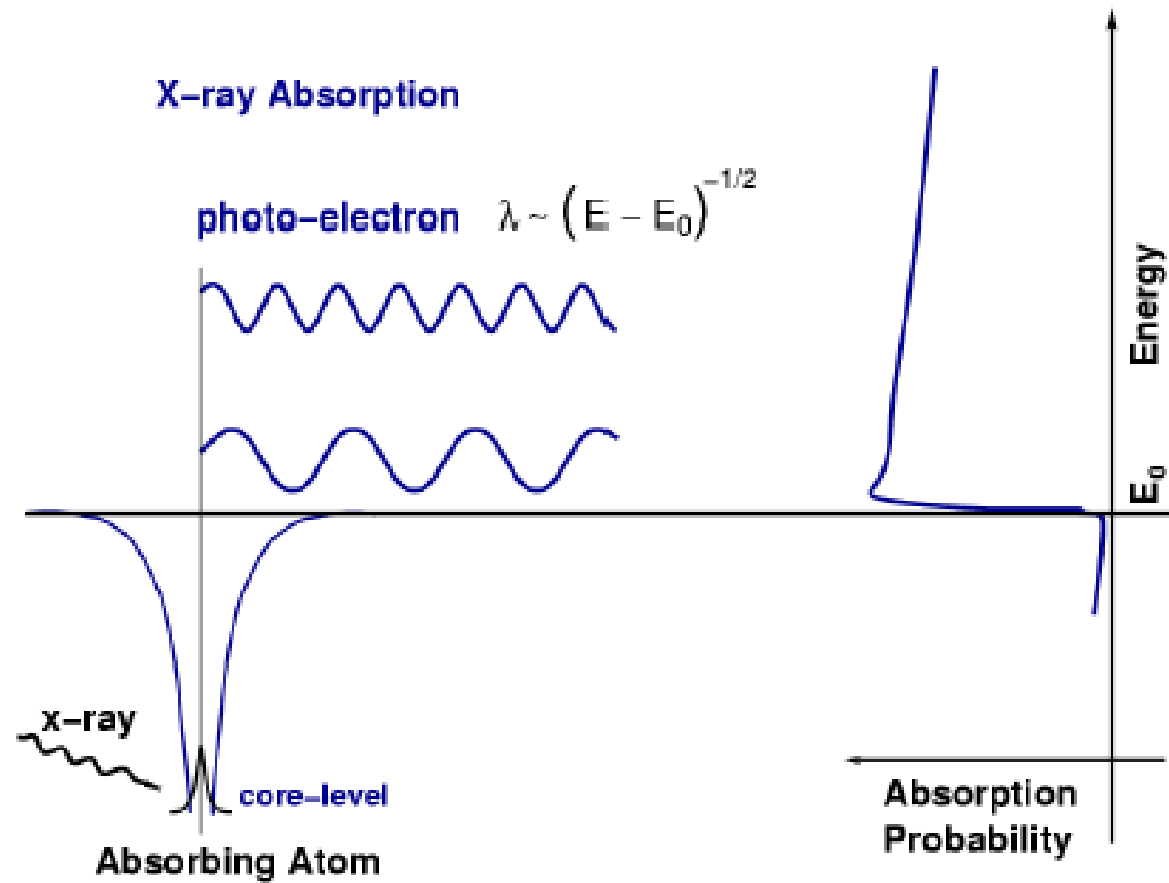
- $E \sim E_b$
- Multiple scattering of photoelectron
- Very intense and complicate resonance features: fingerprinting and theoretial calculations
- Energy of absorption edge depends on oxidation state
 - o Chemical shift of 1-3 eV for each withdrawing e^-



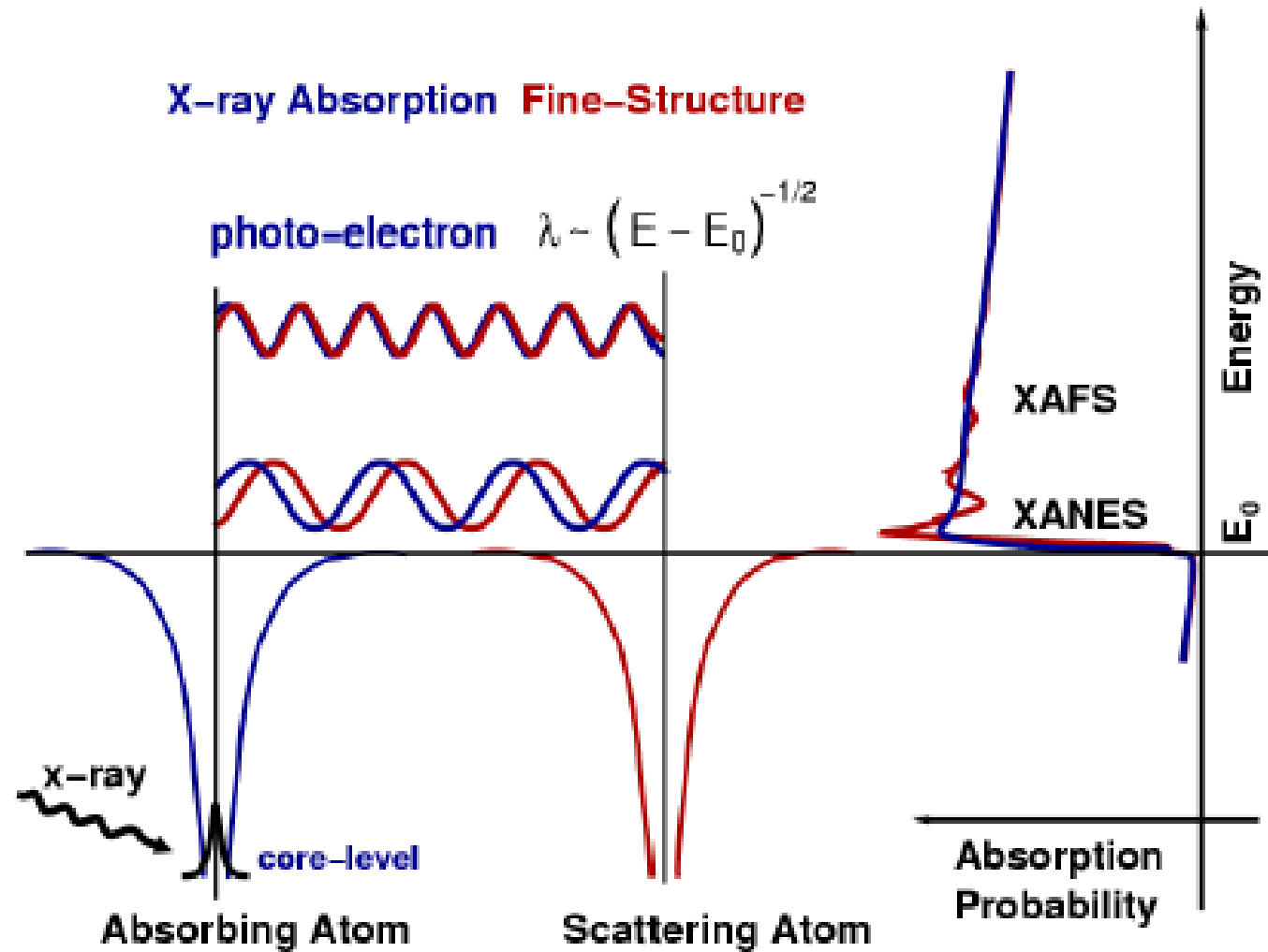


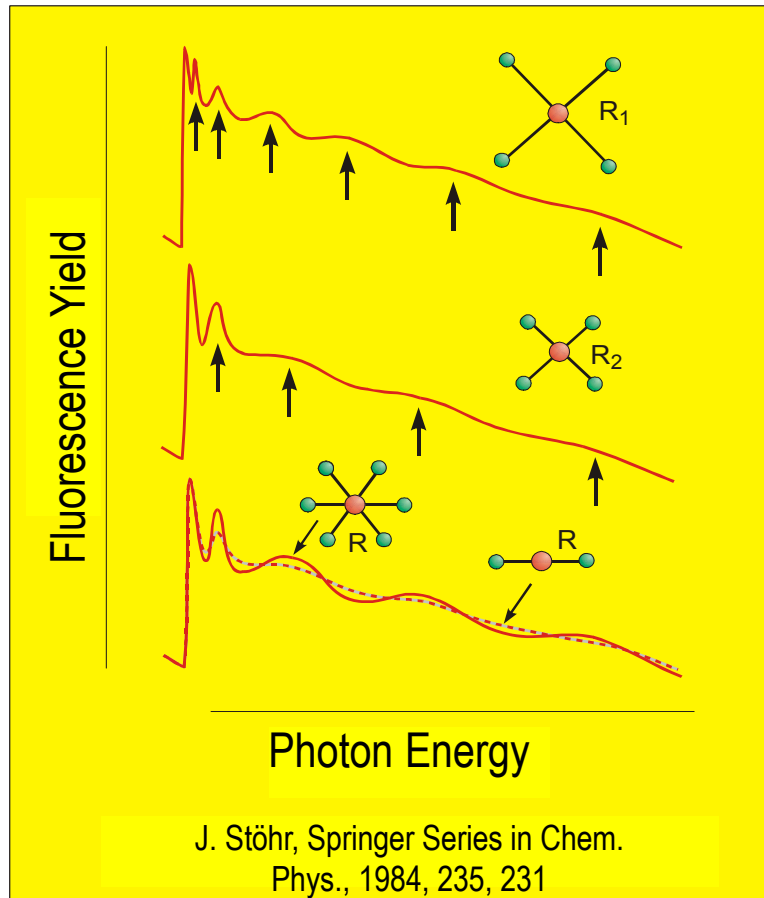
- $E > E_b$
- 50 - 1000 eV above absorption edge
- simplified illustration: constructive & destructive frequencies from the outgoing photoelectron

Free atom



Cluster of atoms

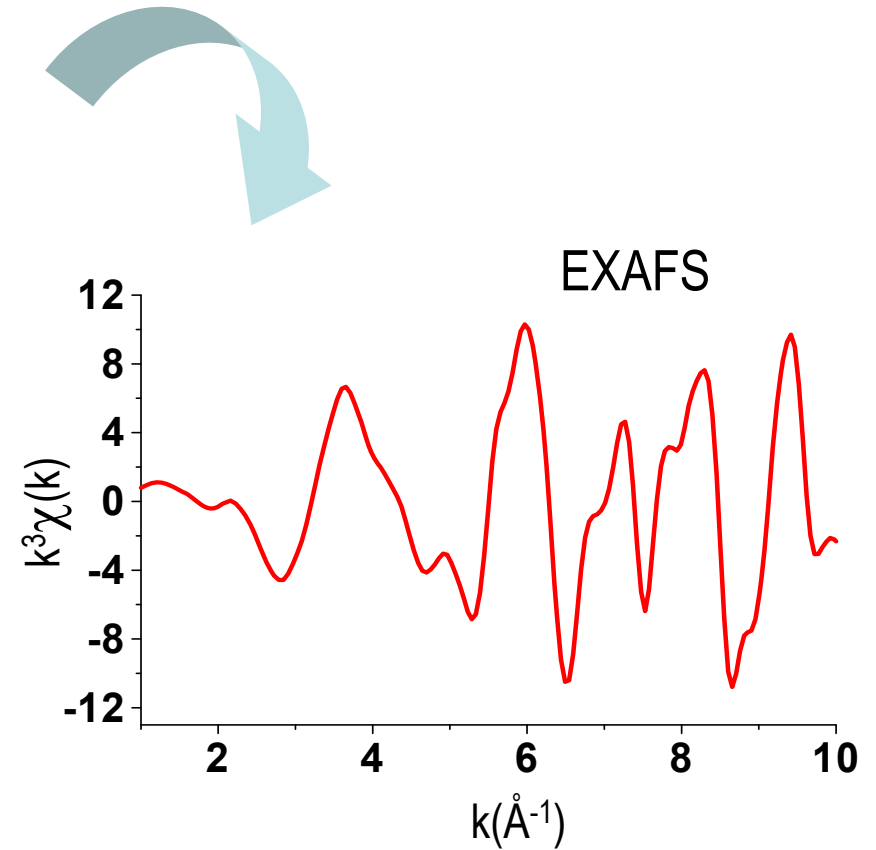
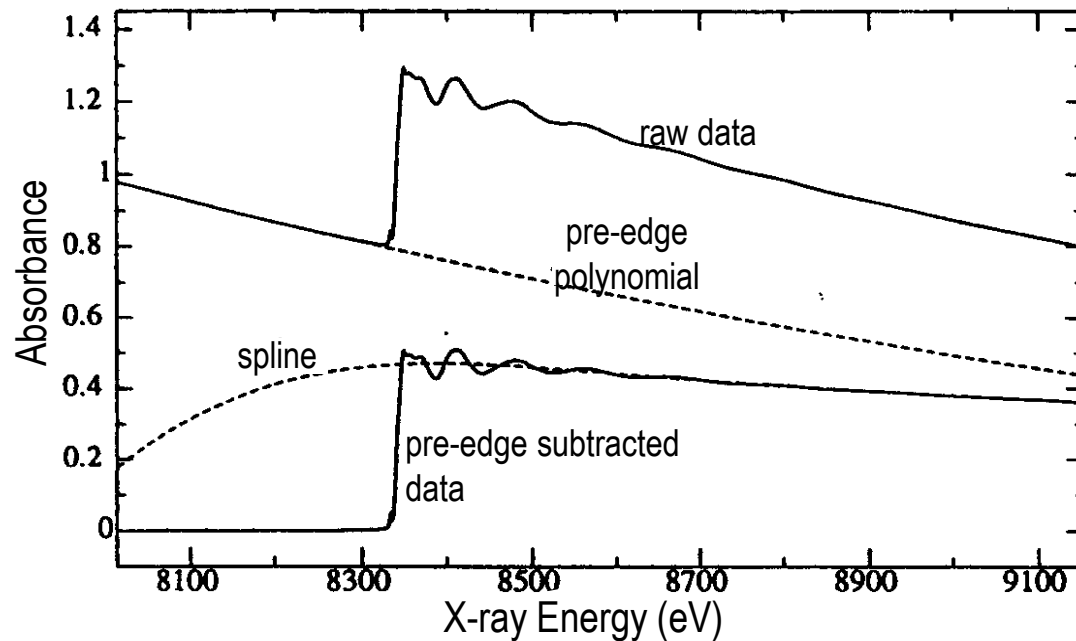




➤ Interference pattern (EXAFS)

- Frequency correlated to bond distance
- Amplitude correlated to coordination number and identity

