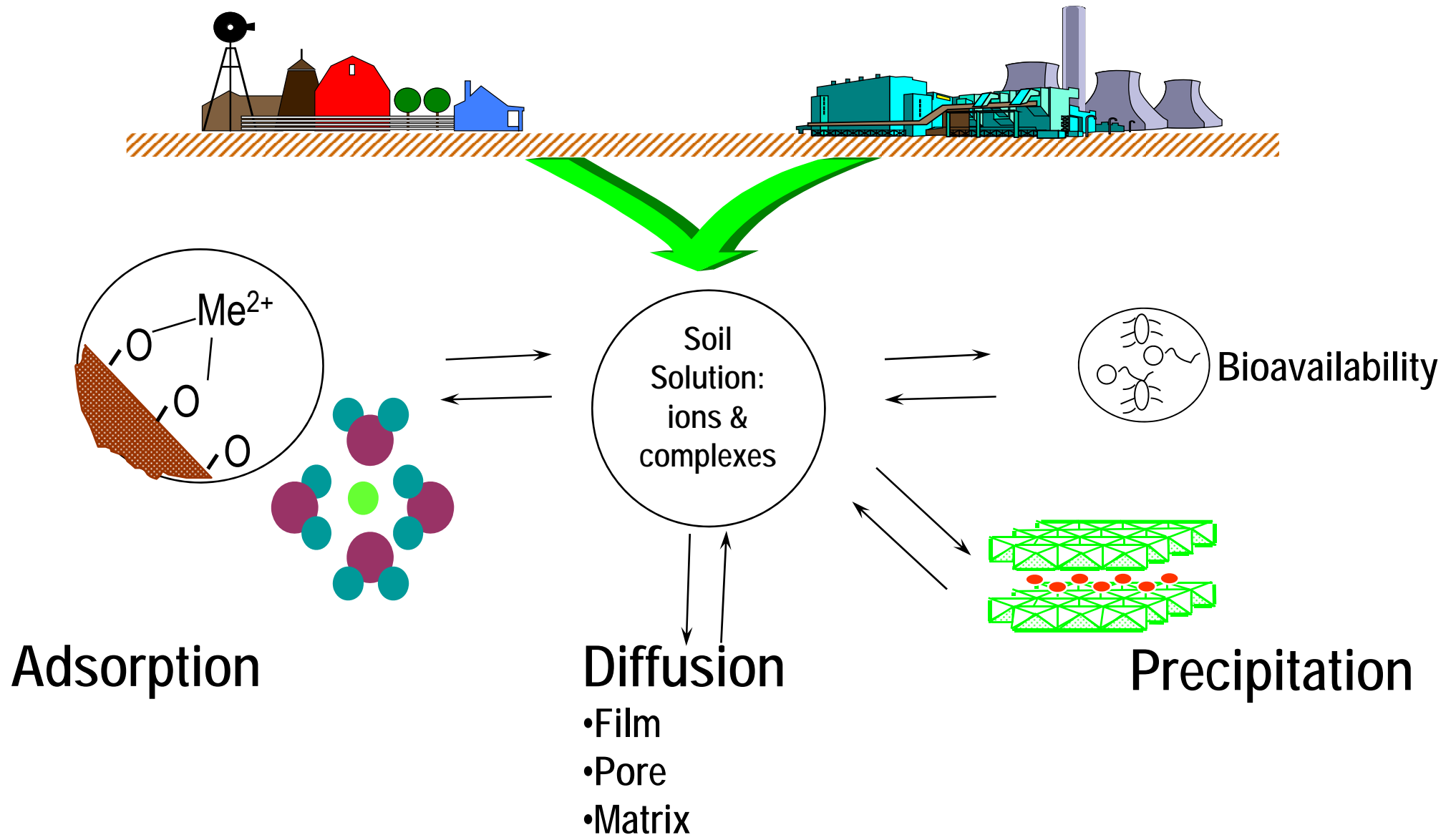Wir schaffen Wissen – heute für morgen

Introduction to EXAFS practical – scientific problem to be analysed

Camelia Borca
Paul Scherrer Institute

Me^{2+}

Soil Solution: ions & complexes

Bioavailability

