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Wir schaffen Wissen – heute für morgen

Shining light on environmental technologies: a bright future for environmental scientists

Maarten Nachtegaal

- In situ X-ray spectroscopy group (IXS), laboratory for bioenergy and catalysis (LBK)/ENE
- SuperXAS beamline, laboratory for catalysis and sustainable chemistry (LSK)/SYN
- Department of environmental system science ETHZ

Outline

In situ passivation of metals (spatially resolved XAS/XRF)

- metal speciation in a Zn smelter contaminated soil

Permeable reactive barriers to reduce organic and metallic compounds (high resolution XANES)

- Cr speciation in a permeable reactive barrier

Intracellular Pb speciation dynamics (RXES)

- Tracking intracellular Pb speciation dynamics in the green alga *C. reinhardtii*

Acknowledgements:

IXS group:

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L. Kluepfel (M.Sc.) (Ph.D. at ETH)
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E. Kleymenov (postdoc) (Mesa Imaging)
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J. Szlachetko (postdoc) (scientist at SwissFEL)
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Support:

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C. Frieh
G. Jud
P. Ascher
M. Birri

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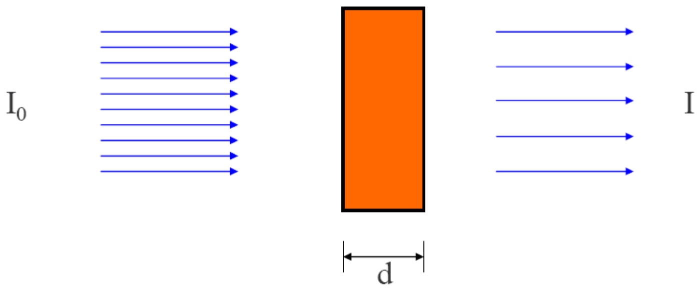
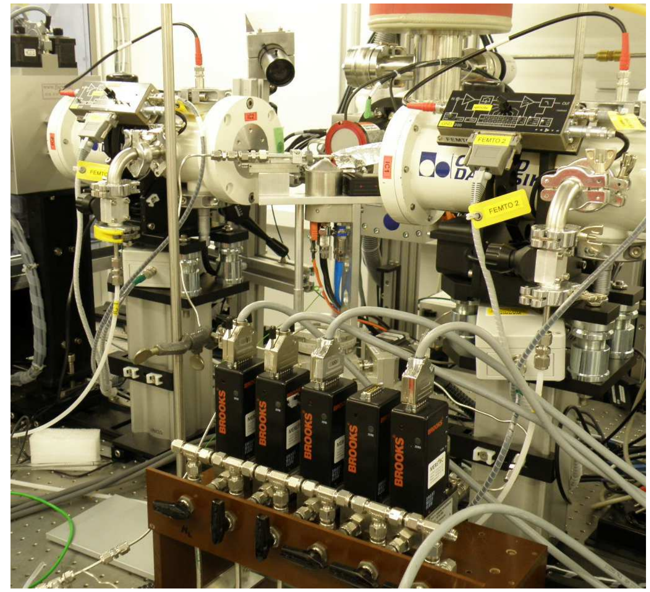
Tool: EXAFS



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:

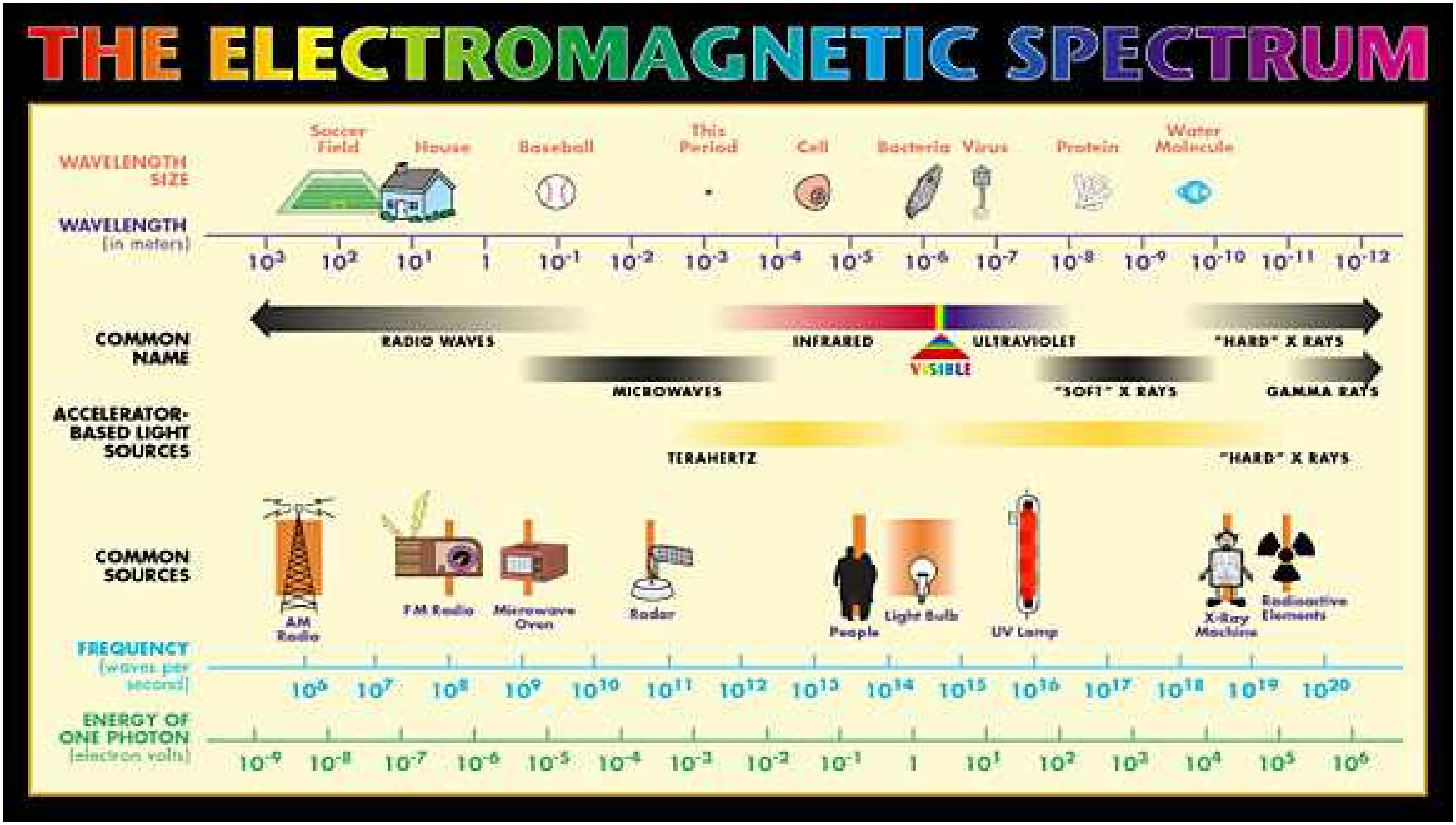
$$\mu \approx \frac{\rho \mathrm{Z}^4}{\mathrm{A}\mathrm{E}^3}$$

What do you measure?