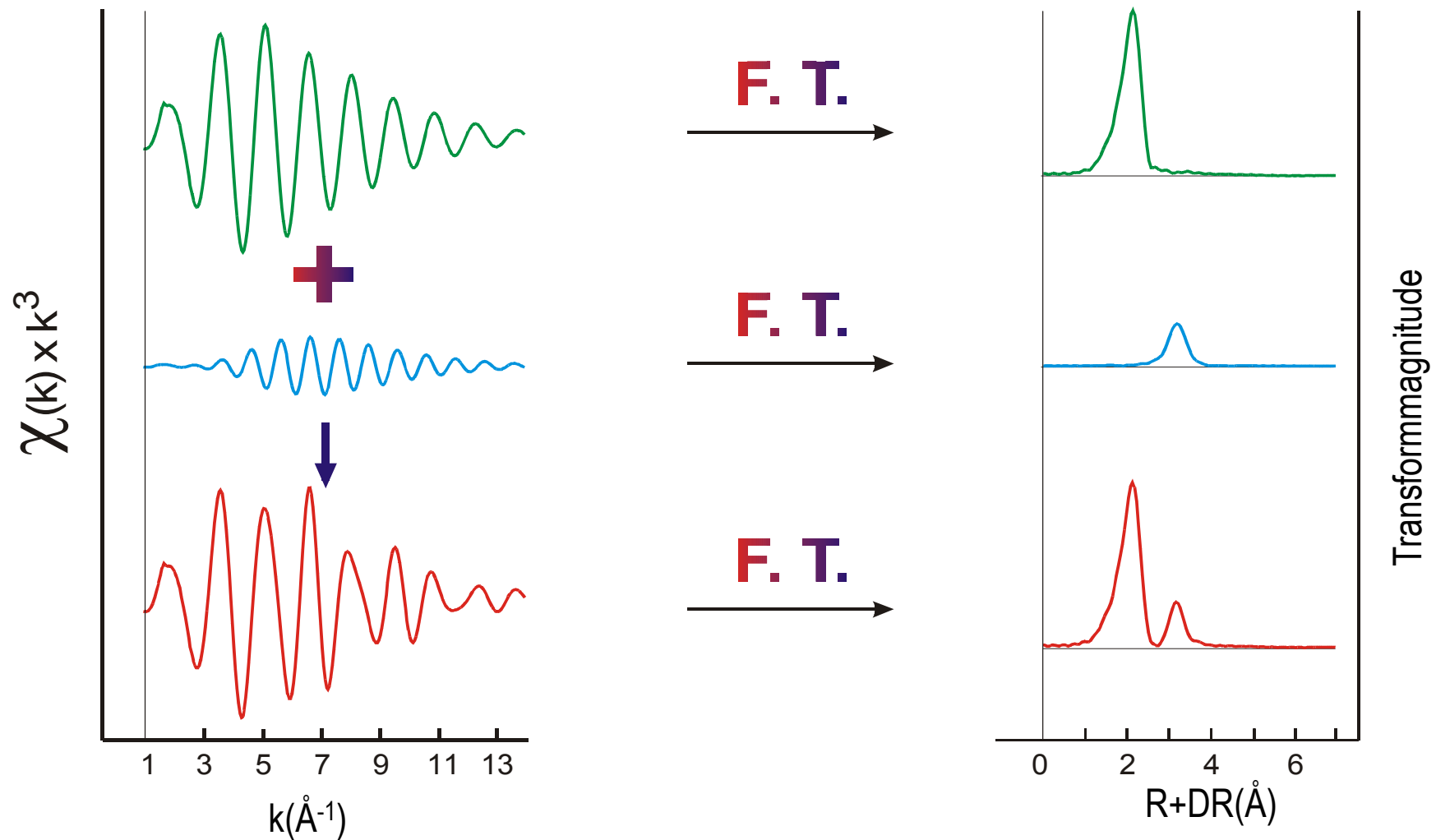
$$\chi(k) = \sum a(k) \sin[2kR + \alpha(k)]$$



➤ extraction of EXAFS

- pre-edge & spline, normalization
- conversion to wave vector $k = (E - E_0) \sqrt{2m/\hbar}$
- normally weighted by k^3

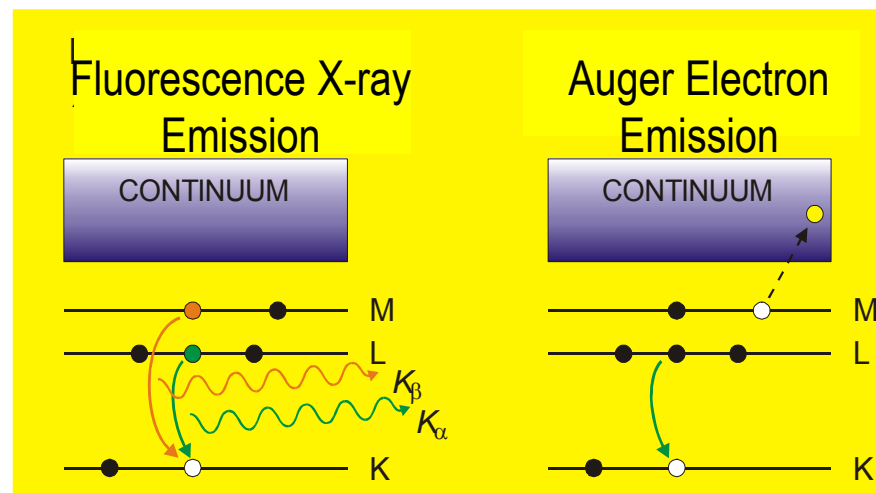
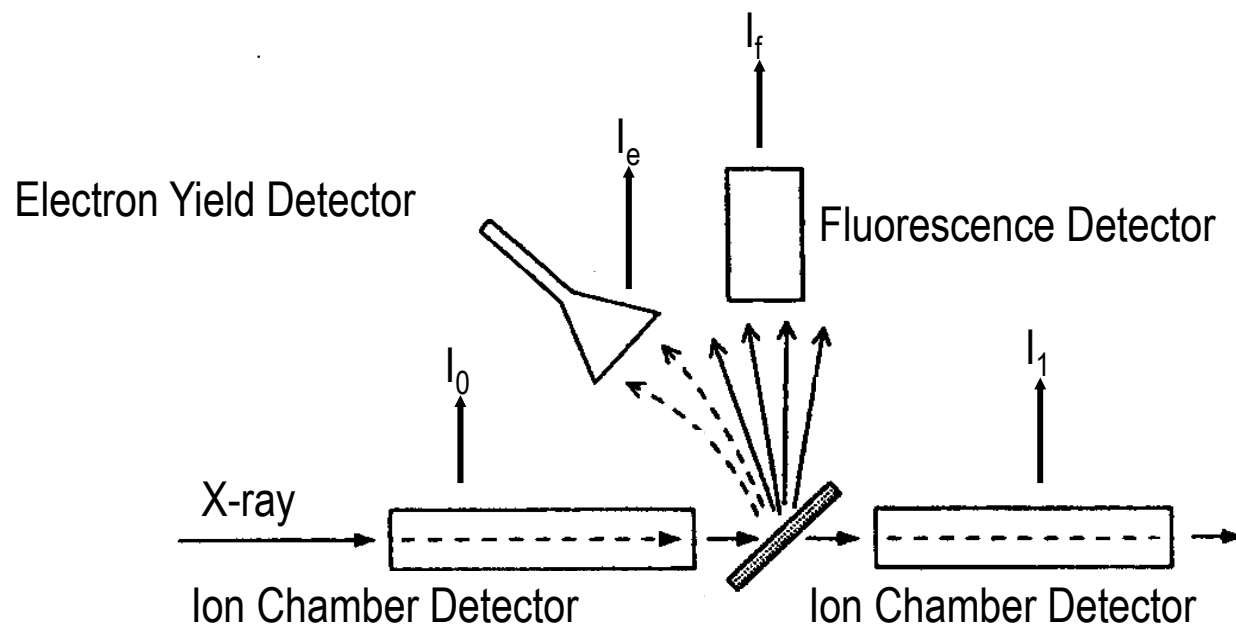
Fourier Transformation

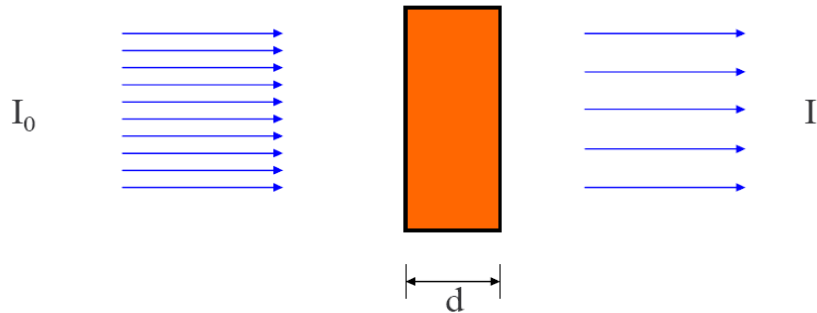


$$\chi(k) = \sum a(k) \sin[2kR + \alpha(k)]$$

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

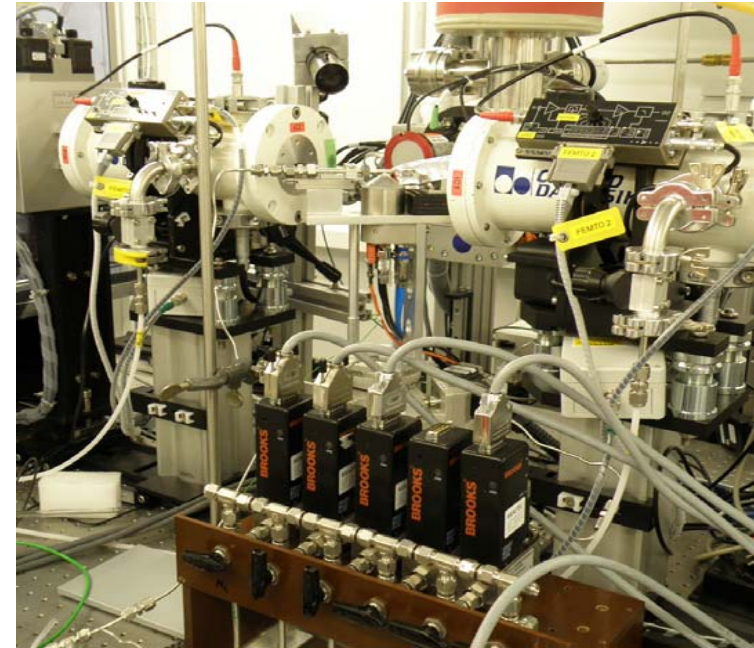




Lambert Beer's Law: $I = I_0 \cdot e^{-\mu d}$

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

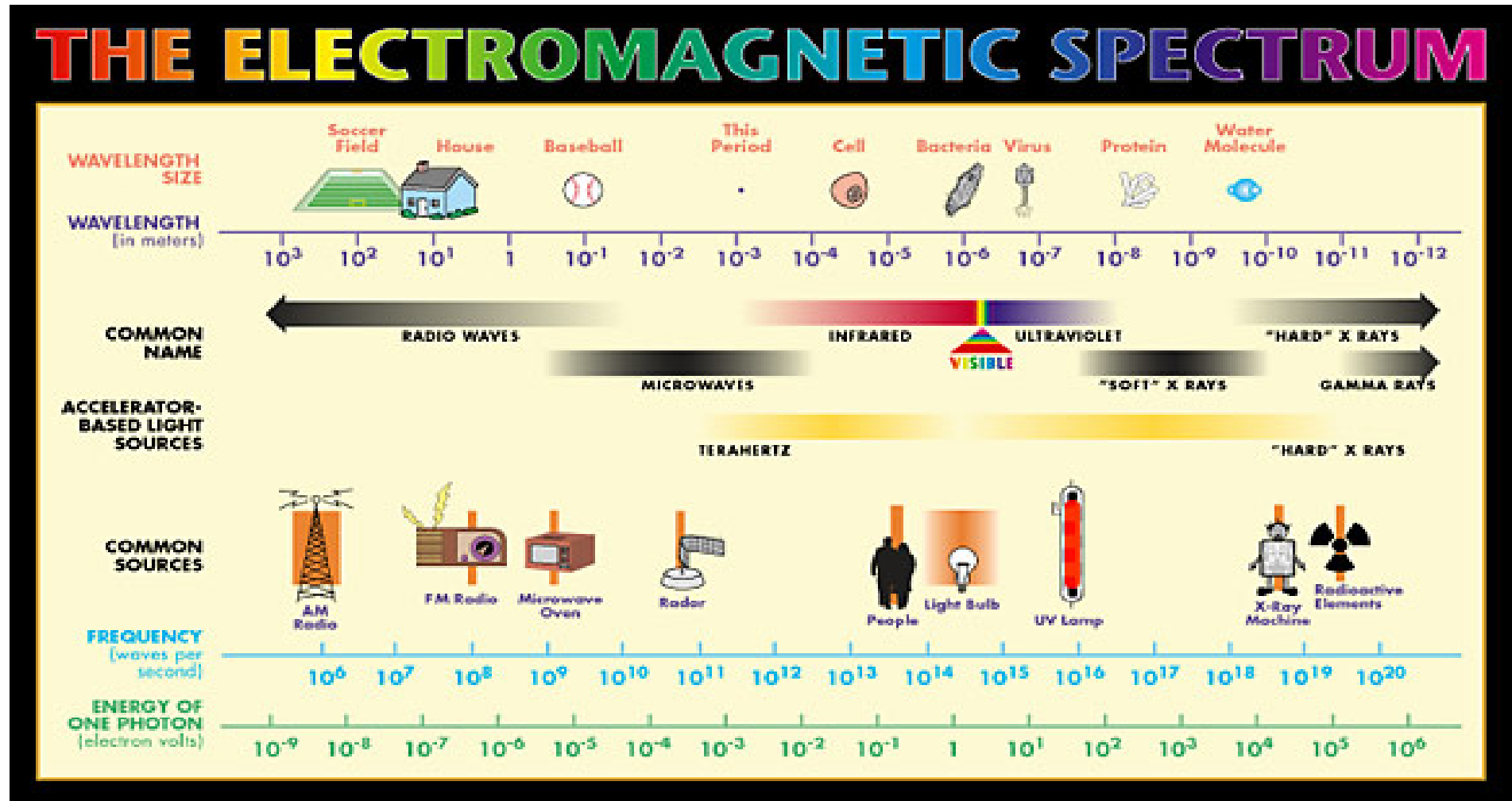


ESRF

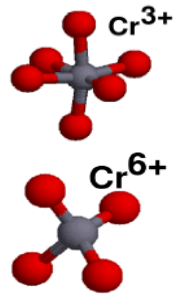
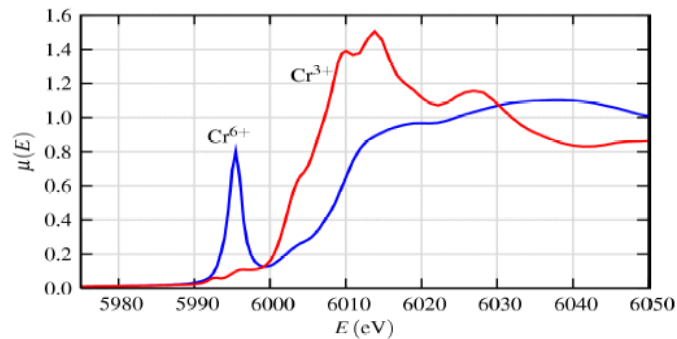


and many more...