Adsorption

Diffusion

- Film
- Pore
- Matrix

Precipitation

- 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

Ferrihydrite
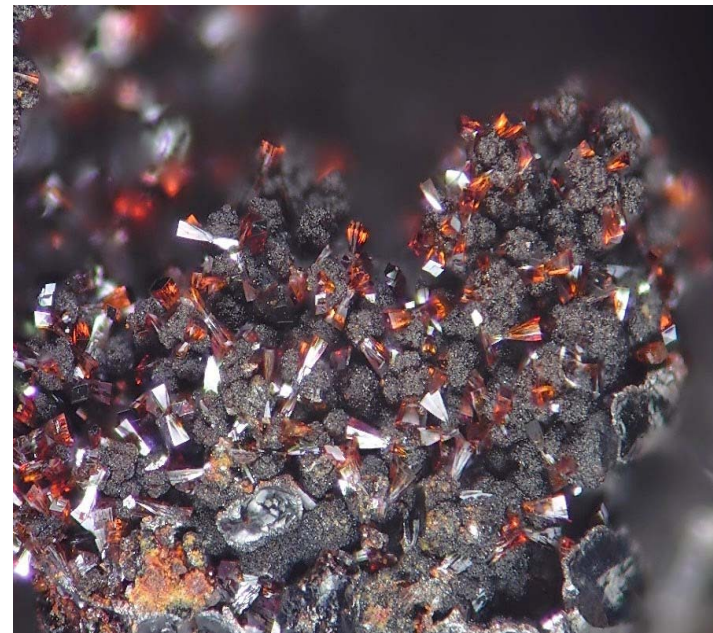
Very common iron hydroxide
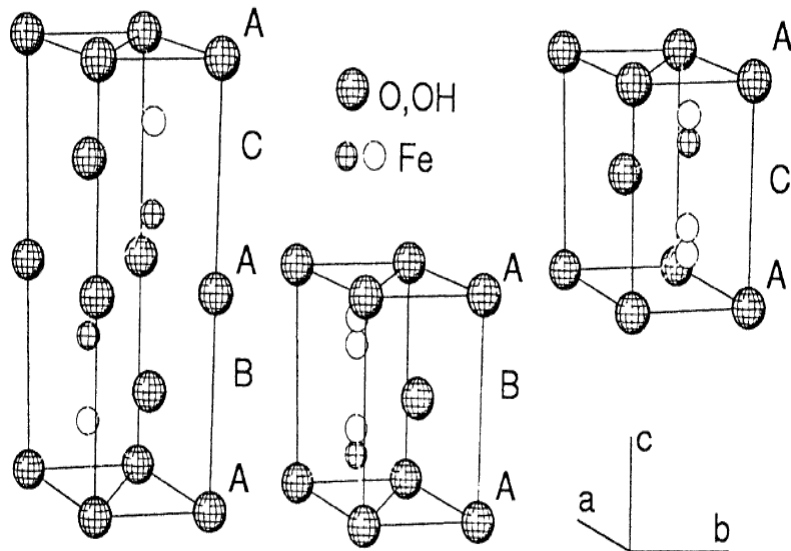
Poorly ordered