- Absorption as function of energy

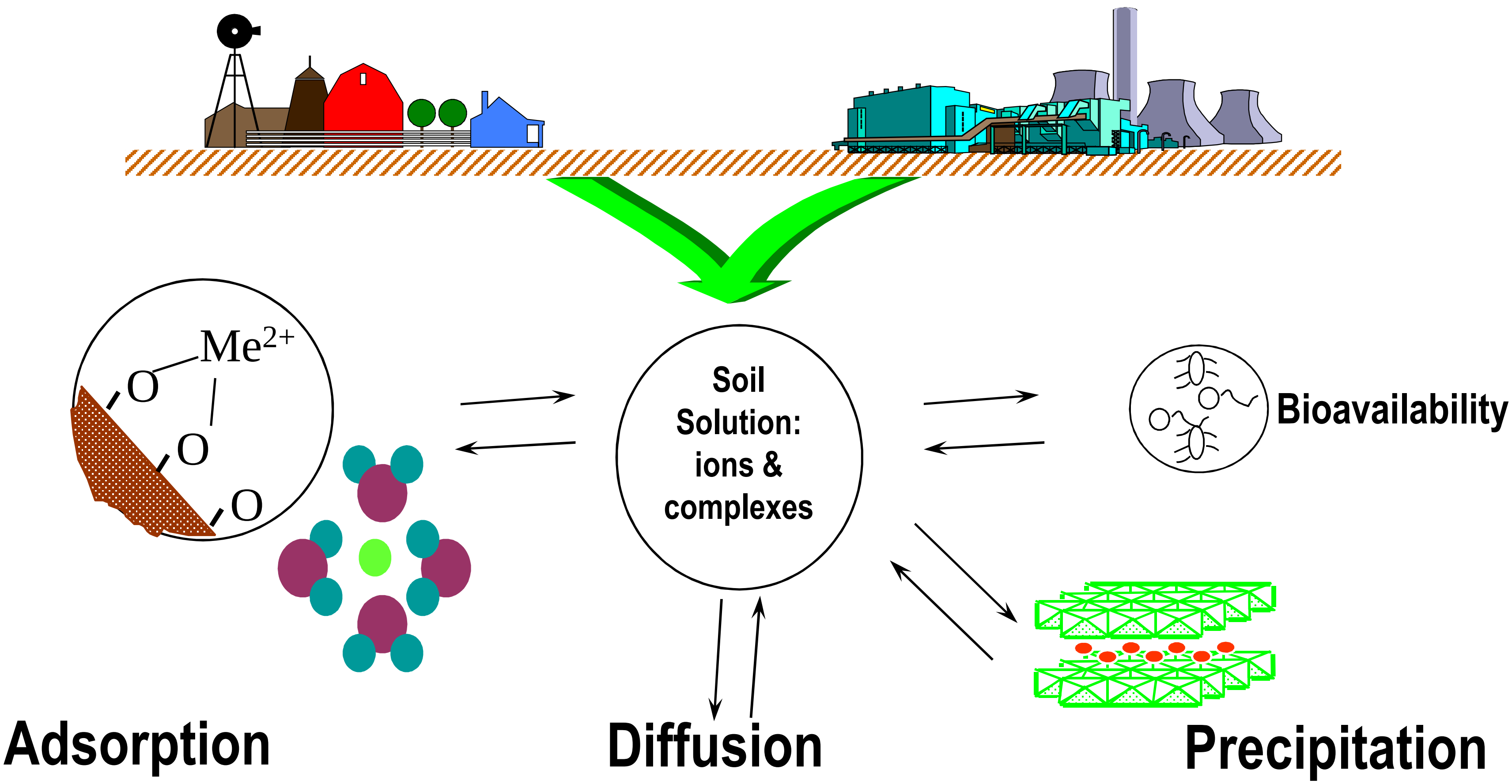
Need a synchrotron…

Synchrotrons produce bright light



Introduction of metals into the environment:

Primary minerals, Agriculture, Industry, Sewage sludge, etc



- Film
- Pore
- Matrix

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Maatheide, Belgium

1990

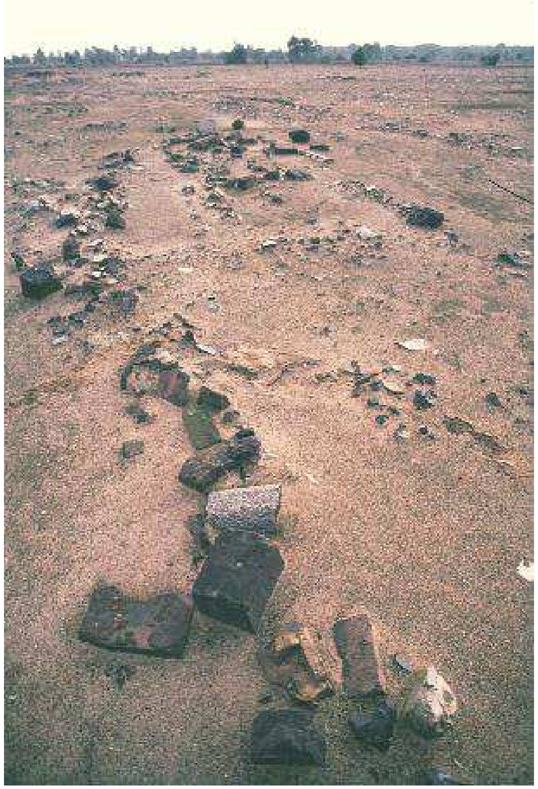
2002

• 135 Ha of bare land due to elevated Zn, Pb, and Cd concentrations from the Zn smelting facility in Maatheide, Belgium.

• Cleanup strategy: *In situ* immobilization of contaminants, by addition of beringite and compost combined with metal tolerant plants.

Zinc Speciation in Smelter Contaminated Soil

Regulatory acceptance of *in situ* immobilization as a secure reclamation method depends on the ability to predict the long–term stability of such remedial treatments.



- How did the speciation change as result of the remediation efforts?

- Do Zn surface precipitates play a significant role in controlling the zinc speciation?

- What is the long term stability with respect to environmental change?

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Experimental Approach:

Scale ↑

Total dissolution

Sequential extraction/ Stirred flow desorption

XRD

Electron microprobe studies/
X-ray microprobe studies

EXAFS

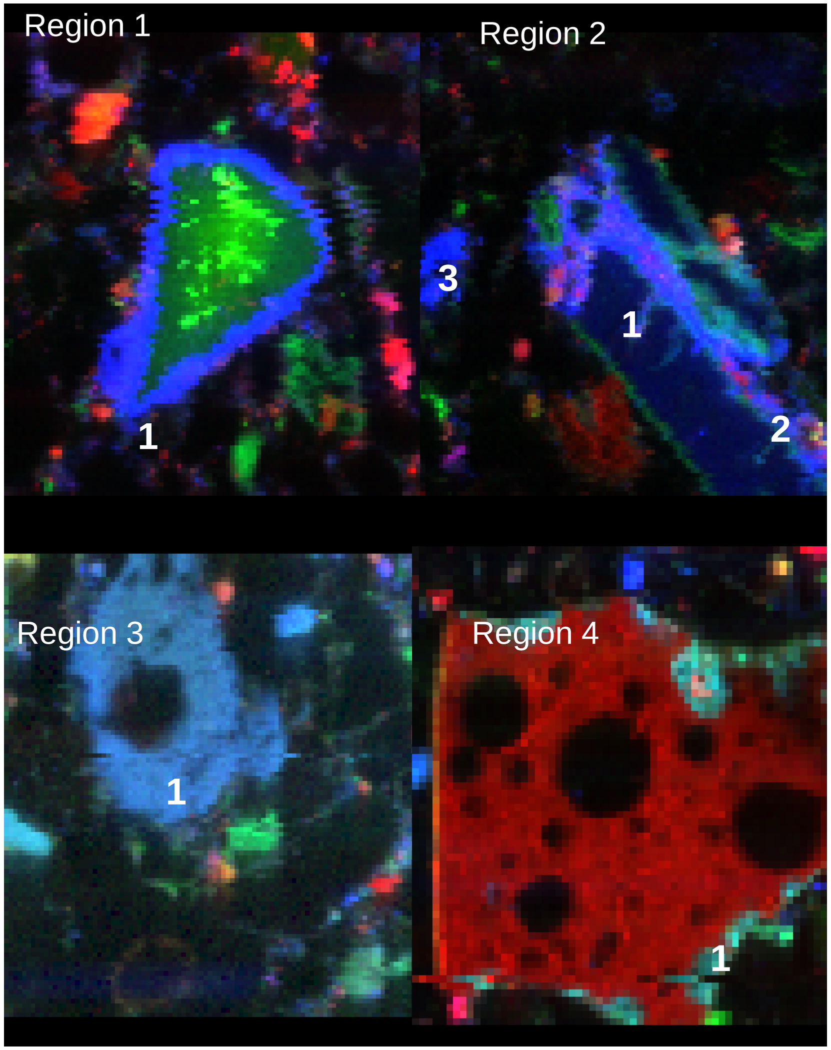
μ-EXAFS in combination with PCA and linear fitting

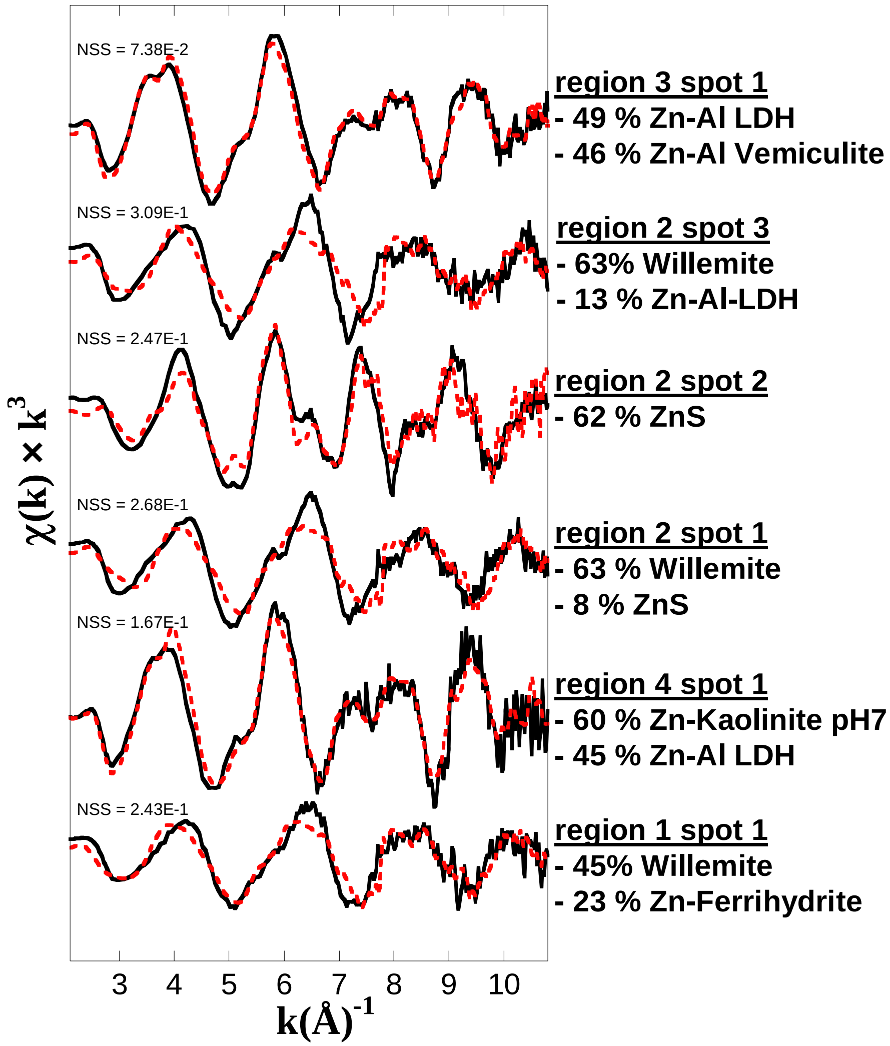
Resolution ↓

Total Dissolution

	Non-Treated pH=6.4 (ppm)	Treated pH=6.7 (ppm)
Fe	47880	21159
Al	18619	23264
Ti	1533	1765
Zr	170	175
Ba	513	368
Mn	1122	573
P	357	819
S	2351	1881
Zn	**20476**	**13144**
Pb	2996	1297
Cu	2132	762
As	312	115
Ni	348	165
Co	41	25
Cd	31	51
Hg	737	779

μ- focused SXRF and EXAFS (non-treated soil)





Conclusions

- Weight percentages Zn in soil, only 30 % of Zn left in primary polluting minerals.