Synchrotrons produce **bright** light

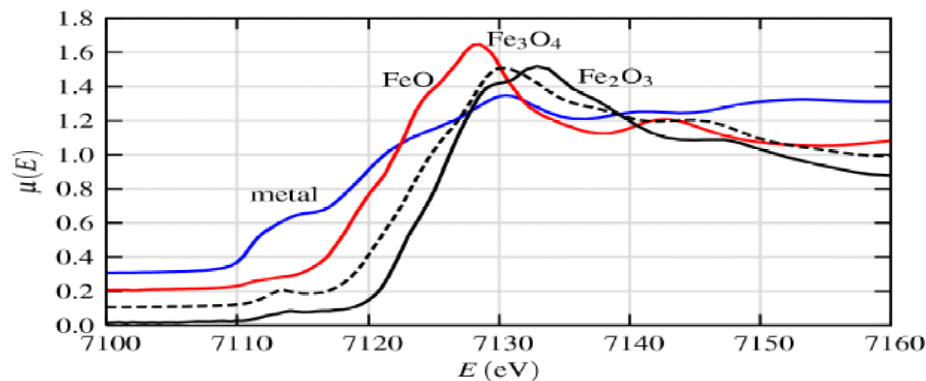


Summary so far:



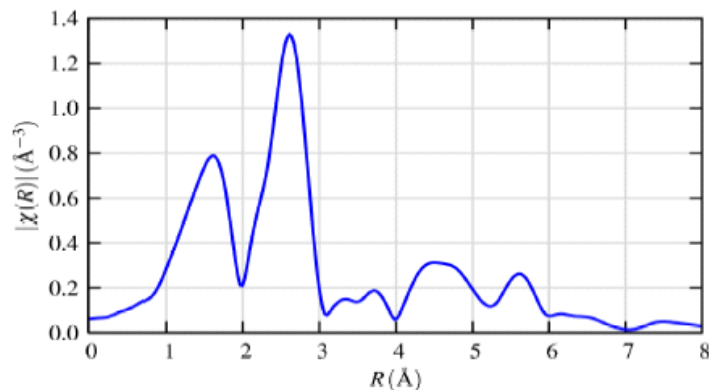
Pre-edge:

- localized electronic states
- coordination chemistry



XANES: (DOS)

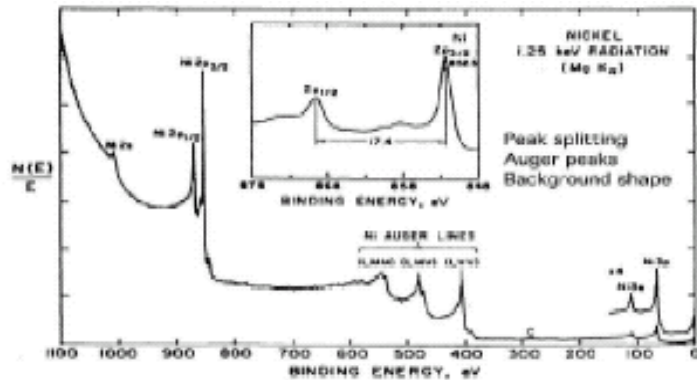
- oxidation state
- band structure
- multiple scattering



EXAFS:

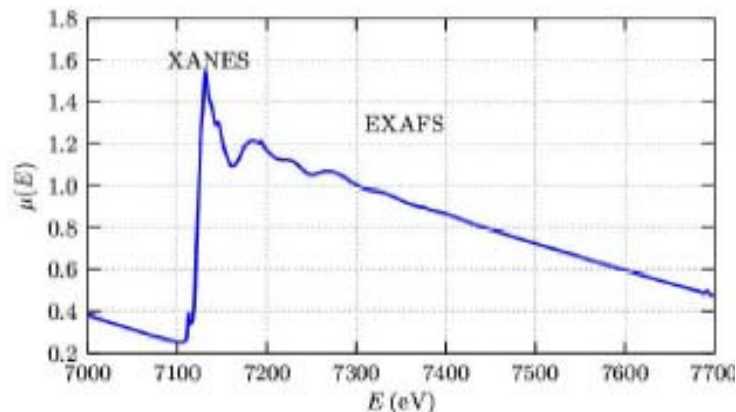
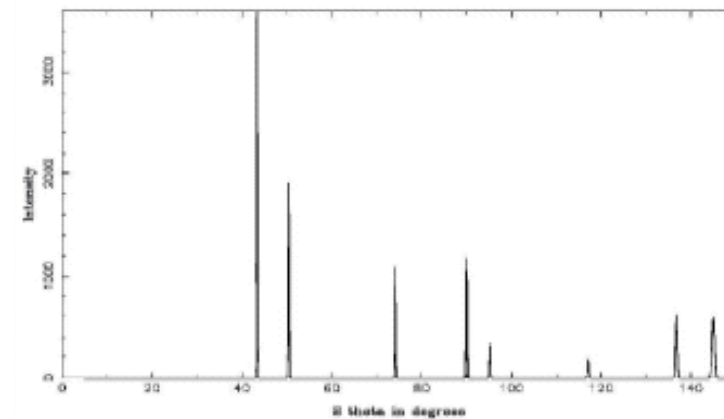
- Identity of nearest neighbors
- Bond distances
- Coordination numbers
- Amount of disorder

Comparison: XPS, XRD, XAS



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

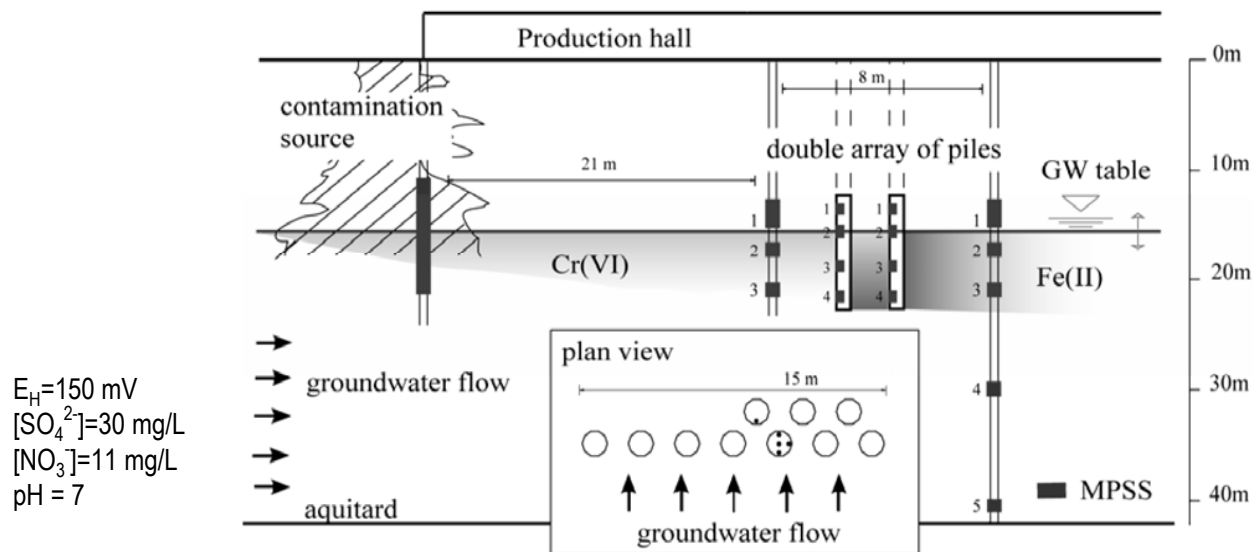
- structural information
- bulk technique
- In-situ
- long range order



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

Example: Fe-oxides as contaminant sorbent

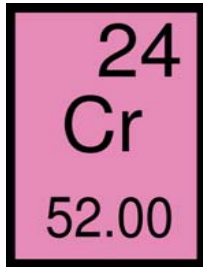
24
Cr
52.00



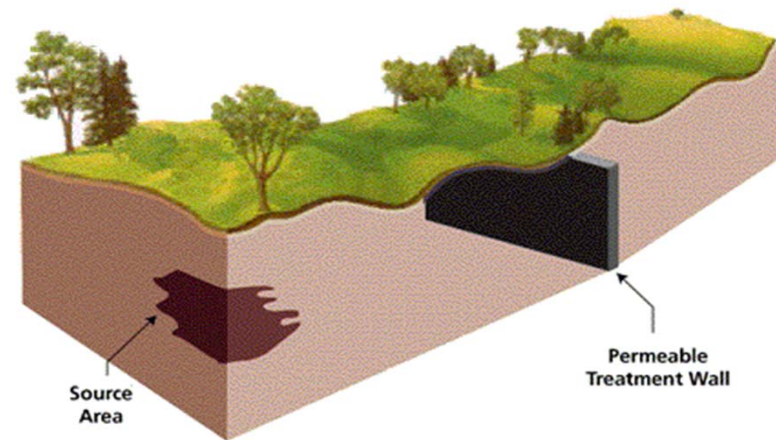
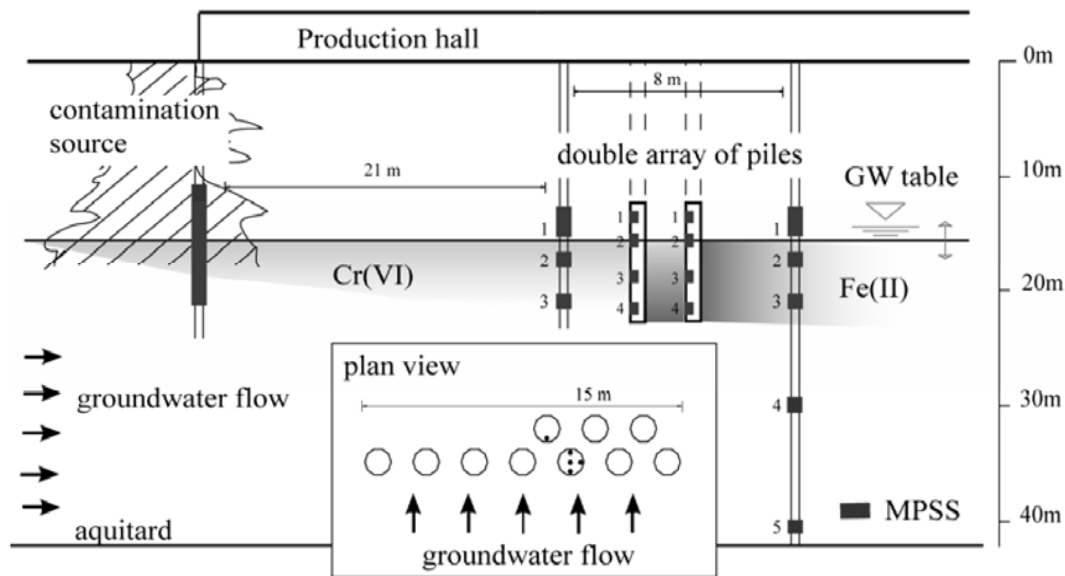
- Contaminants Cr(VI), Cu
- ~1 t Cr at a depth of 3-12 m
- Groundwater protection zone
 $[\text{Cr(VI)}]_{\text{max}} = 0.01 \text{ mg/L}$



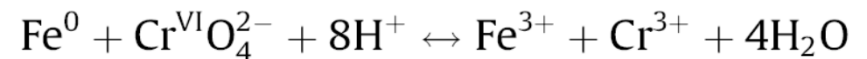
Permeable reactive barrier

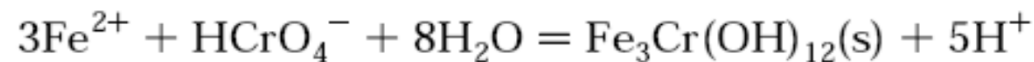
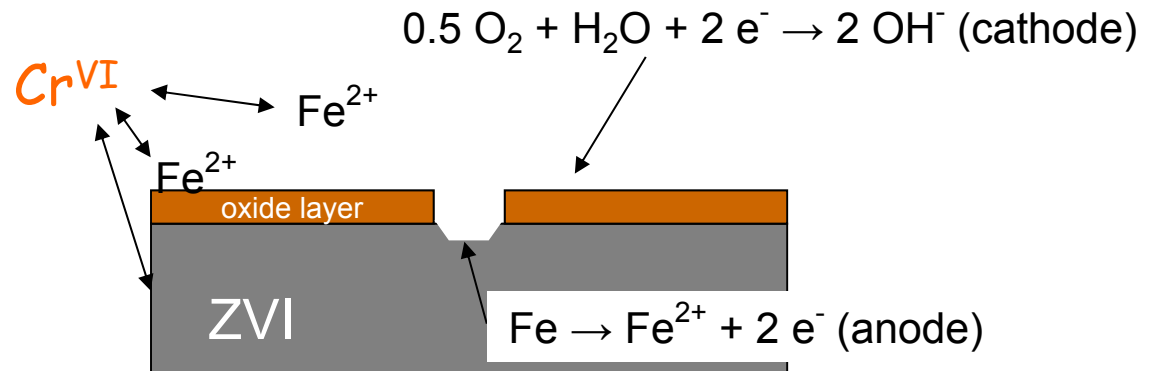
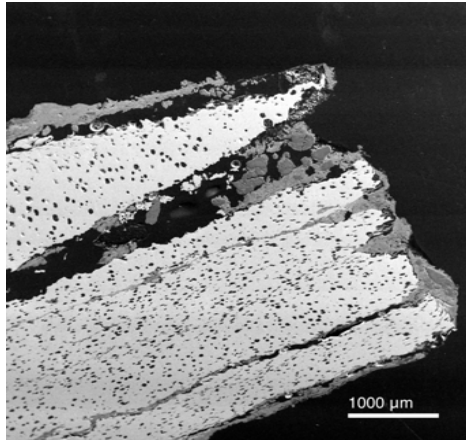


Permeable Reactive Barrier (PRB):
couple the oxidation of Fe(0) with
the reduction of Cr(VI)



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





- homogeneous redox reaction (Buerge & Hug, 1997)
- heterogeneous redox reaction (Buerge & Hug, 1999)
- ZVI- Cr^{VI} -direct reaction (Liu et al., 2008)

Molecular Cr/Fe ratio:

1/3

Hansel et al., 2003

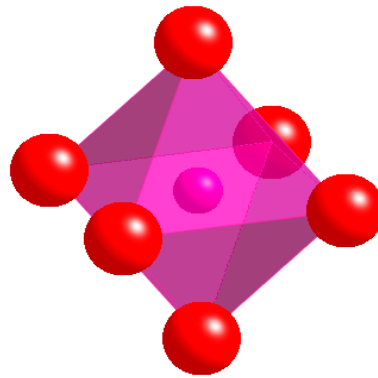
>1/3 (Cr clusters)

Grolimund et al., 1999

?