Structure/chemical formula unclear
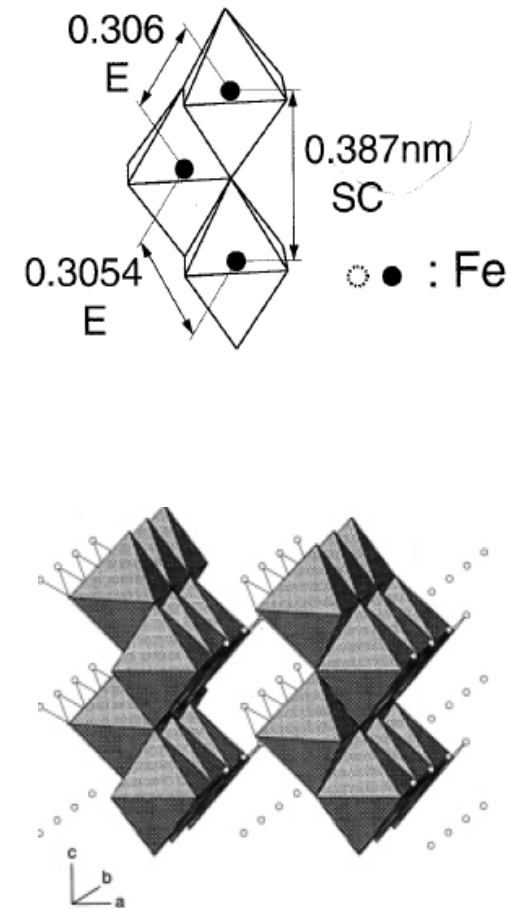

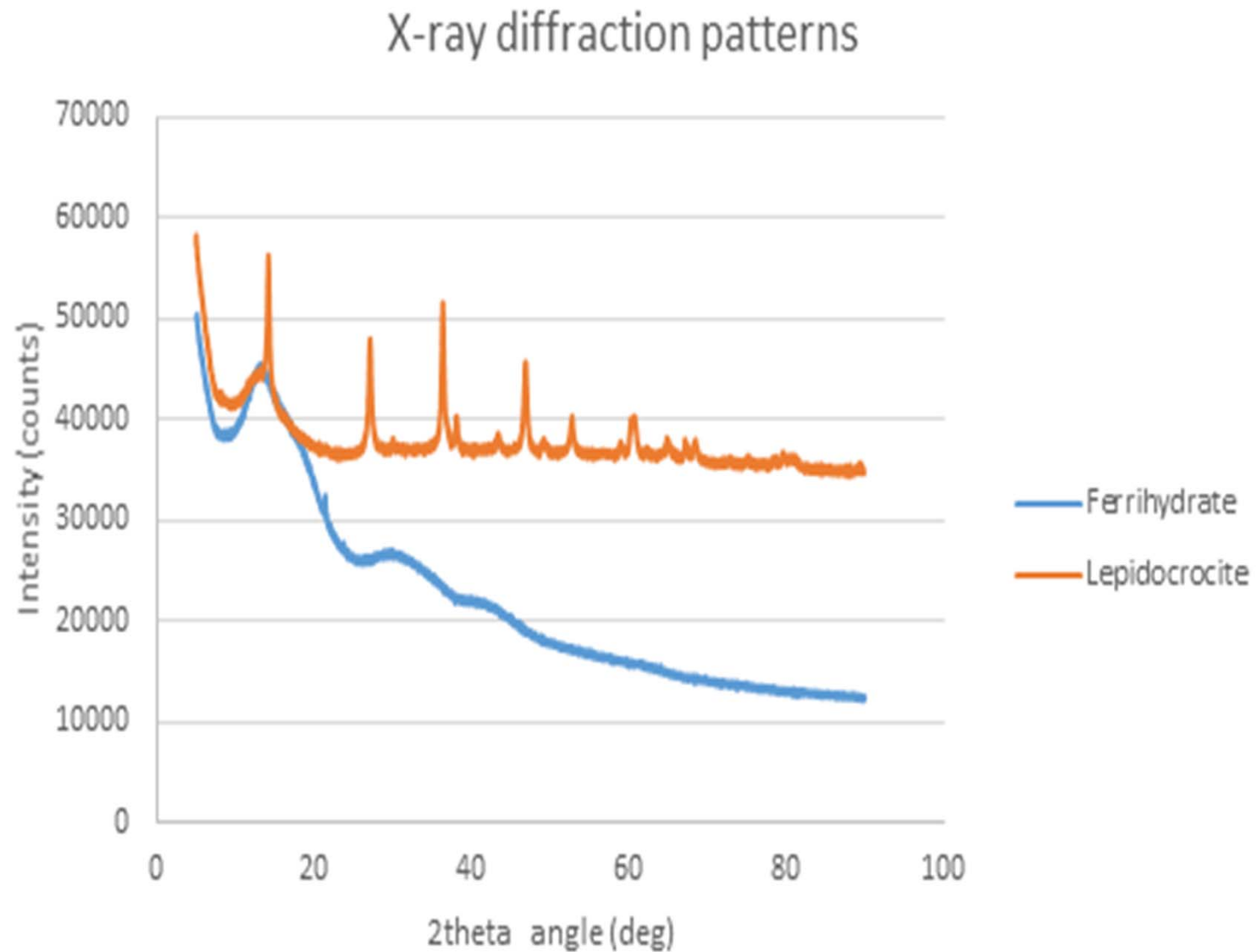## Lepidocrocite

Orthorhombic crystal structure

Well-crystalized

Webmineral.com

Ferrihydrite $Fe_5O_8H \cdot 4H_2O$(?)