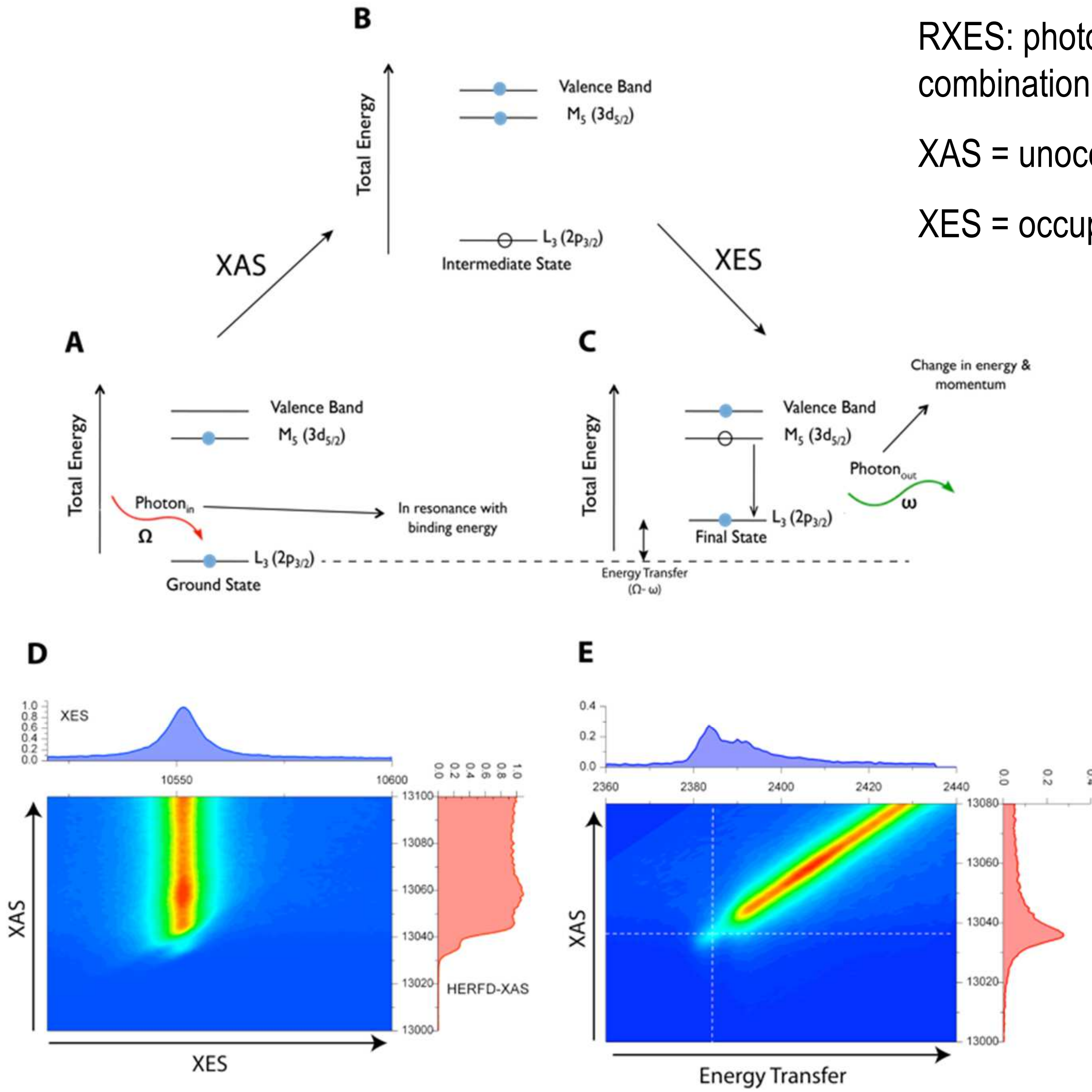
- EXAFS and μ-EXAFS studies show that zinc containing surface precipitates make up 60 % of the total zinc fraction in both the treated and non-treated soils. With the formation of a more stable Zn phyllosilicate in the treated soil.

- No difference in speciation between treated and non-treated soil, which is reflected by desorption studies.

Effects of *in situ* Remediation on the Speciation and Bioavailability of Zinc in a Smelter Contaminated Soil

2005 Nachtegaal, M., Sonke, J.E., Markus, M.A., Vangronsveld, J., Livi, K.,van der Lelie, N., and Sparks, D.L. *Geochimica Cosmochica Acta* **69**, 4649-4664

Tool: high resolution XAS (HERFD-XAS)



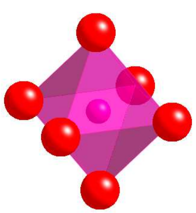
RXES: photon-in photon-out technique, a combination of XAS and XES spectroscopy

XAS = unoccupied density of states

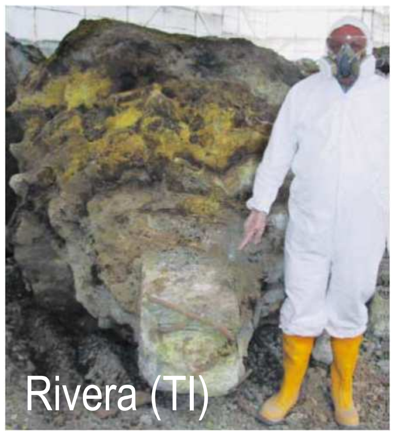
XES = occupied electronic states.

Cr(III)

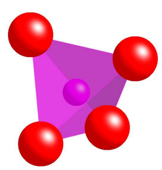
Essential micronutrient



Cr(VI)
(chromate)



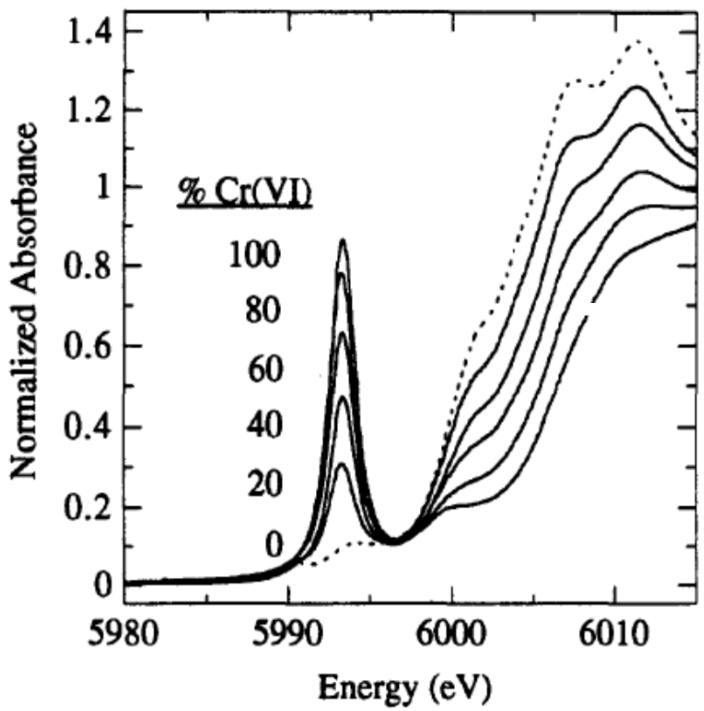
Chemical carcinogen



24
Cr
52.00

Solid state Cr speciation

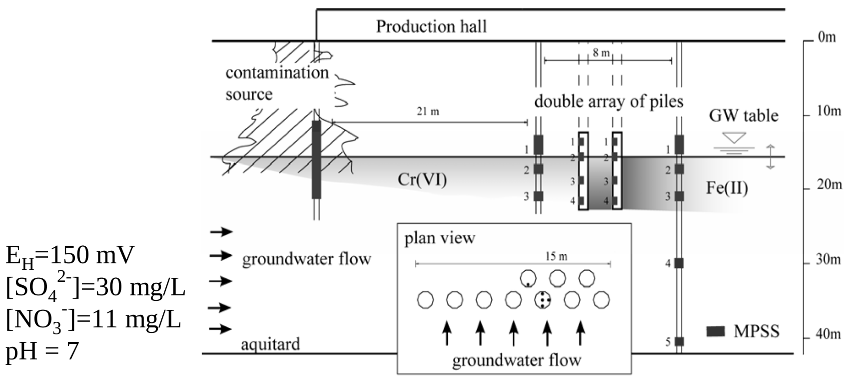
M. L. Peterson et al.