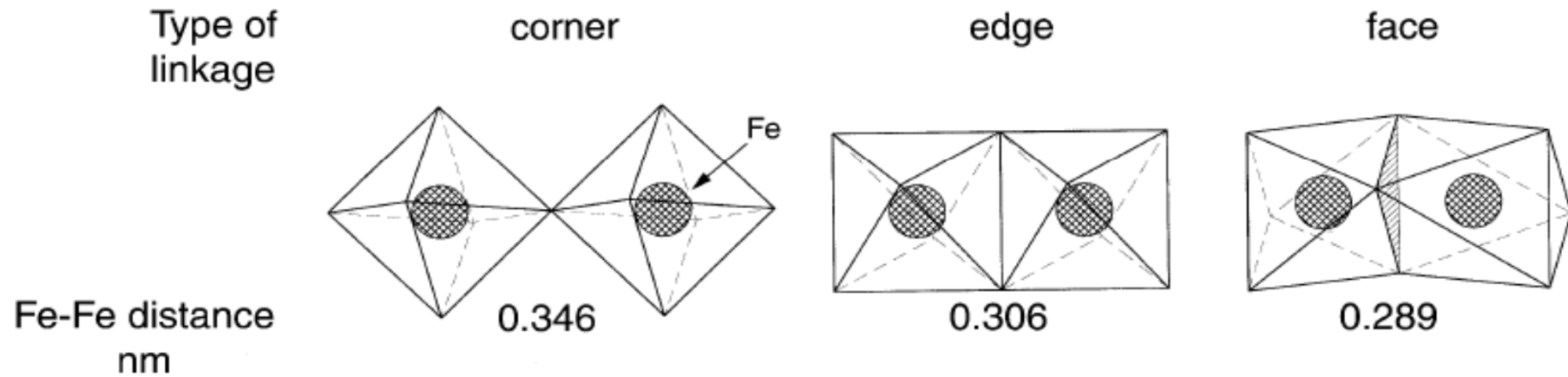
Local structure ↔ Mechanism

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

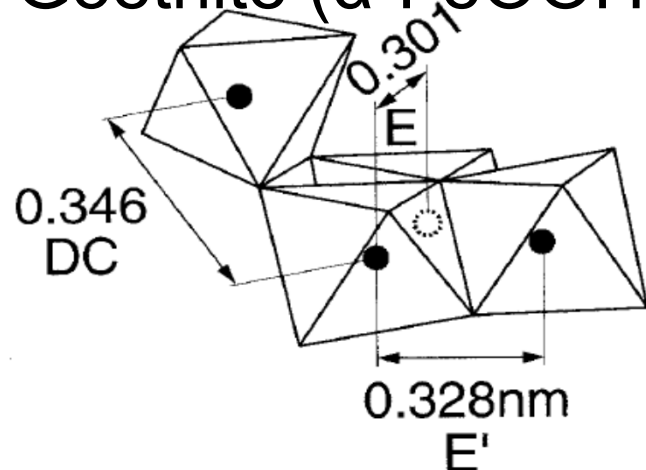


FeO_6 octahedron
(also: $\text{CrO}_3(\text{OH})_3$ $\text{FeO}_3(\text{OH})_3$)

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
($\alpha\text{-Cr}_2\text{O}_3 - \alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$)

Relation to molecular Fe/Cr
(\rightarrow mechanism)

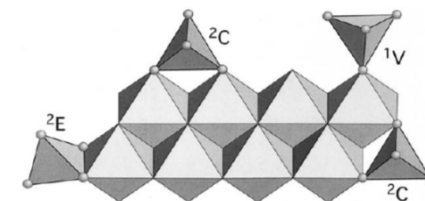
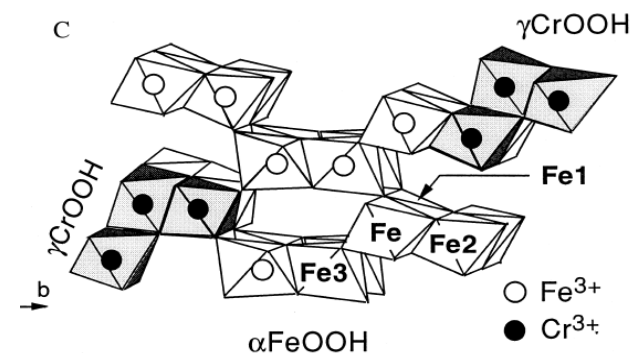
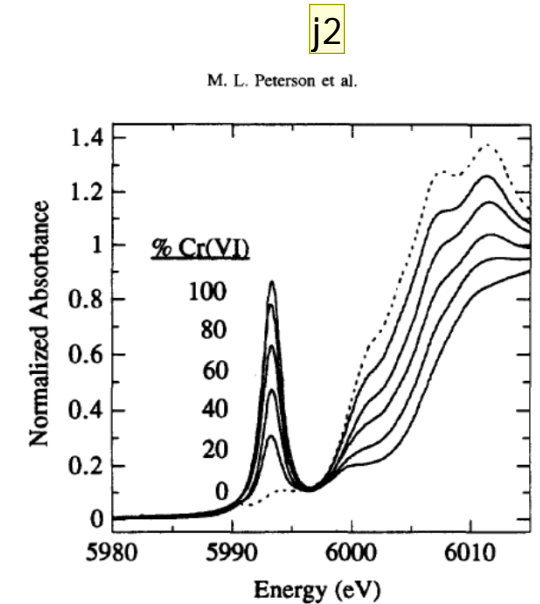
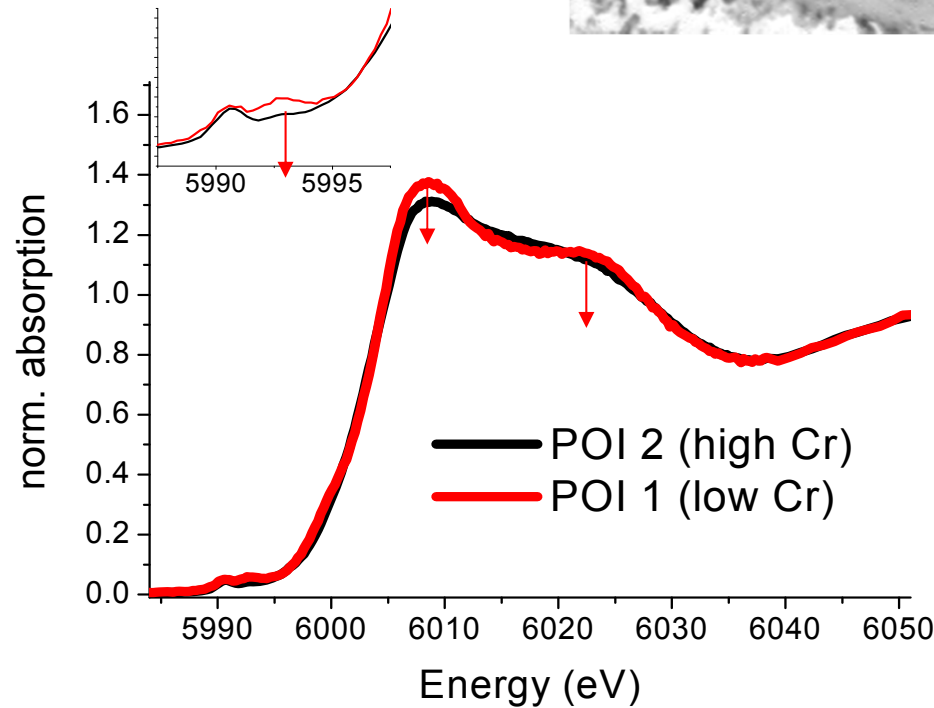
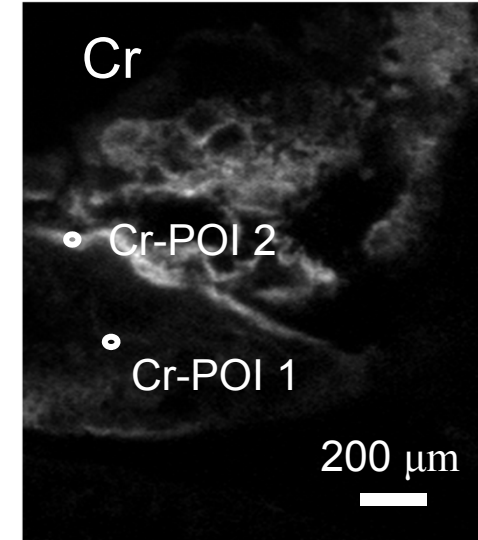
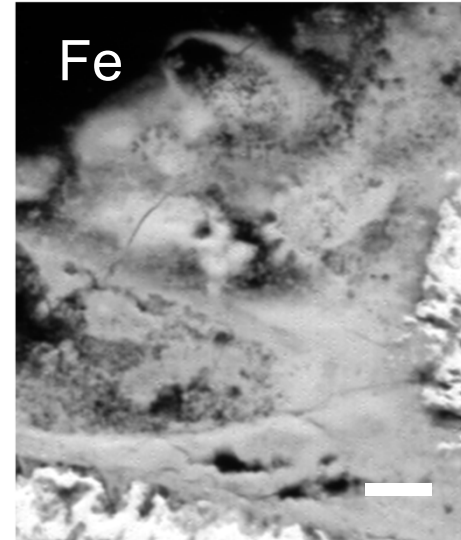
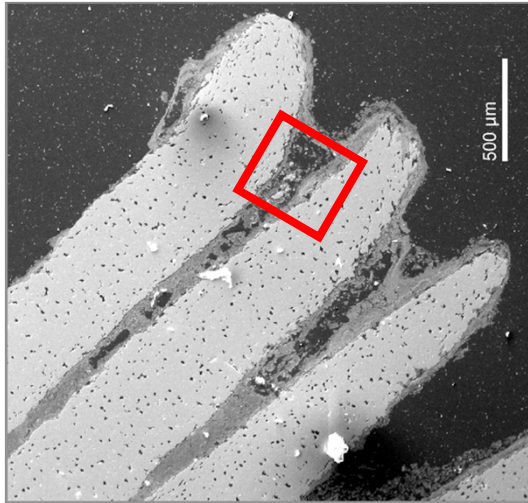


Fig. 1. Possible surface complexes of AsO_4 tetrahedra on goethite.

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



Permeable reactive barrier



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

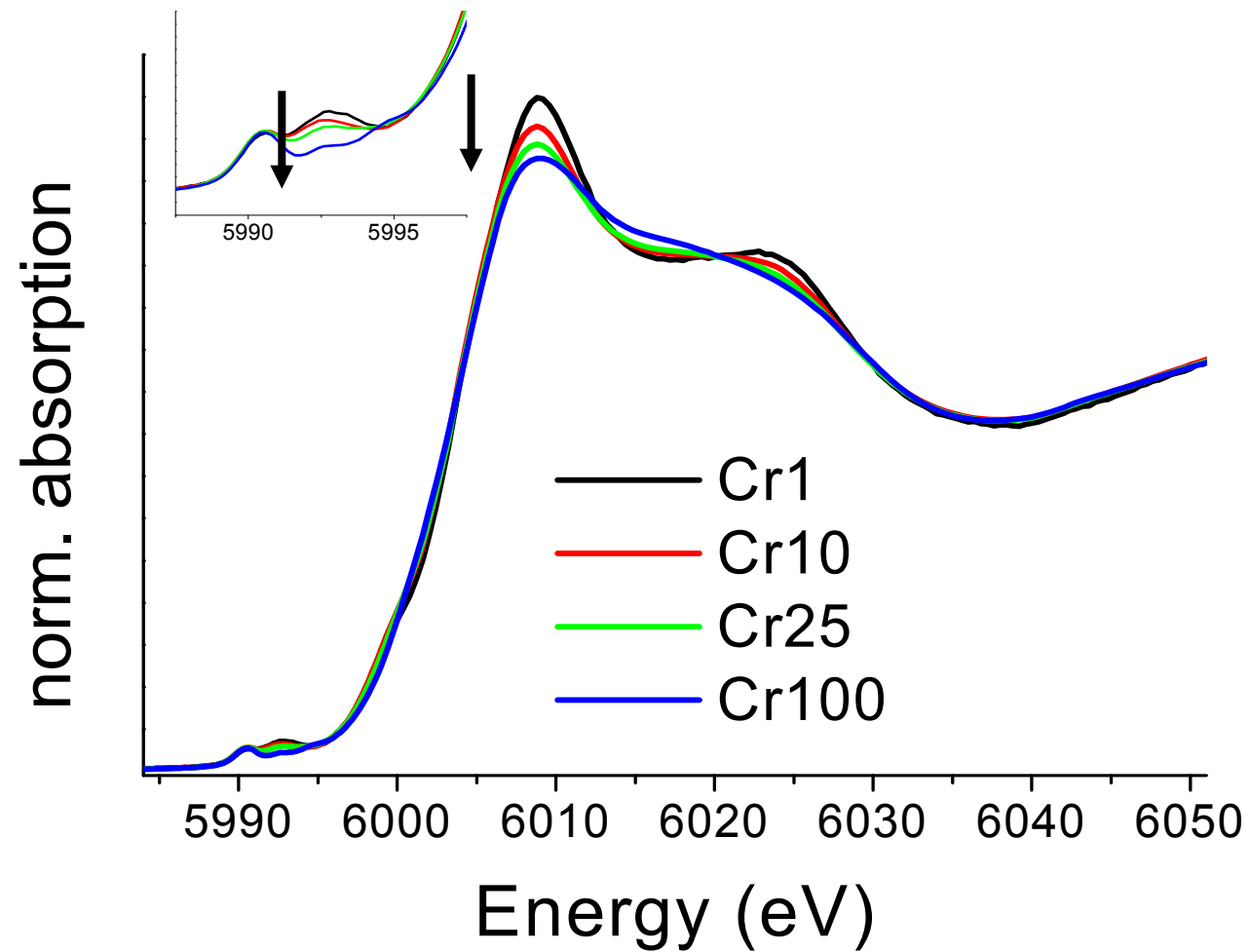
j2

noch vergrößerung des pre-edge

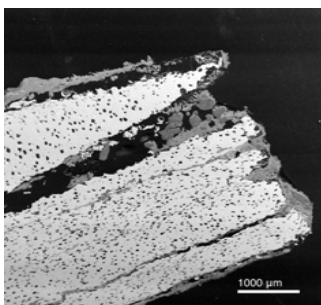
ggf. noch vor und nachteile EXAFS aufzeigen