Lepidocrocite (γ-FeOOH)

(Cornell, 2003)

The debate is still ongoing

✓ 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)

Absorbance

X-ray Energy E

Visible light
λ ~ 0.5 µm
E ~ 2 eV

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

valence electrons

Continuum

M

L

Energy

K

core electrons

Photoelectric Absorbtion

CONTINUUM

M

L

K

X-ray Absorbtion Near Edge Structure; XANES

Extended X-ray Absorption Fine Structure, EXAFS

Pre-edge

Absorbtion a.u

-200   0   200   400   600   800   1000

Relative Energy

After Bertsch et al., 1995

> 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

- 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

  - o   Chemical shift of 1-3 eV for each withdrawing e$^-$

X-ray Photon

I Electron

🔴 Absorber Atom

🟢 Backscattering Atom

Outgoing Wave

Backscattered Wave

➢ E>Eb

➢ 50 - 1000 eV above absorption   edge

➢ simplified illustration: constructive & destructive   frequencies from the outgoing   photoelectron

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

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

> extraction of EXAFS
> - pre-edge & spline, normalization
> - convertion to wave vector $k = (E-E_o)\sqrt{2m/\hbar}$
> - 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

I_f

I_e

Electron Yield Detector

Fluorescence Detector

I_0

X-ray

I_1

Ion Chamber Detector

Ion Chamber Detector

Fluorescence X-ray Emission

Auger Electron Emission

CONTINUUM

CONTINUUM

M

L

K_β

K_α

K

M

L

K

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

SLS

Diamond

Soleil

ESRF

and many more…

Summary so far:

Cr^{3+}

Cr^{6+}

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

- 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

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

$$0.5\ O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-\ \text{(cathode)}$$

Cr^{VI} $\leftrightarrow$ Fe^{2+}

Fe^{2+}

oxide layer

ZVI

$$Fe \rightarrow Fe^{2+} + 2\ e^-\ \text{(anode)}$$

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

- 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: $CrO_3(OH)_3$ $FeO_3(OH)_3$)

Local structure

Type of linkage | corner | edge | face

Fe

Fe-Fe distance nm | 0.346 | 0.306 | 0.289

Goethite (α-FeOOH)

0.301
E
0.346 DC
0.328nm
E'

- interatomic distances
- 3D-arrangement

Nucleation, growth, aggregation of mineral phases

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

Sorption complexes

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

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

Relation to molecular Fe/Cr
 (-> mechanism)

Permeable reactive barrier

Fe

Cr

Cr-POI 2

Cr-POI 1

200 μm

500 μm

j2

M. L. Peterson et al.

POI 2 (high Cr)
POI 1 (low Cr)

norm. absorption

Energy (eV)

% Cr(VI)

100
80
60
40
20
0

Normalized Absorbance

Energy (eV)

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

j2   noch vergrösserung des pre-edge
ggf. noch vor und nachteile EXAFS aufzeigen
jafromme; 01.10.2008

Cr/Fe < 1/10

POI1: Cr/Fe > 1/3

POI2: Cr/Fe ~ 1/3

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

1. Extract EXAFS signal

- Subtract smooth background

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

Normalized oscillatory part of absorption coefficient

Measured Absorption coefficient

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

Evaluated at the Edge step (E_0)