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

Wood impregnation in Willisau, CH

24
Cr
52.00

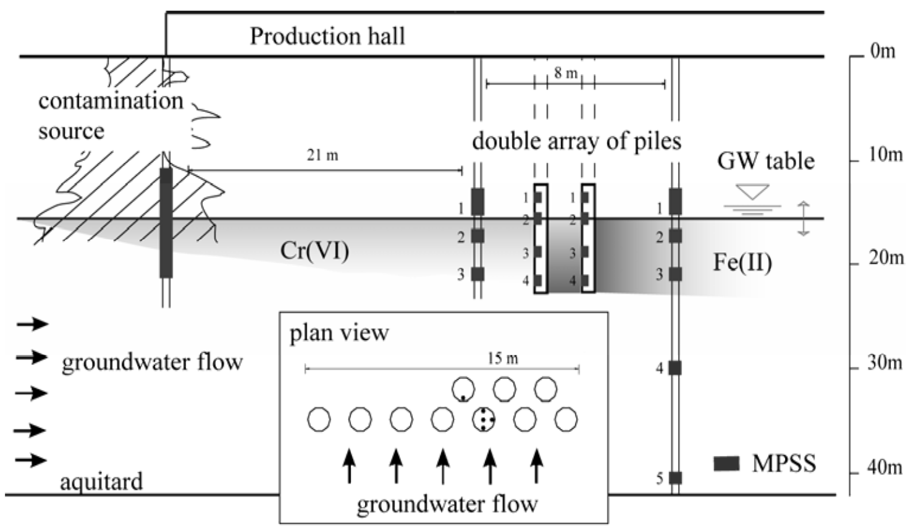


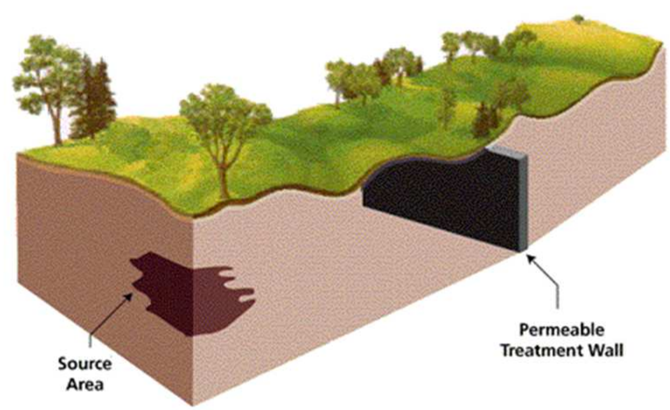
- Contaminants Cr(VI), Cu
- ~1 t Cr at a depth of 3-12 m
- Groundwater protection zone ([Cr(VI)]max = 0.01 mg/L)

Permeable reactive barrier

24
Cr
52.00

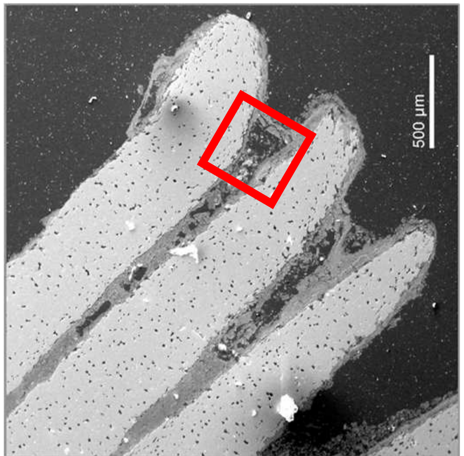
Permeable Reactive Barrier (PRB): couple the oxidation of Fe(0) with the reduction of Cr(VI)

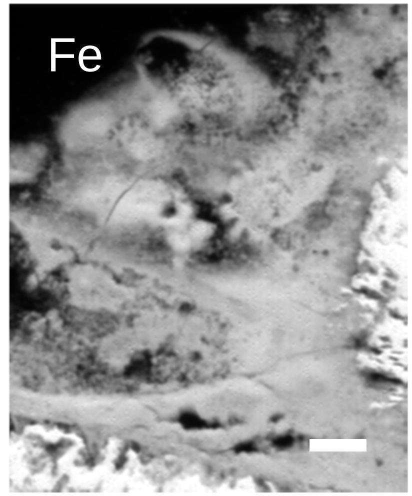


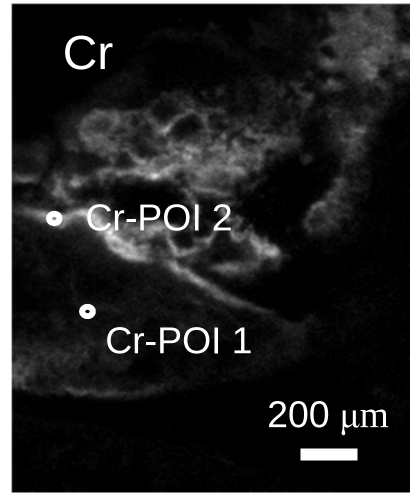


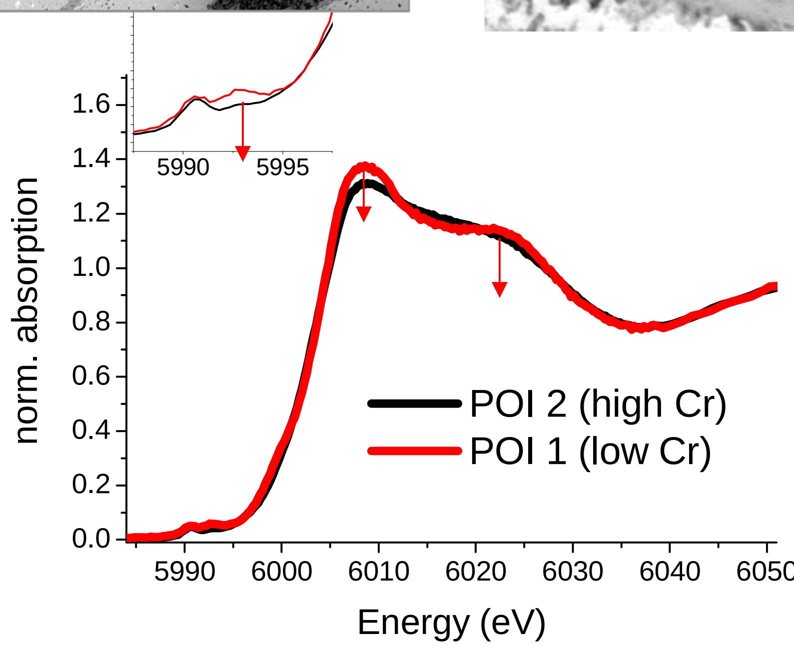
- Contaminants Cr(VI), Cu
- ~1 t Cr at a depth of 3-12 m
- Groundwater protection zone ([Cr(VI)]max = 0.01 mg/L)

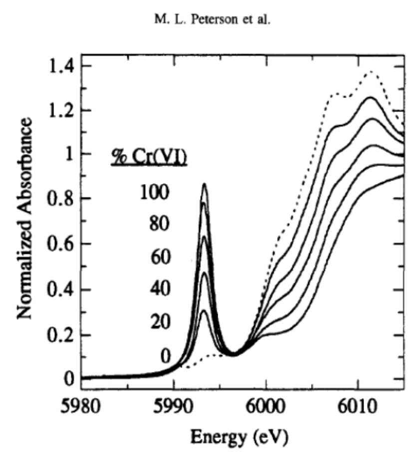
$$Fe^0 + Cr^{VI}O_4^{2-} + 8H^+ \leftrightarrow Fe^{3+} + Cr^{3+} + 4H_2O$$



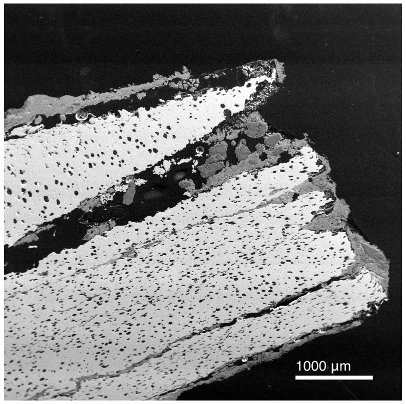


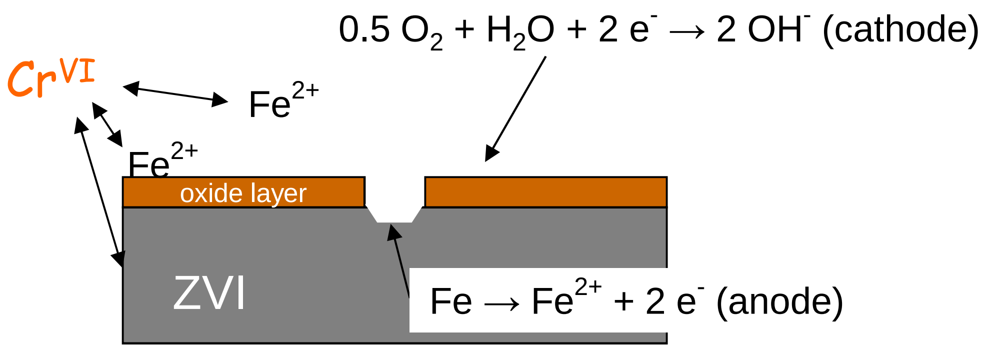






Peterson et al., *GCA* 61: 3399, 1997.





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

- 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

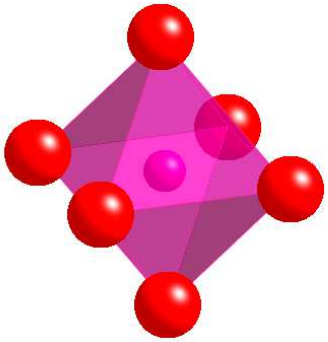
?