jafromme; 01.10.2008

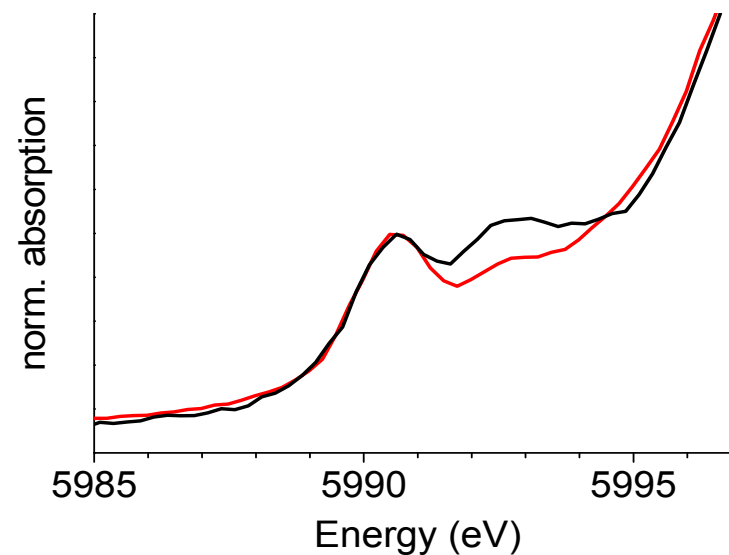
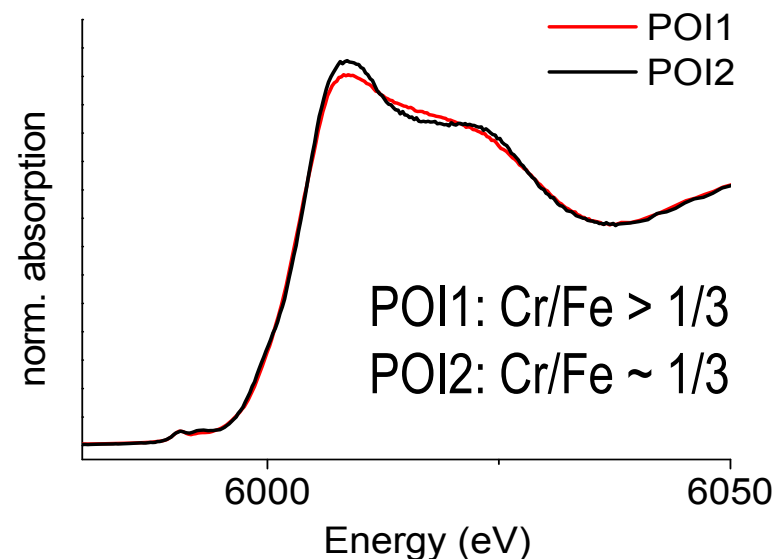
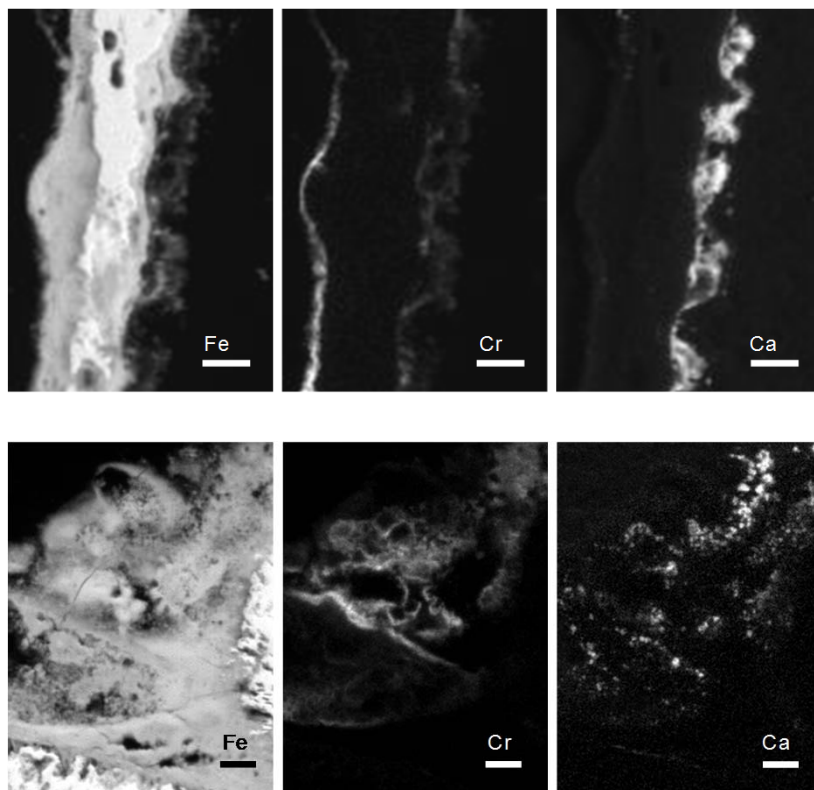
XANES



Back to the beginning: Permeable Reactive Barrier



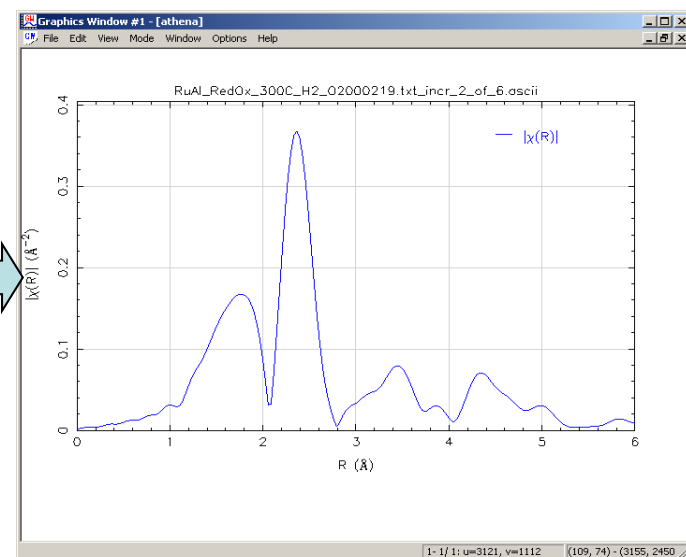
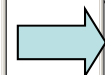
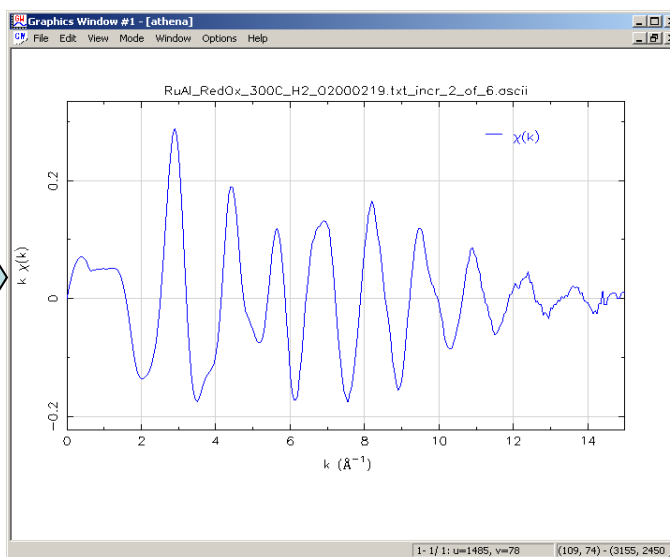
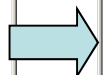
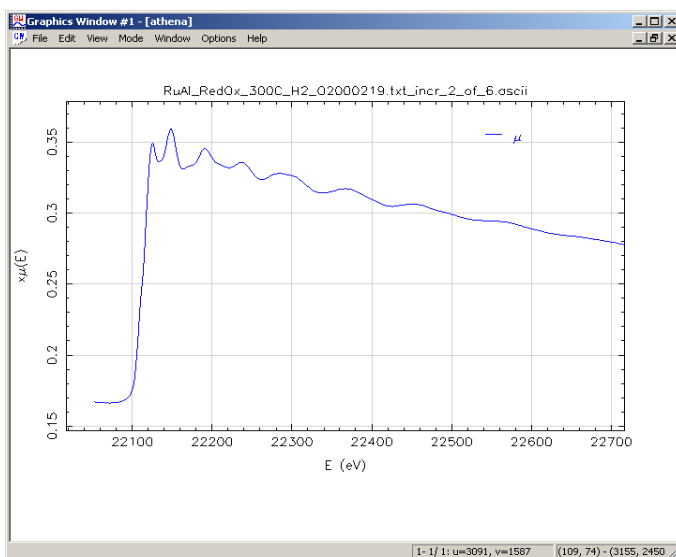
Cr/Fe < 1/10



homogeneous & heterogeneous
redox reactions

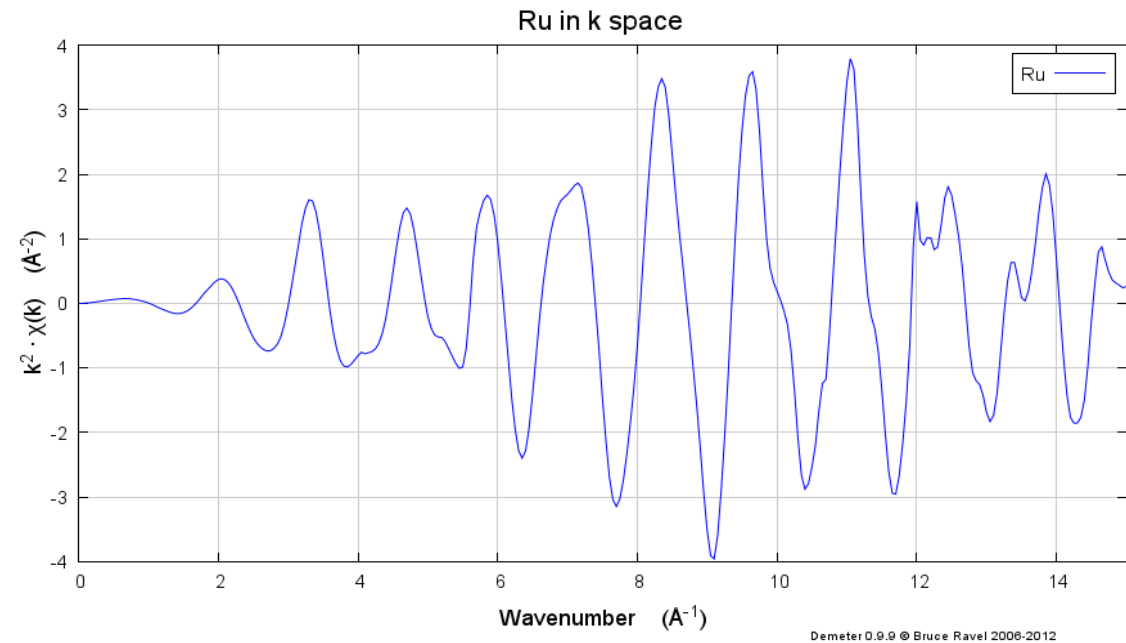
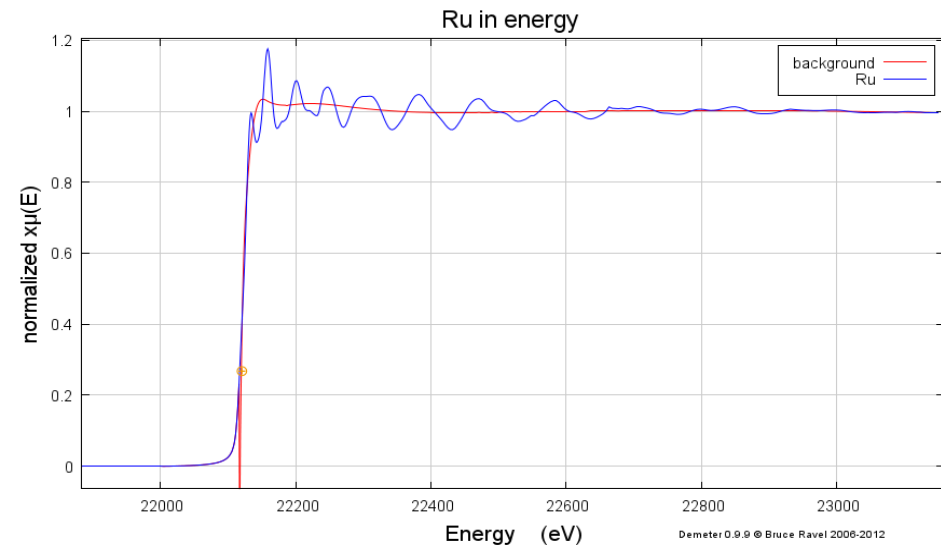
Basic data reduction steps of