Ru in energy

Ru in k space

Photon

Photoelectron

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

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

Fourier Transform Button

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

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

Fourier transformed of the EXAFS signal

Remember: FT creates a complex function

→ always show magnitude AND real or imaginary part

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

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

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

Feff calculation

Calculate EXAFS signal of model compound! → FEFF

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

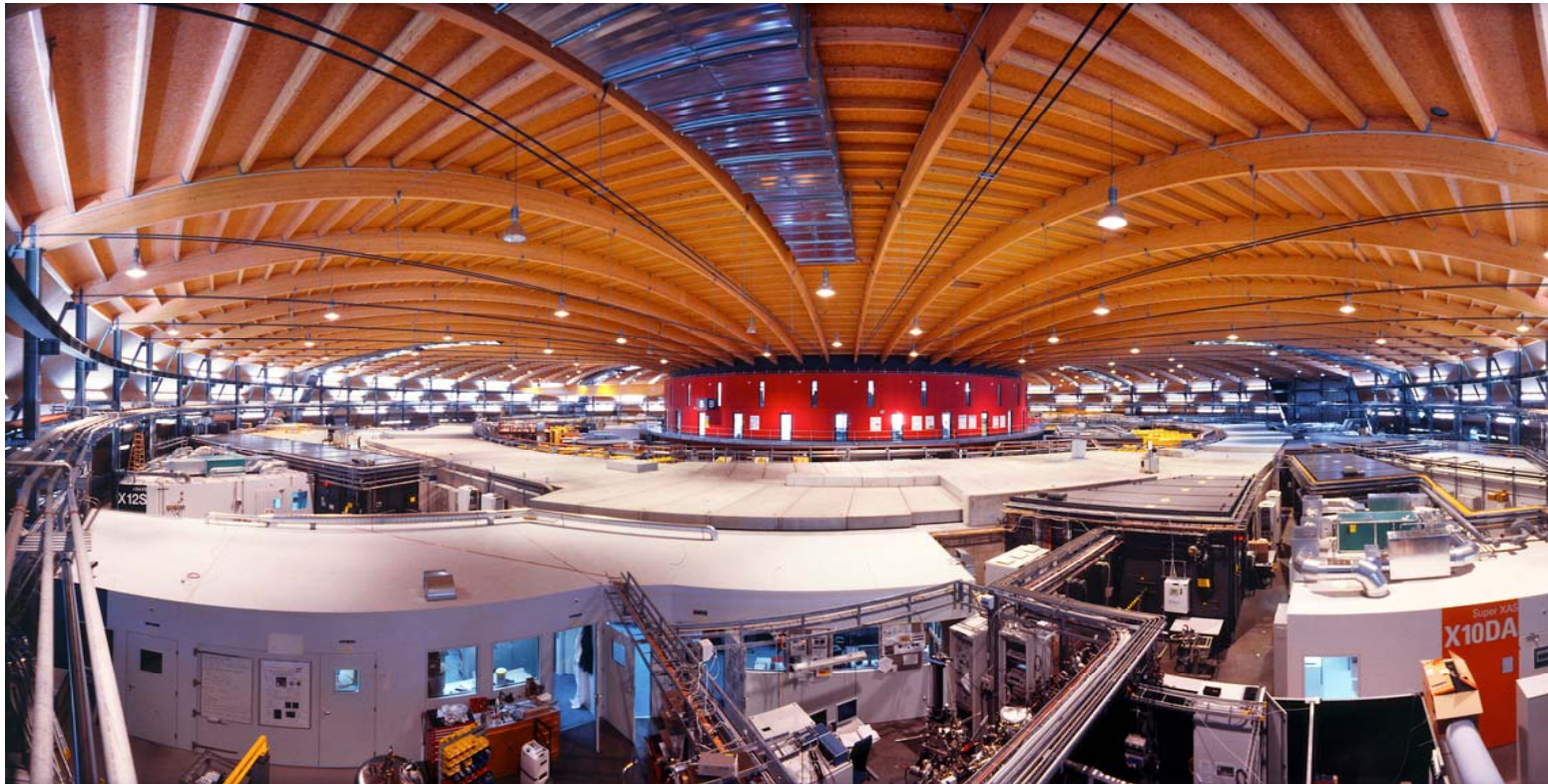| Beamline	Energy Range (keV)	Spot Size (µm)	K-Edges	Absorption	Fluorescence	Electron yield	Speciality
PHOENIX	0.8 - 8	2 x 2	Na - Co	x	x	x	**Energy Range Variable Polarization**
MicroXAS	5 - 23	1 x 1	Ti - Mo	x	x		**Femto Diffraction radioactive samples**
SuperXAS	6 - 40	5 x 10	Cr - La	x	x		**Absorption, Fluorescence, Quick, Chemical 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?