Local structure ↔ Mechanism

Poorly Crystalline Chromium-Iron (Oxy)Hydroxides

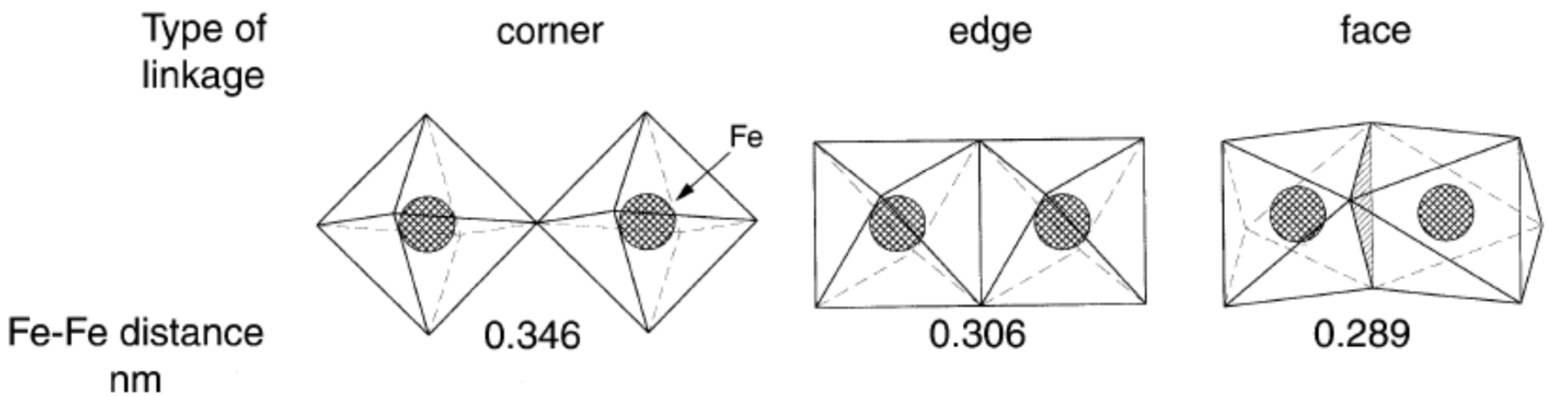
(small excursion)

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

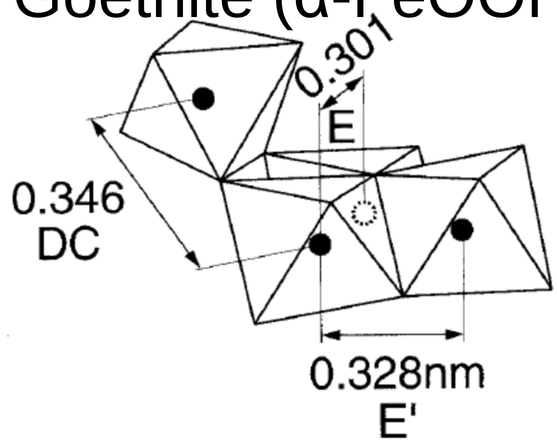


CrO_6 / FeO_6 octahedron
(also: $CrO_3(OH)_3$ $FeO_3(OH)_3$)

local structure



Goethite (α-FeOOH)



- interatomic distances
- 3D-arrangement

why study local (~5Å) structure ?

Nucleation, growth, aggregation of mineral phases

Sorption complexes

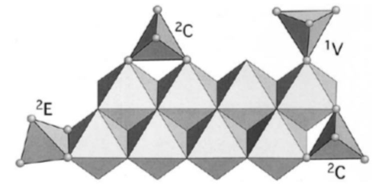


Fig. 1. Possible surface complexes of AsO_4 tetrahedra on goethite.

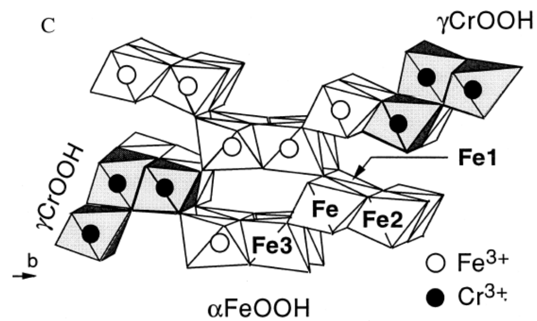
Sherman & Randall, GCA, 67 (2003), 4223.

Important properties e.g. color

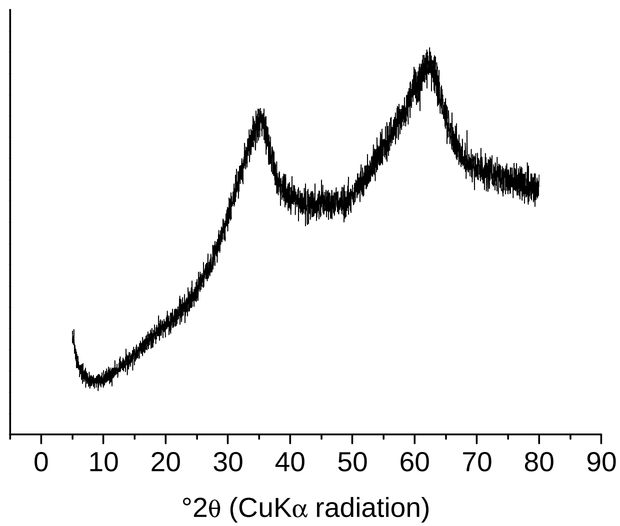
(α-Cr_2O_3 – α-Al_2O_3:Cr^{3+})

Relation to molecular Fe/Cr

(-> mechanism)



XRD ferrihydrite



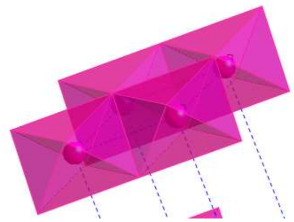
Model Cr(III) Phases

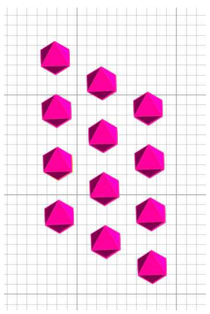
Fe-Cr-hydroxides of different composition (0-100 % Cr)

Grimaldiite (CrOOH):

Pure Cr-Oxyhydroxide

Octahedral polymerization





Active Cr-Hydroxide ($Cr(OH)_3 \bullet 3H_2O$):

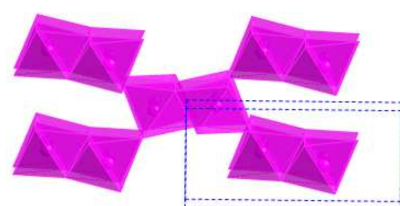
Pure Cr-Hydroxide

Hydrogen bonded isolated Cr-octahedra

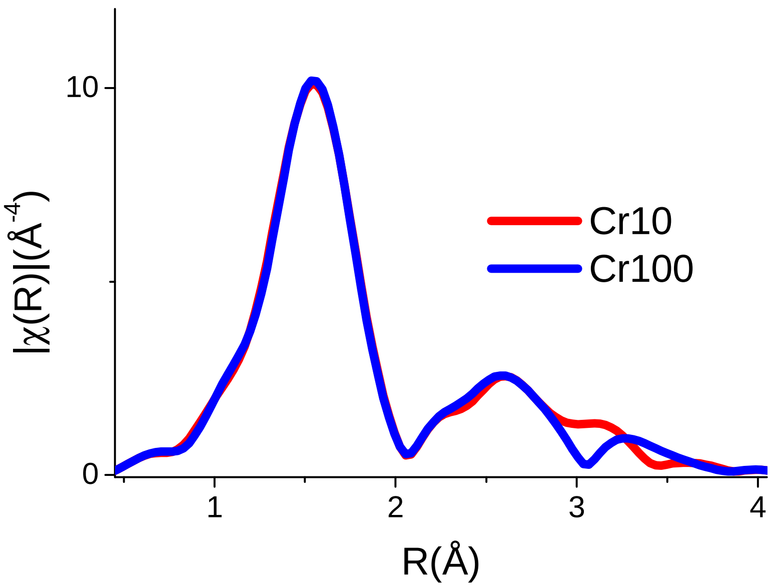
Cr-goethite:

α-FeOOH with 10% Cr substitution

Octahedral polymerization

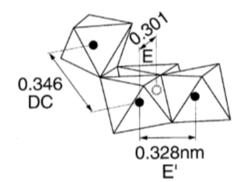


EXAFS



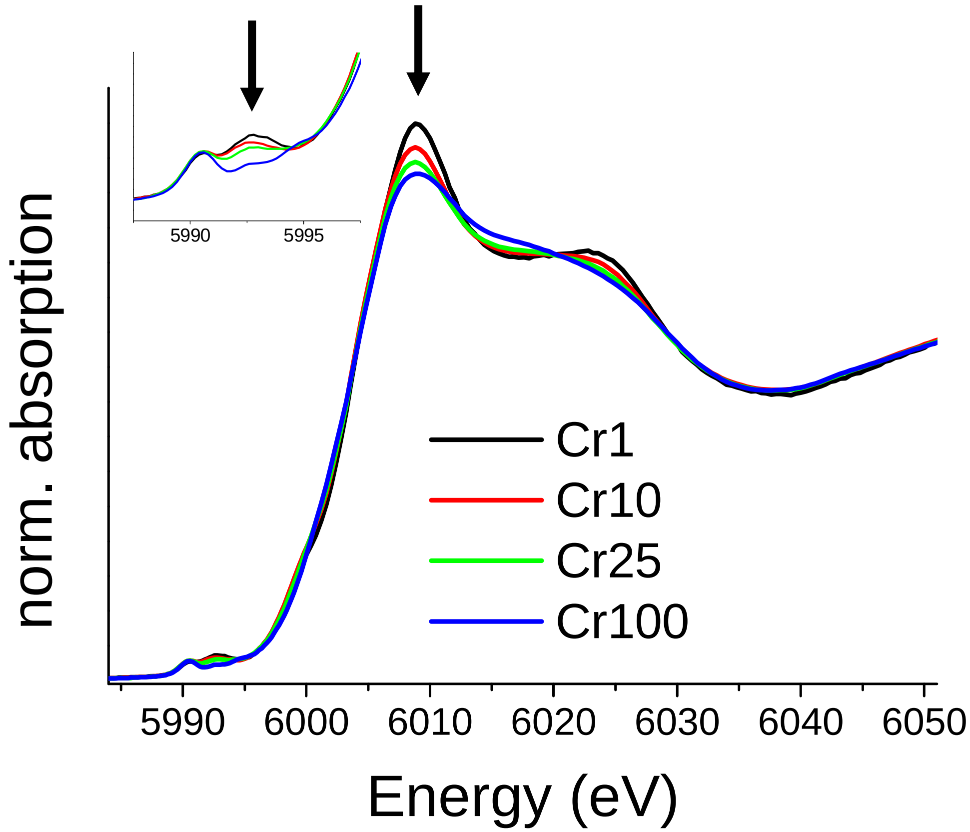
Cr10	R(Å)	N	σ^2 (Å^2)
O	1.98 ± 0.01	6	0.006 ± 0.001
Fe	3.05 ± 0.01	4	0.016 ± 0.002
Fe	3.44 ± 0.04	2	0.015 ± 0.005
R-factor	1.40%		

Cr100	R(Å)	N	σ^2 (Å^2)
O	1.98 ± 0.01	6	0.006 ± 0.001
Fe	3.00 ± 0.01	2	0.010 ± 0.001
Fe	3.35 ± 0.03	2	0.010 ± 0.001
Fe	3.56 ± 0.02	2	0.008 ± 0.001
R-factor	0.80%		



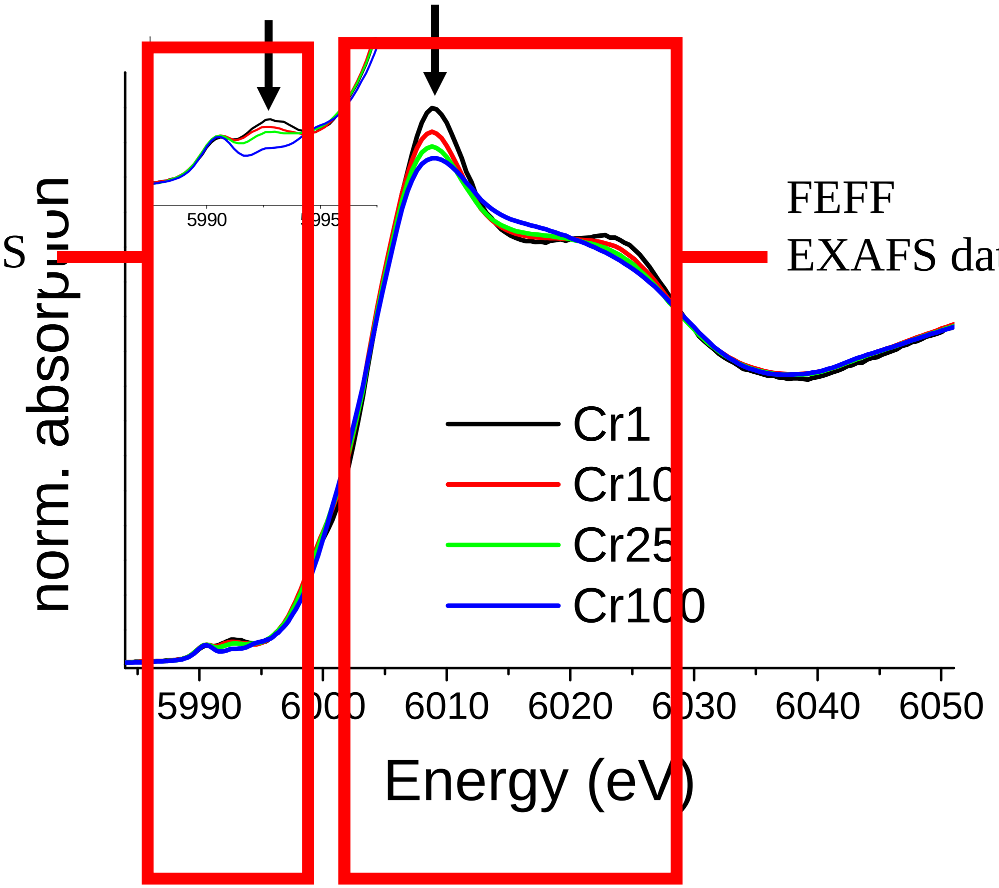
- No indication for single corner Fe at 4 Å, suggests end member in the series is not gamma, but beta CrOOH
- low [Cr] → more coherent 1st metal shell
- ΔZ(Cr,Fe) = 2

XANES



5990
5995
Cr1
Cr10
Cr25
Cr100
norm. absorption
5990
6000
6010
6020
6030
6040
6050
Energy (eV)