- 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

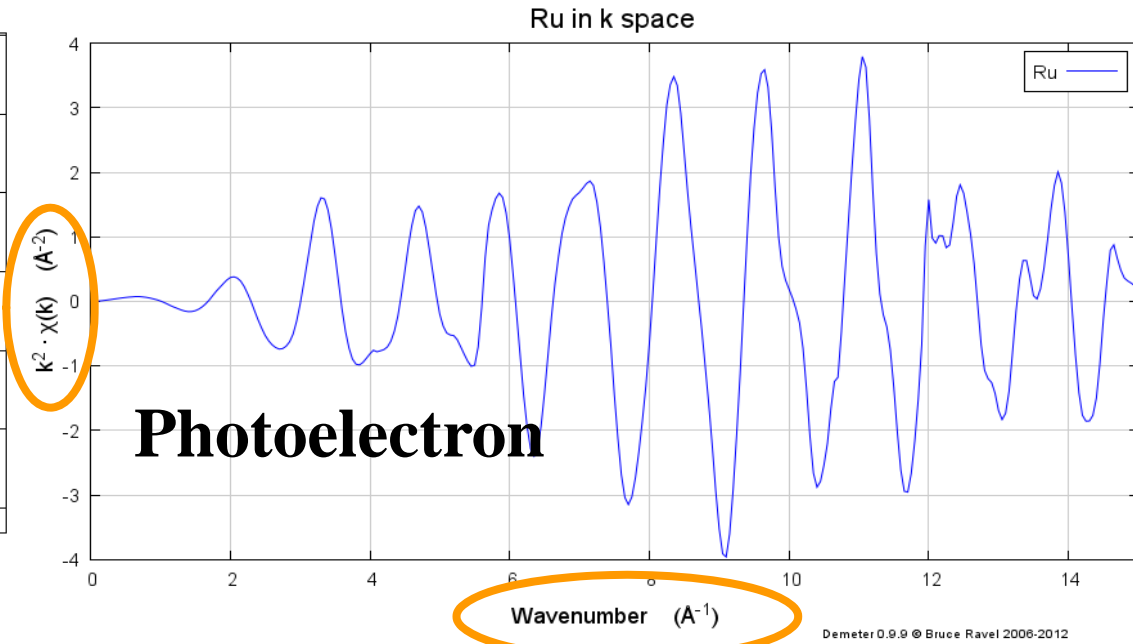
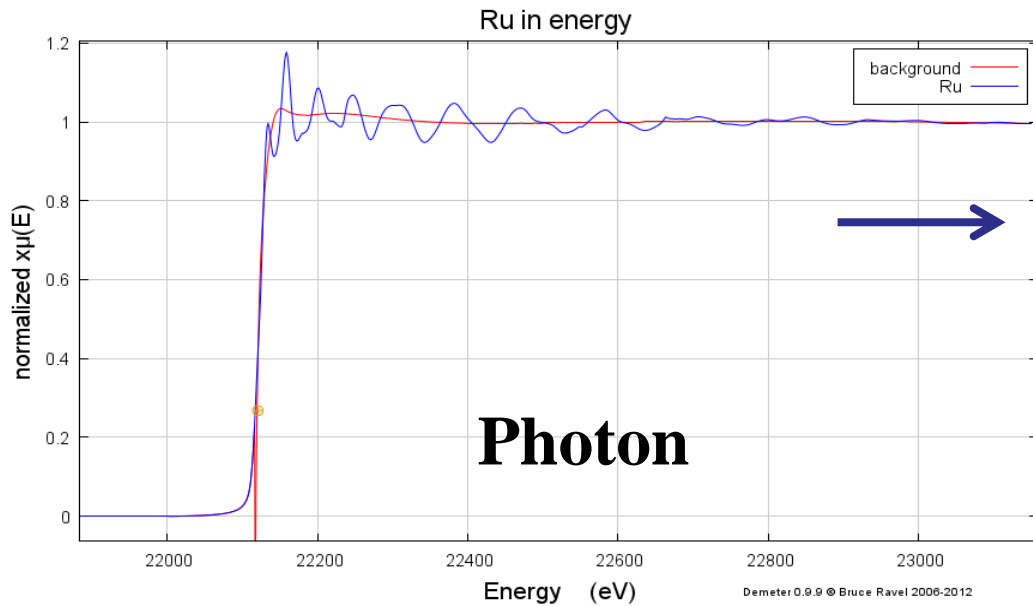
Measured Absorption coefficient

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)

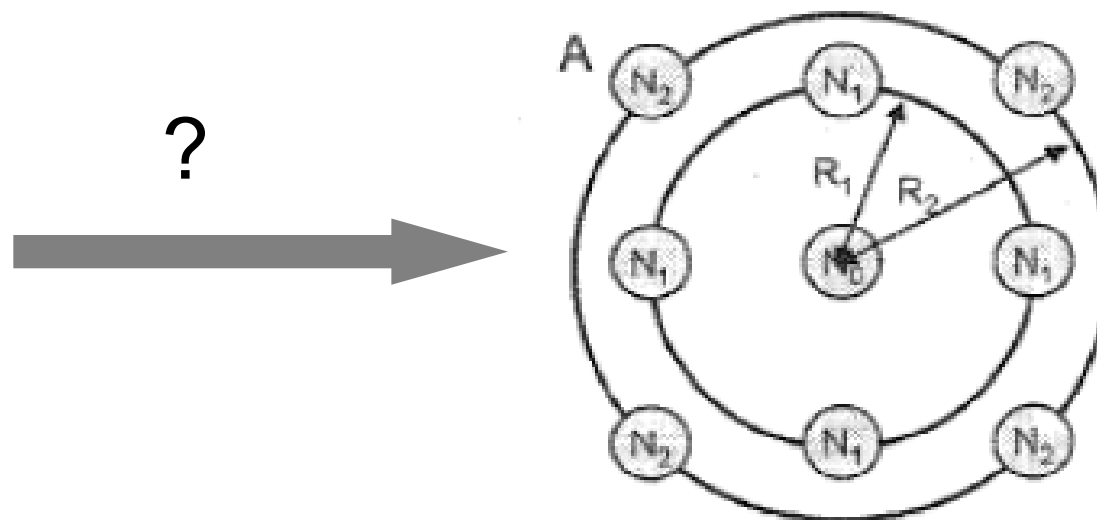
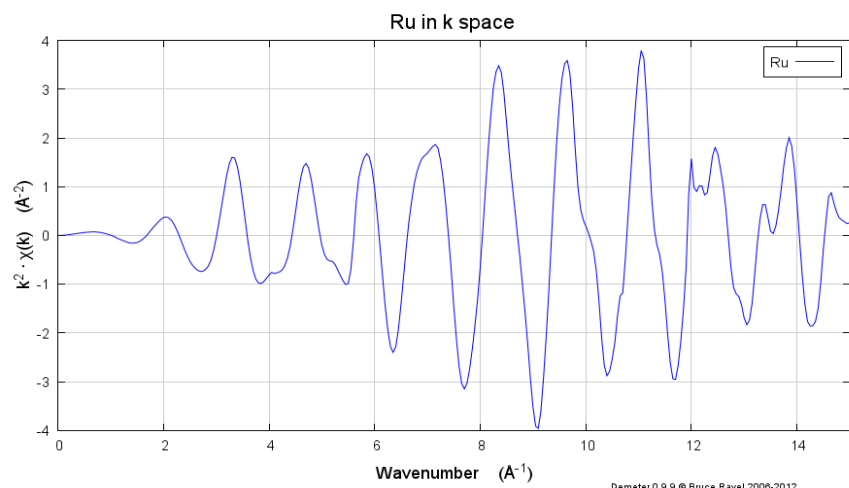
$$k^2 = \frac{2m_e(E-E_0)}{\hbar^2} \sim \frac{\Delta E}{3.81}$$

Mass of electron

Edge Energy

Plank's constant

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

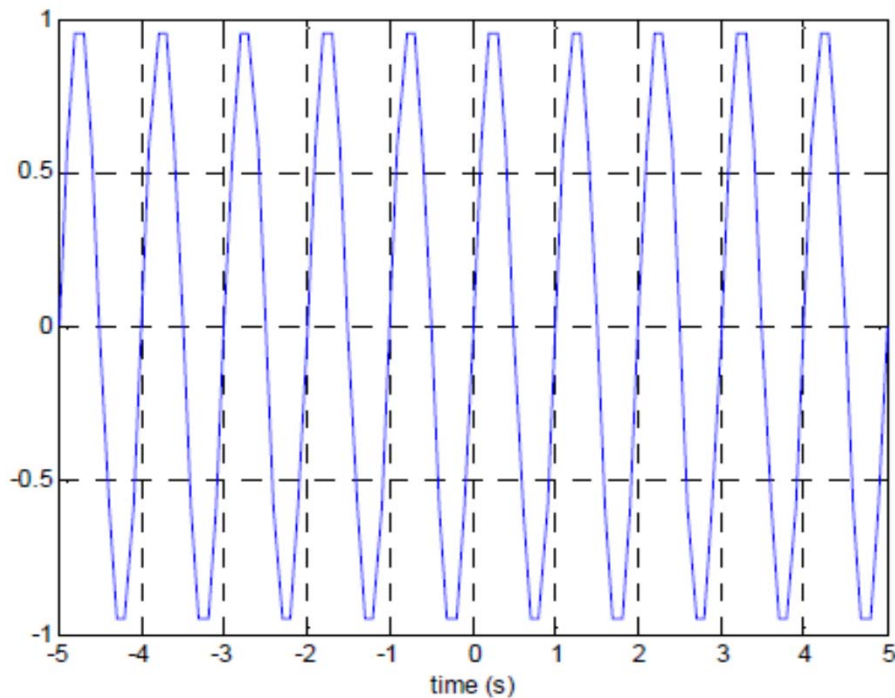


- N_0 X-ray absorbing atom
- N_1 1st neighboring scatterer (shell)
- N_2 2nd neighboring scatterer (shell)

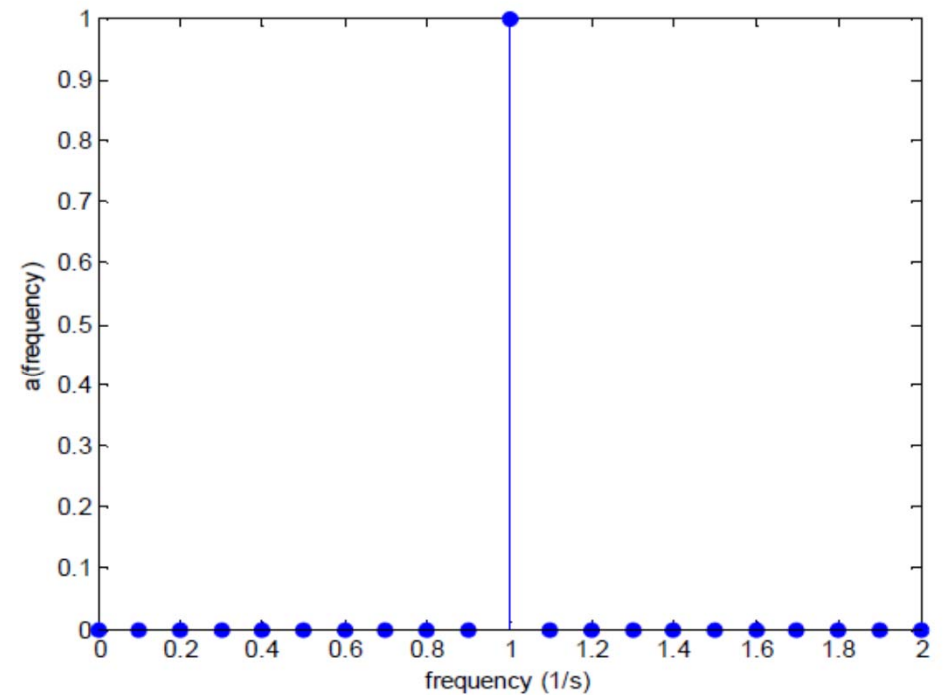
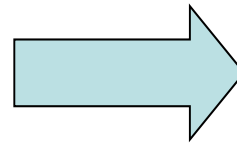
R_x distance between absorber and scatterer

Fourier transformation crash course

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



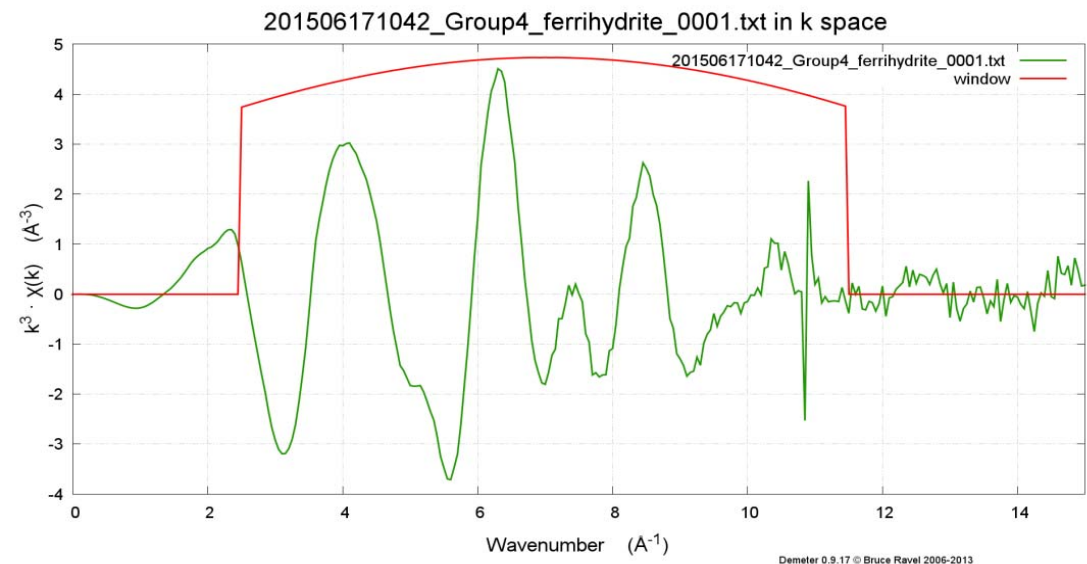
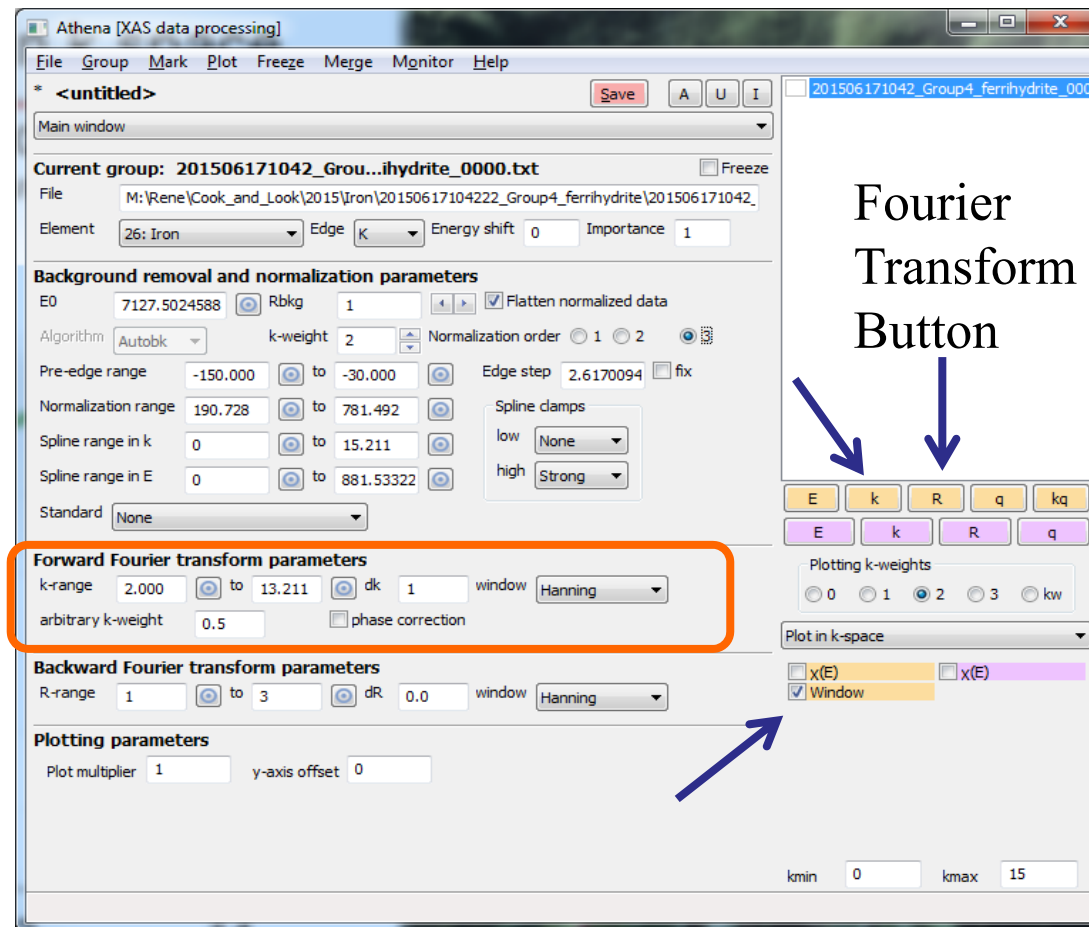
Wave function with period length of 1 s