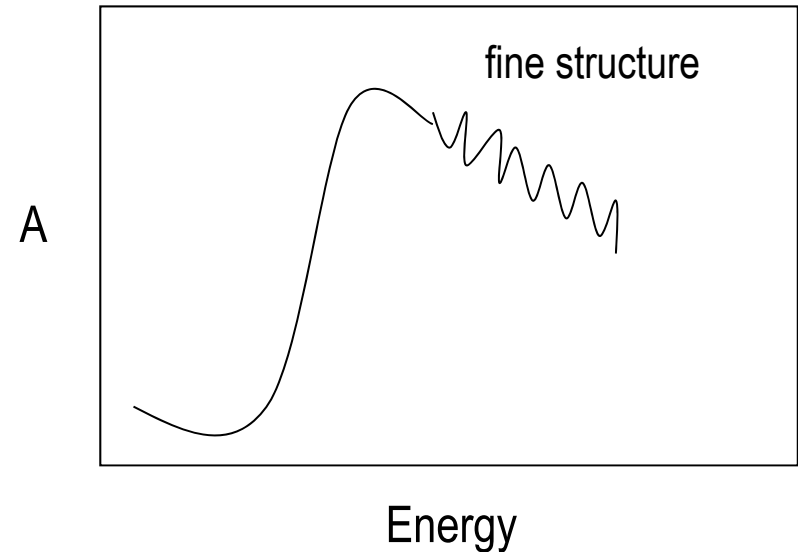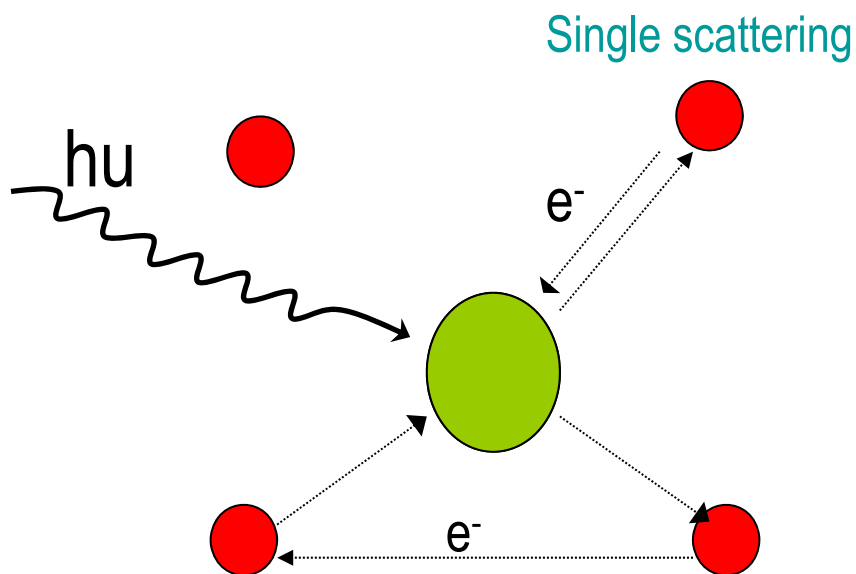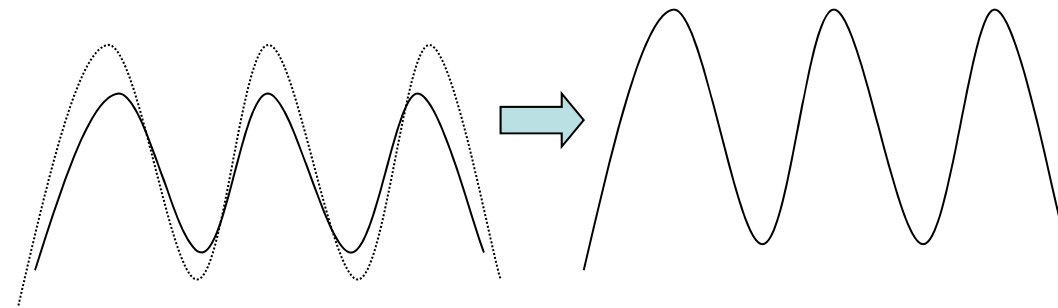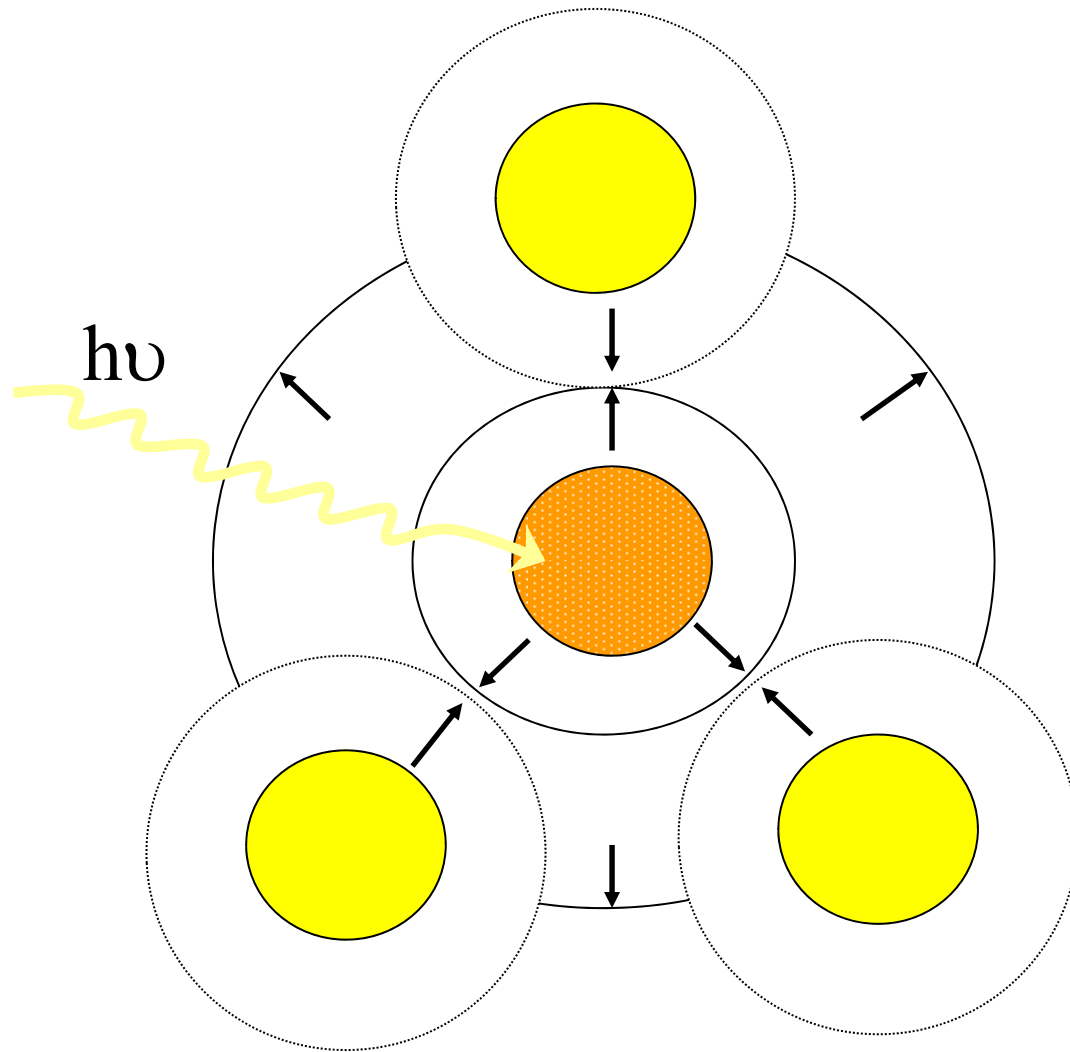X-rays (light with wavelength 0.06- 12 Å or energy 1-200 keV) are absorbed by all matter through the photo-electric effect:
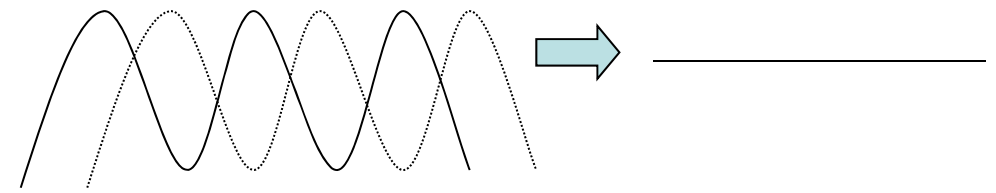
An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core level electron (K, L, or M shell) which is subsequently ejected from the atom. Any excess energy from the X-ray is given to the ejected photo-electron.

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.

hʋ

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.