XANES



FEFF & RXES

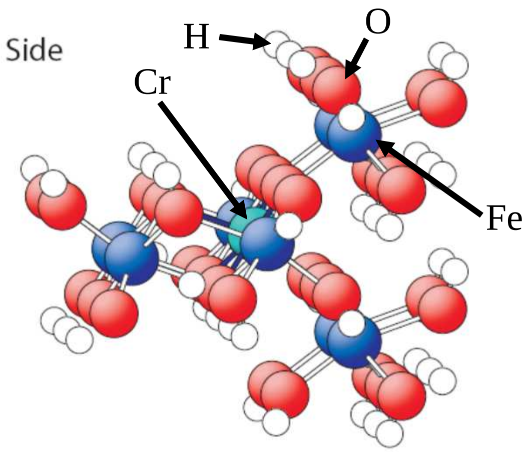
FEFF
EXAFS data as starting point

II.
„pre-edge“

I.
main edge

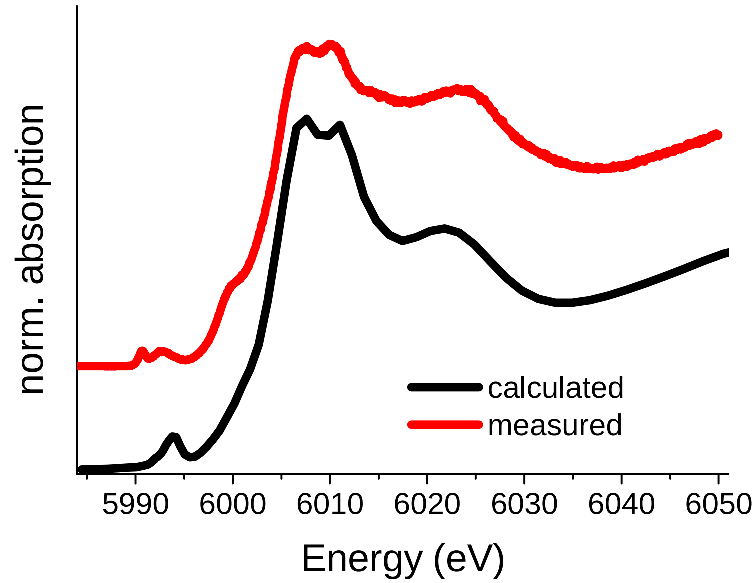
FEFF-Modeling

(Cr-) Goethite

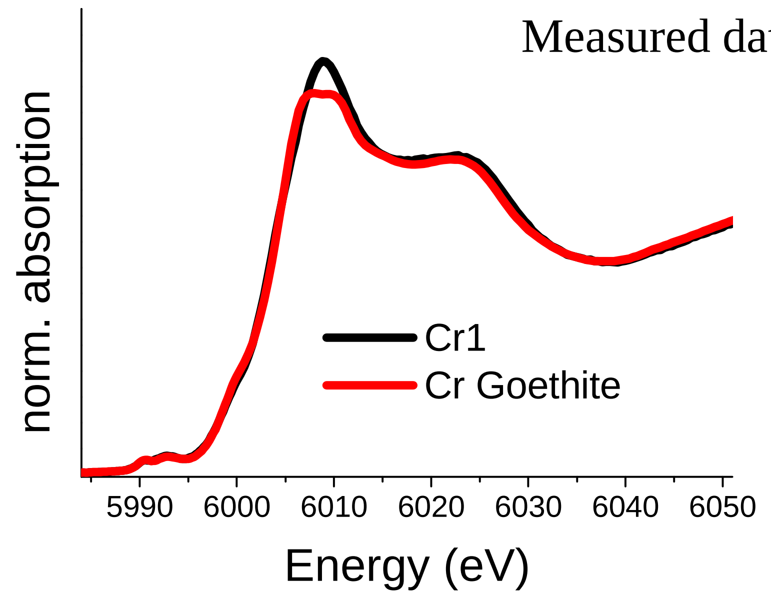


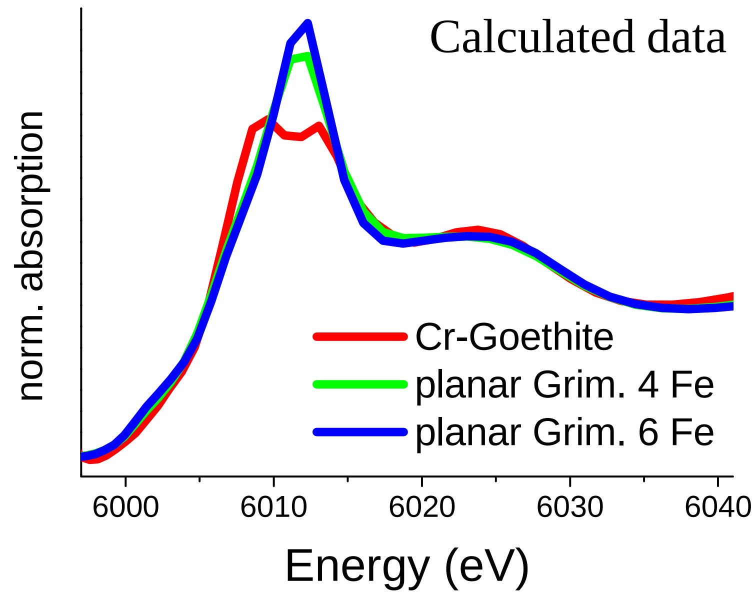
structural relaxation
(DFT)

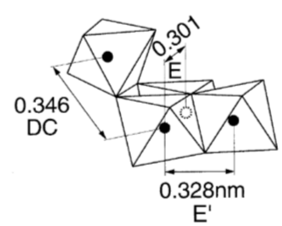
FEFF: FMS-SCF

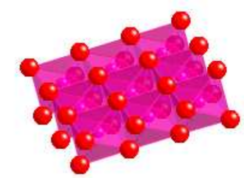


FEFF-Modeling







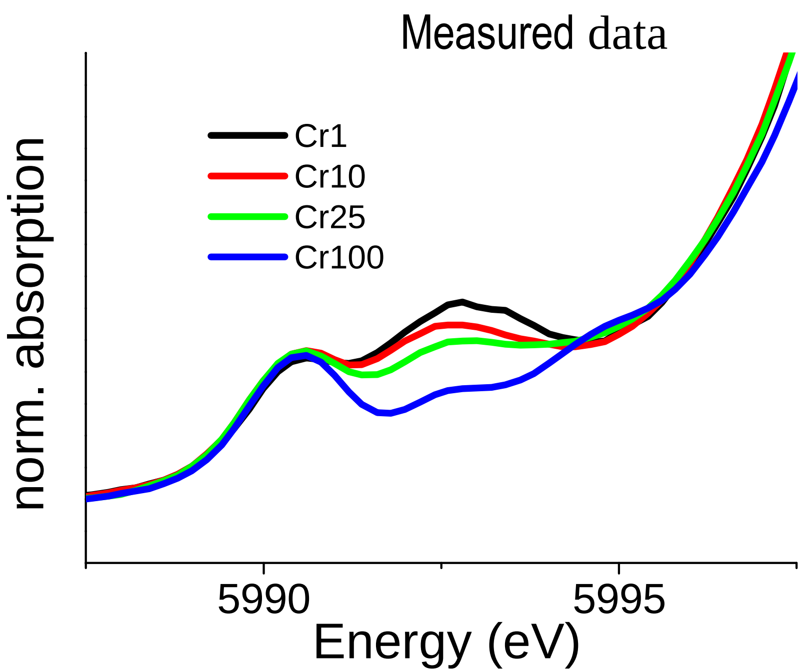


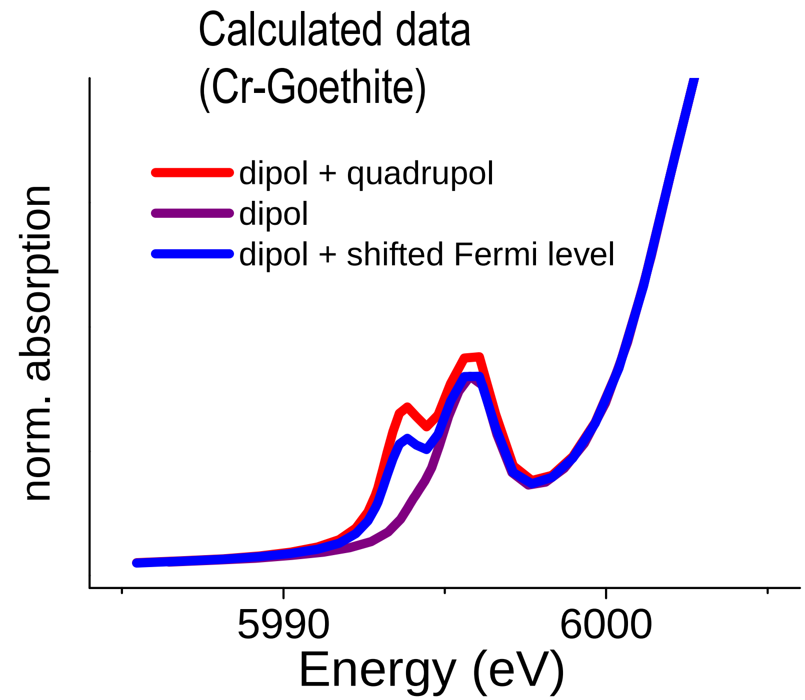
XANES corroborates EXAFS results

„Pre-“edge

Probes 3d states

Basis for important properties: e.g. magnetism, redox properties





Pre-edge consists of dipolar and quadrupolar transitions

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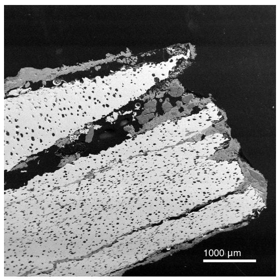
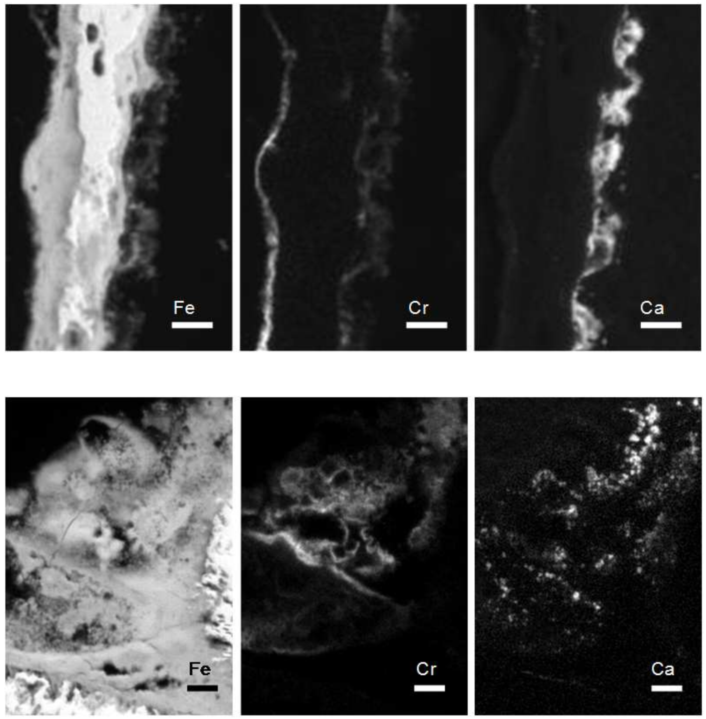
X-ray absorption and emission spectroscopy of CrIII(hydr)oxides: Analysis of the K pre-edge region. 2009. J. Frommer, M. Nachtegaal, I. Czekaj, T. Weng, R. Kretzschmar. *Journal of Physical Chemistry A* **113** 12171–12178

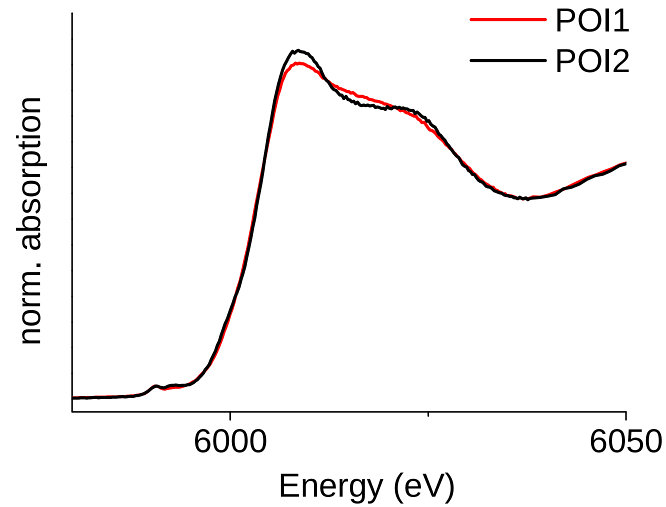
The Cr X-ray absorption *K*-edge structure of poorly crystalline Fe(III)-Cr(III)-oxyhydroxides. 2010. J. Frommer, M. Nachtegaal, I. Czekaj, R. Kretzschmar *American Mineralogist* **95**, 1202-1213