Frequency of 1 Hz

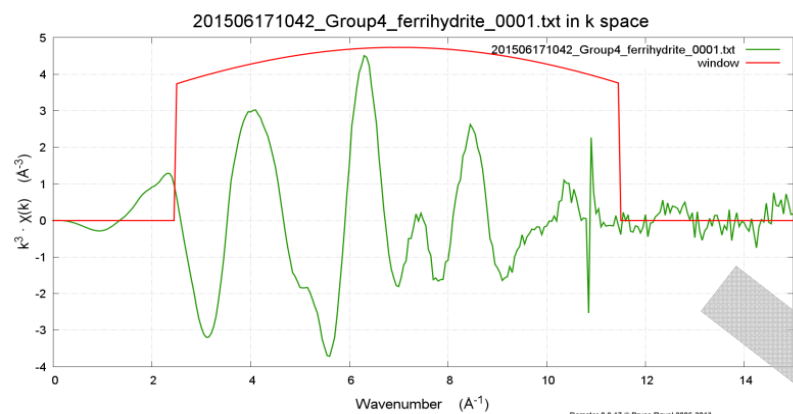
Define k-range for Fourier transformation

Lower limit: $2\text{--}3 \text{ \AA}^{-1}$; 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 \AA^{-1} to \AA)



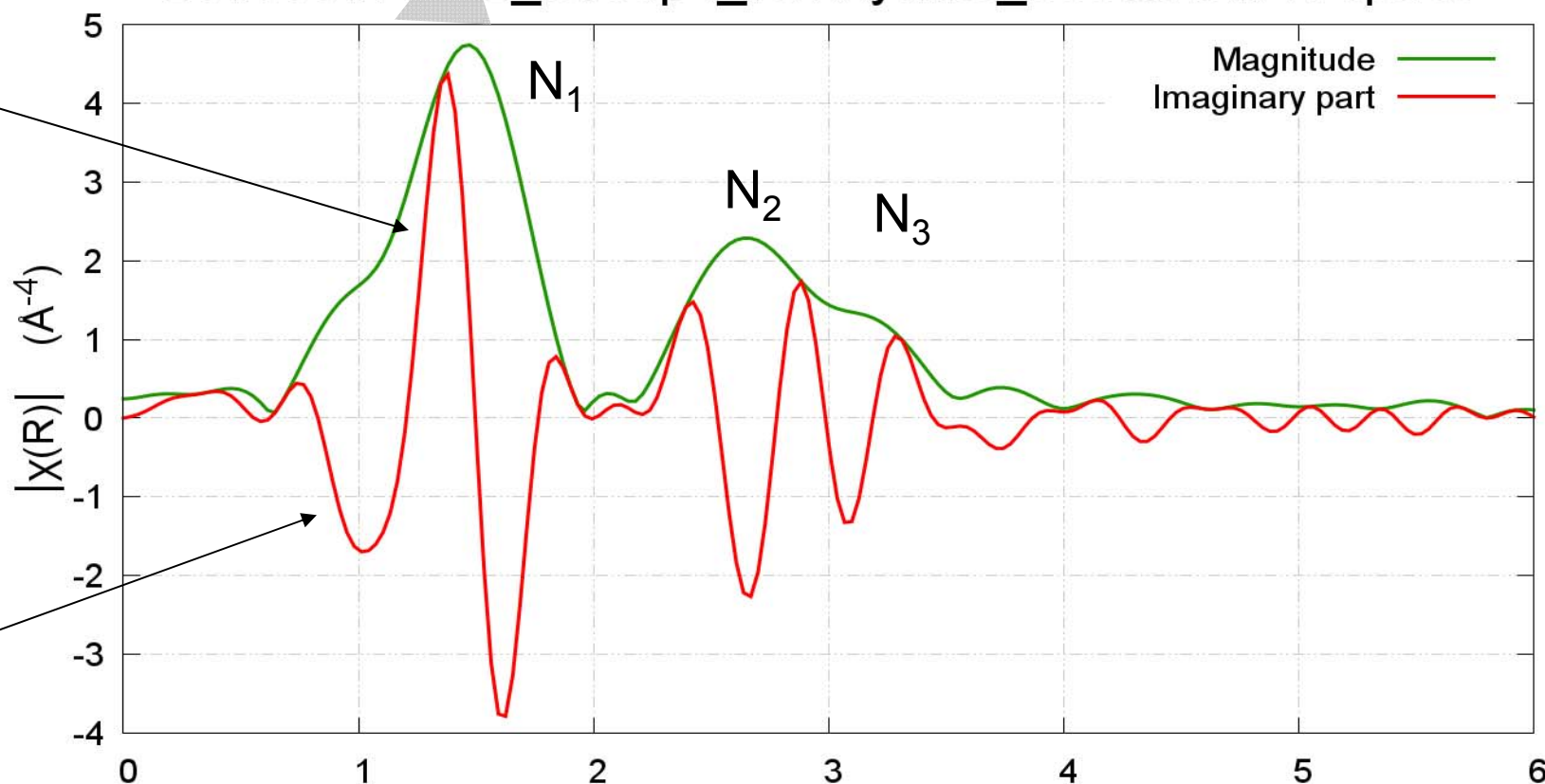
Fourier transformed of the EXAFS signal

Remember: FT creates a complex function

→ always show magnitude AND real or imaginary part

201506171042_Group4_ferrihydrite_0001.txt in R space

magnitude



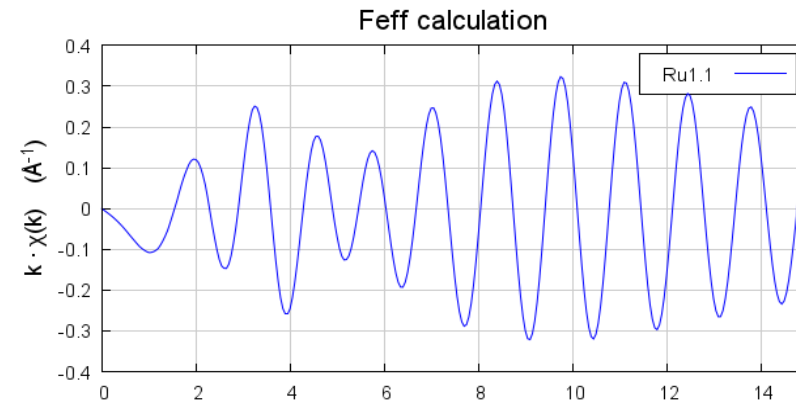
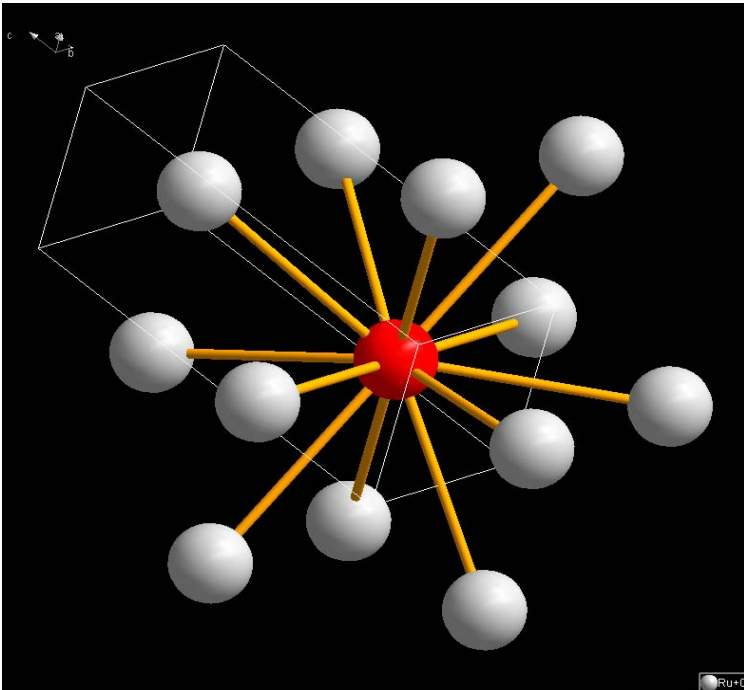
Imag part

Radial distance (\AA)

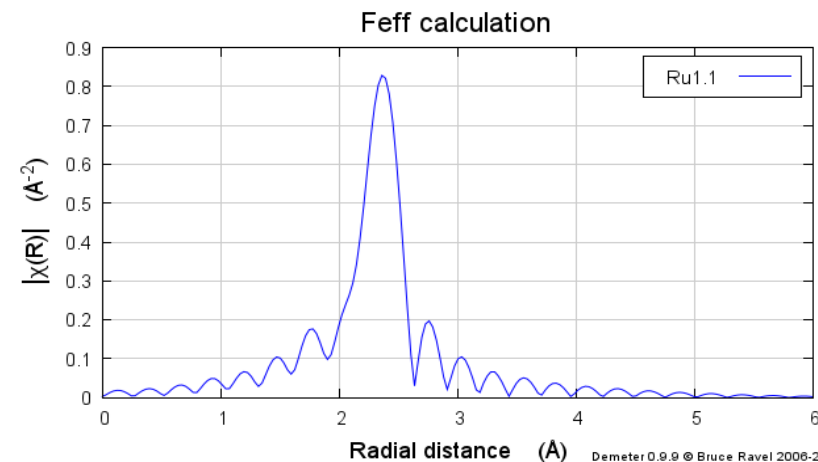
Part 2: Fitting of EXAFS data

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

What information can we extract from a fit?

EXAFS function

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

Diagram illustrating the EXAFS function with arrows pointing to the terms:

- N_i : Coordination number (amplitude)
- $F_i(k)$: Scattering amplitude
- S_0^2 : Amplitude reduction factor
- $k R_i^2$: Radial distance (frequency)
- $e^{\frac{-2R_i}{\lambda}}$: Exponential decay factor
- $e^{-2\sigma_i^2 k^2}$: Damping factor
- $\sin(2kR_i + \phi_i(k))$: Sine wave phase

Sum of damped sine functions with a pre-factor

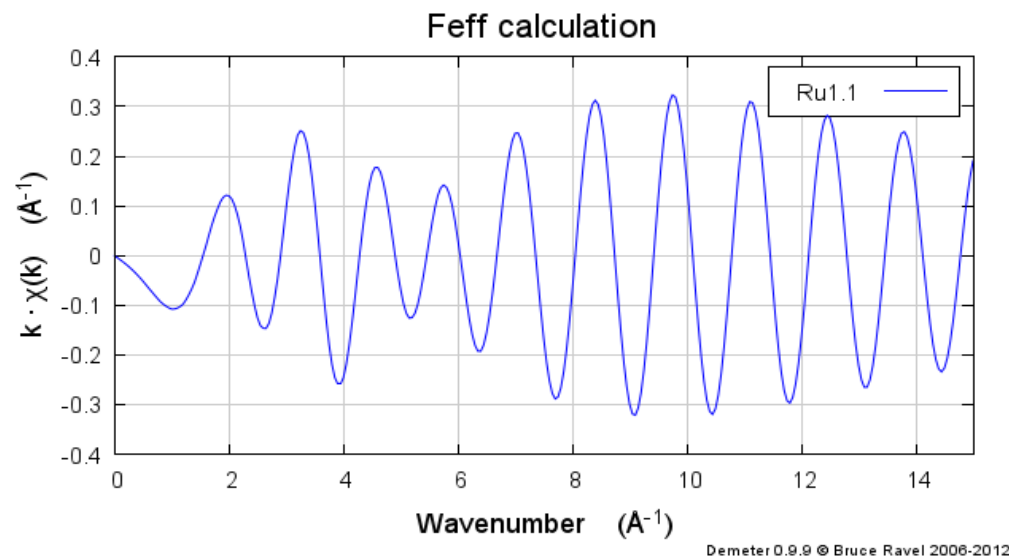
Structural Parameters:

N: coordination number → amplitude

R: radial distance → frequency

σ^2 : pseudo Debye waller factor → damping

Theoretical first Ru-Ru shell of metallic ruthenium

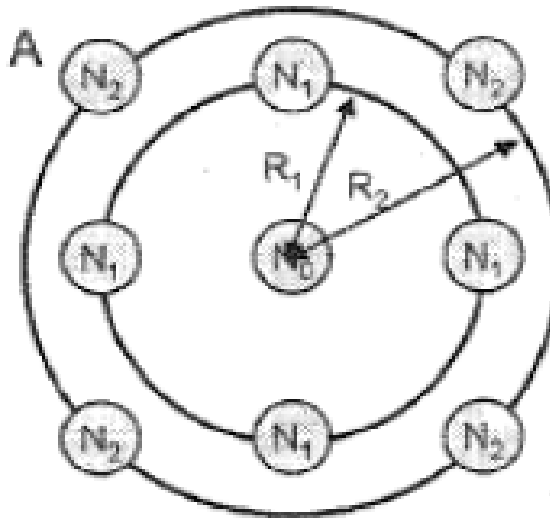


Calculate EXAFS signal of model compound! → FEFF

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

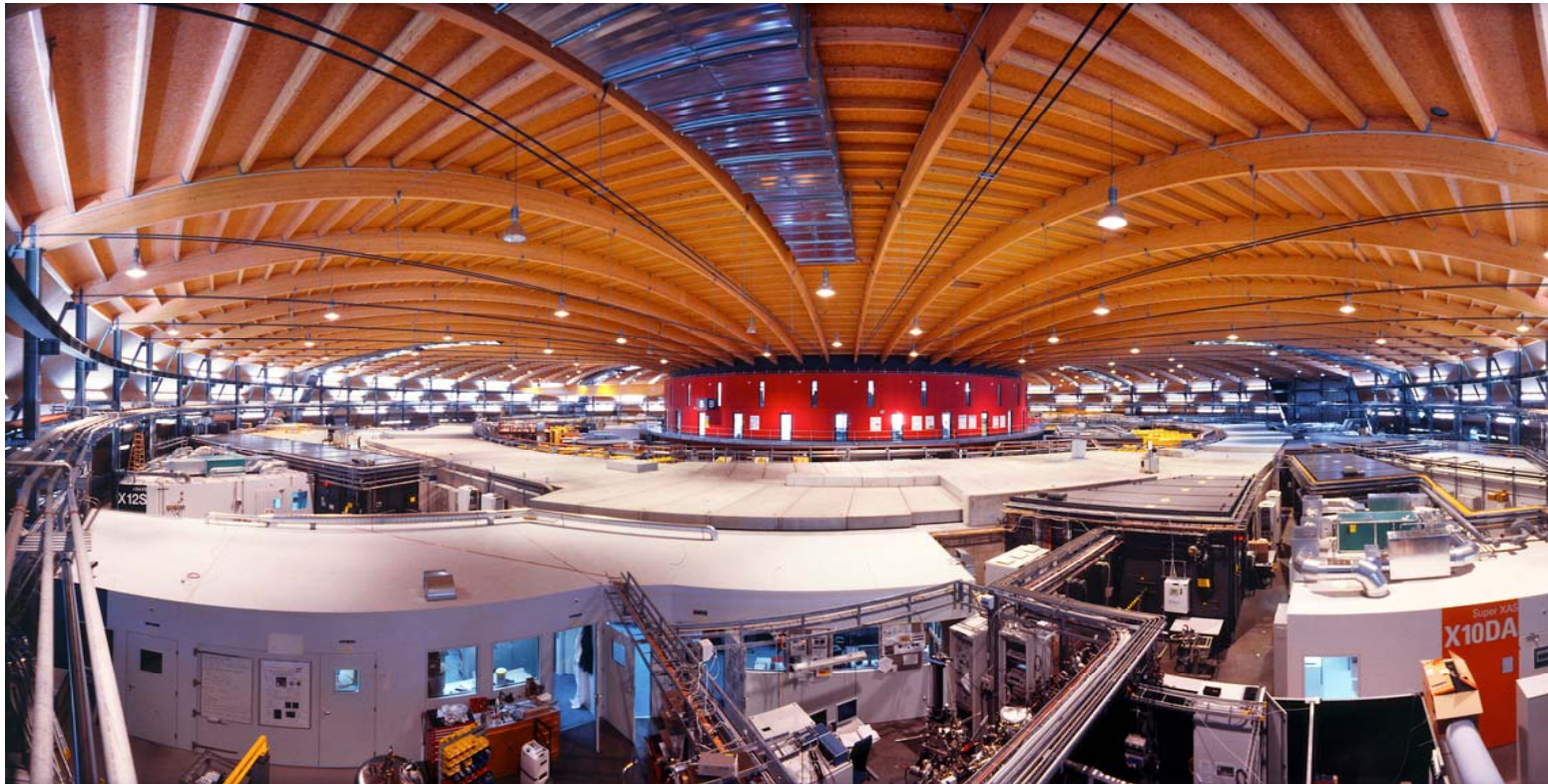


From fitting of EXAFS data information about

- the distance R of each shell from the absorbing atom
- the number of atoms in each shell (coordination number) is obtained.

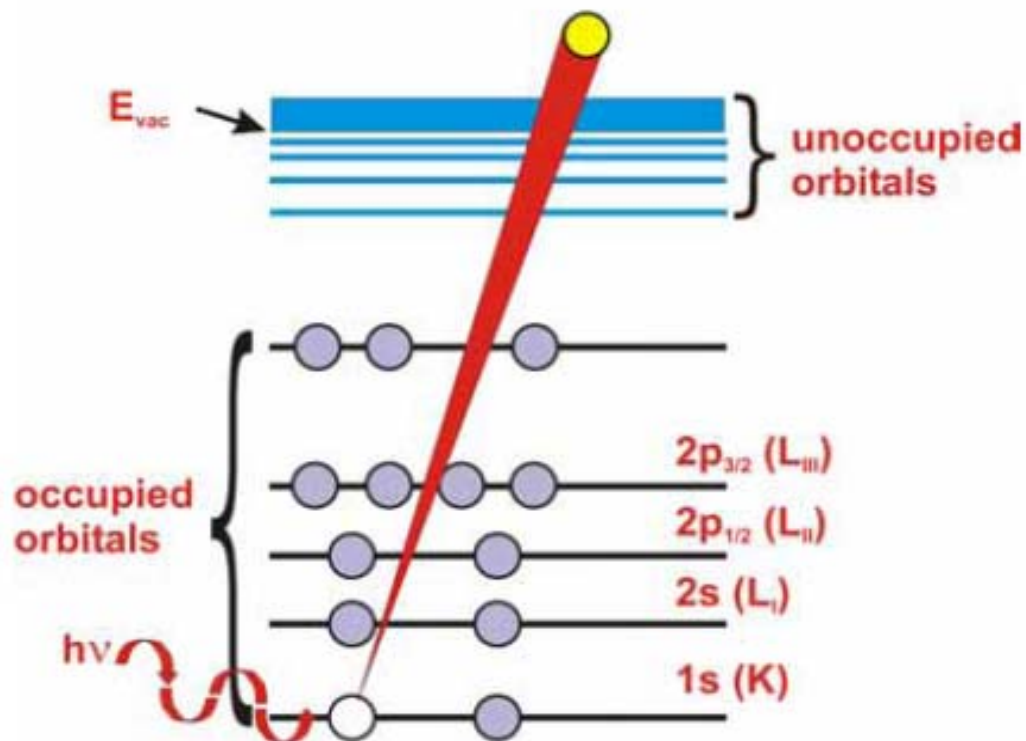
XAS at the Swiss Light Source

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 Polarization
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 environments
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?

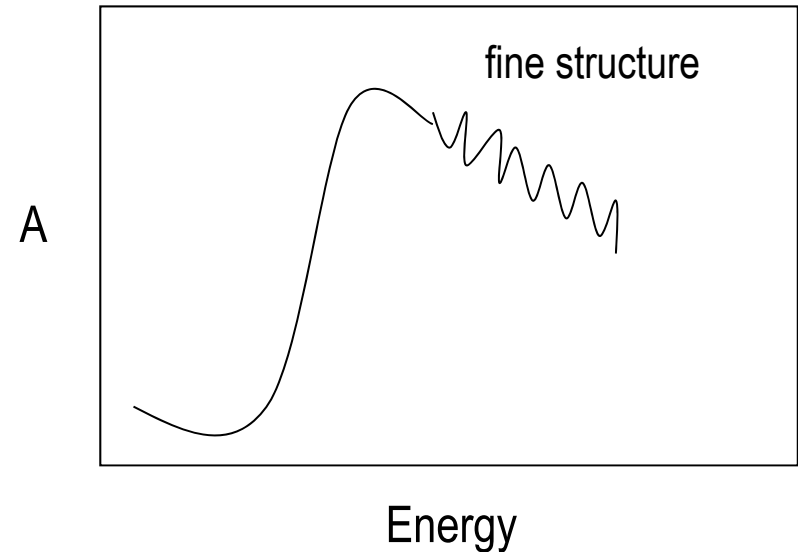
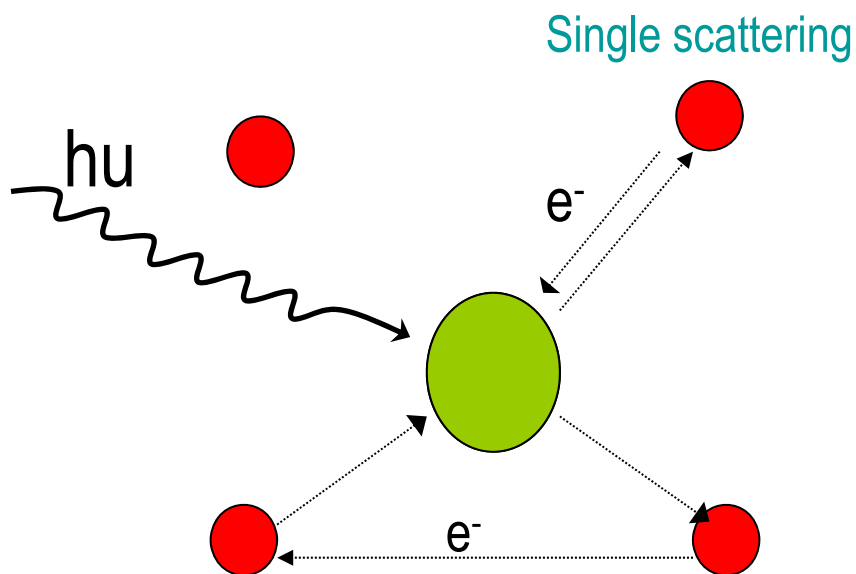
The basic concept of XAFS

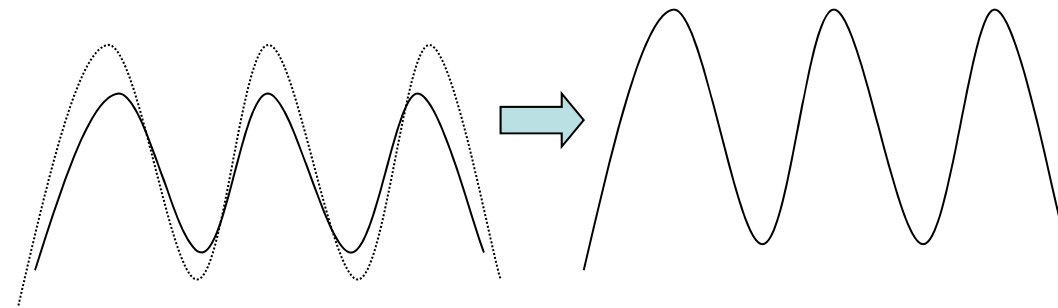
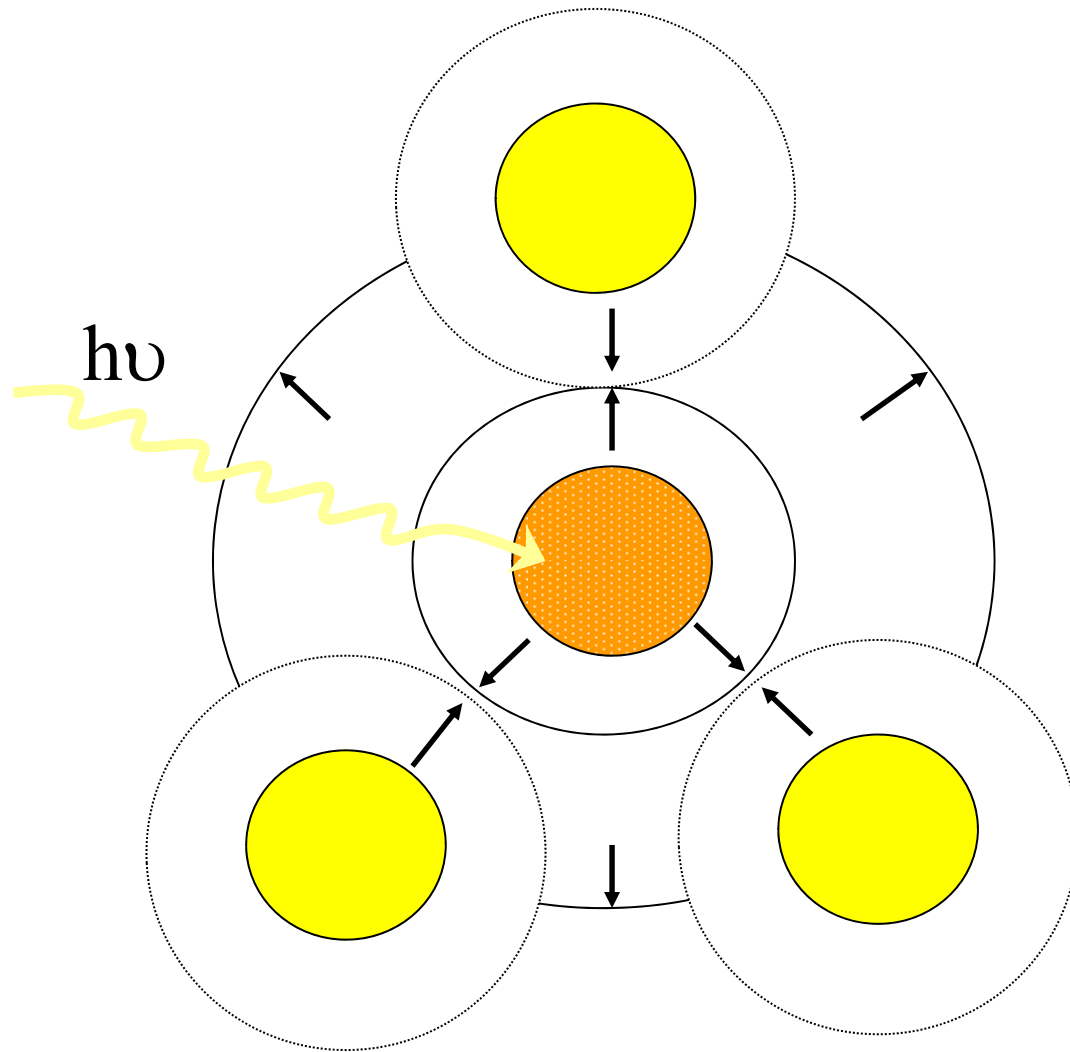


X-rays (light with wavelength 0.06- 12 Å or energy 1-200 keV) are absorbed by all matter through the **photo-electric effect**:

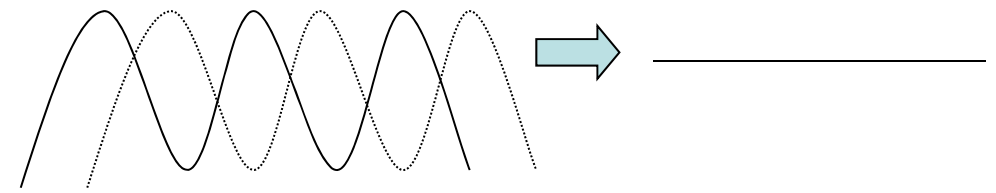
An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core level electron (K, L, or M shell) which is subsequently ejected from the atom. Any excess energy from the X-ray is given to the ejected photo-electron.

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.