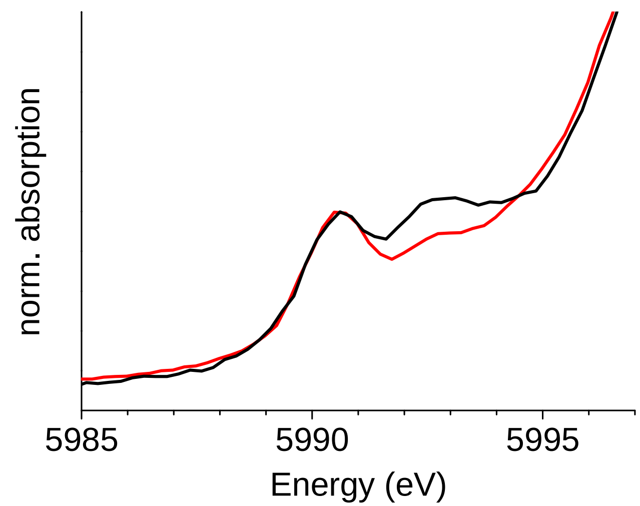
Back to the beginning: PRB



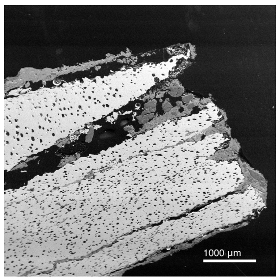
Cr/Fe < 1/10



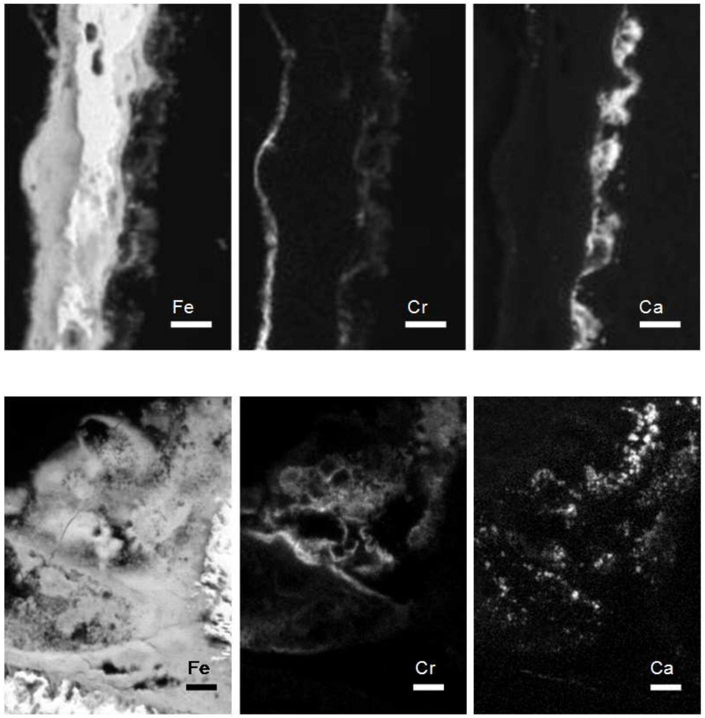


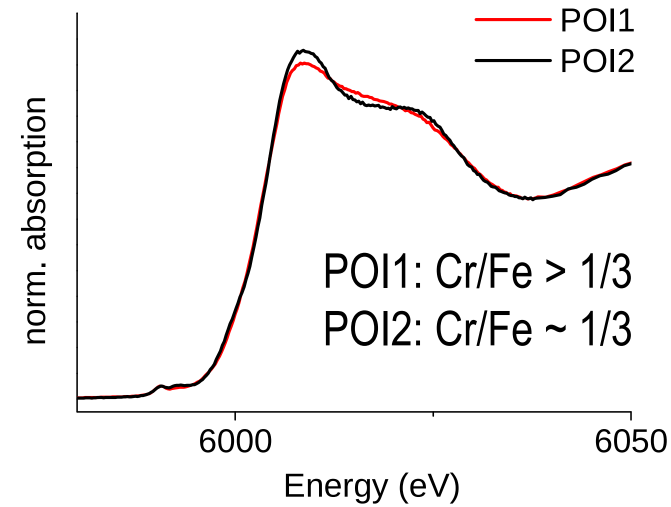


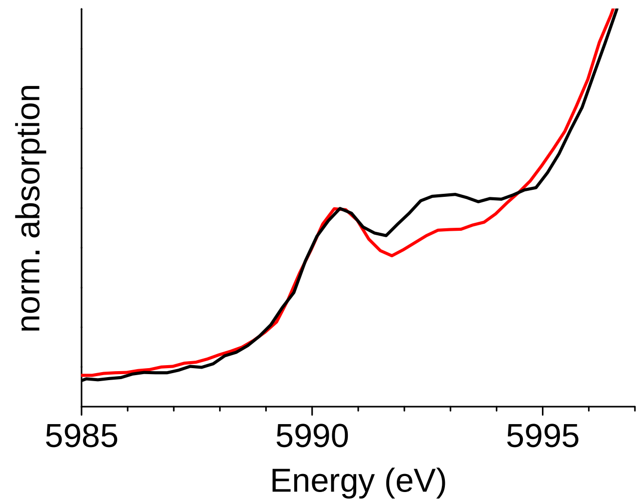
Back to the beginning: PRB



Cr/Fe < 1/10







homogeneous & heterogeneous redox reactions

Assessment of long-term performance and chromate reduction mechanisms in a field scale permeable reactive barrier

2009. B. Flury, J. Frommer, U. Eggenberger, U. Mäder, M. Nachtegaal, R. Kretzschmar. *Environ. Sci. Tech.* **43,** 6786-6792

ES&T best papers 2009. First runner up in the category `environmental technology`

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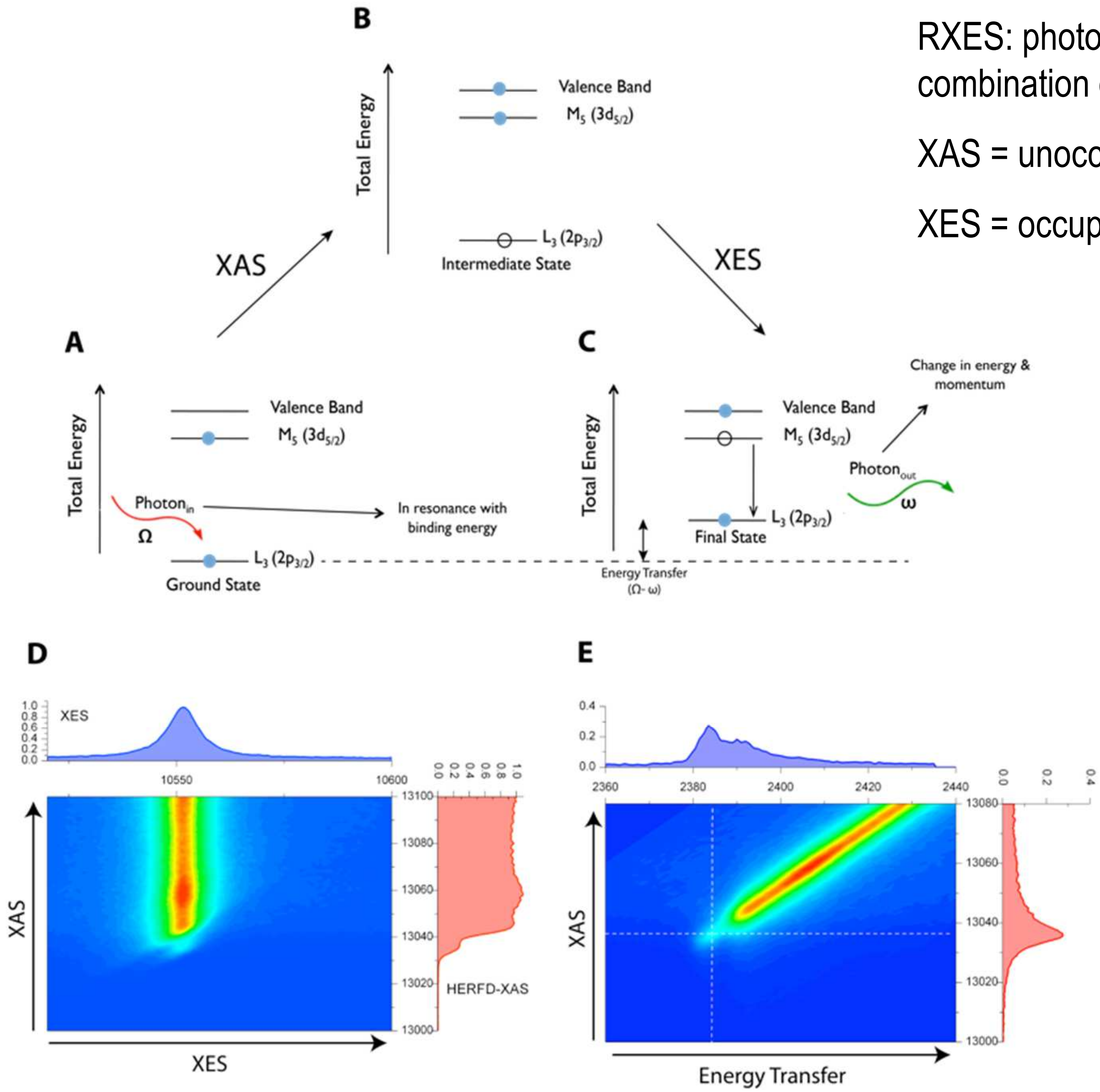
Tool: RXES spectroscopy

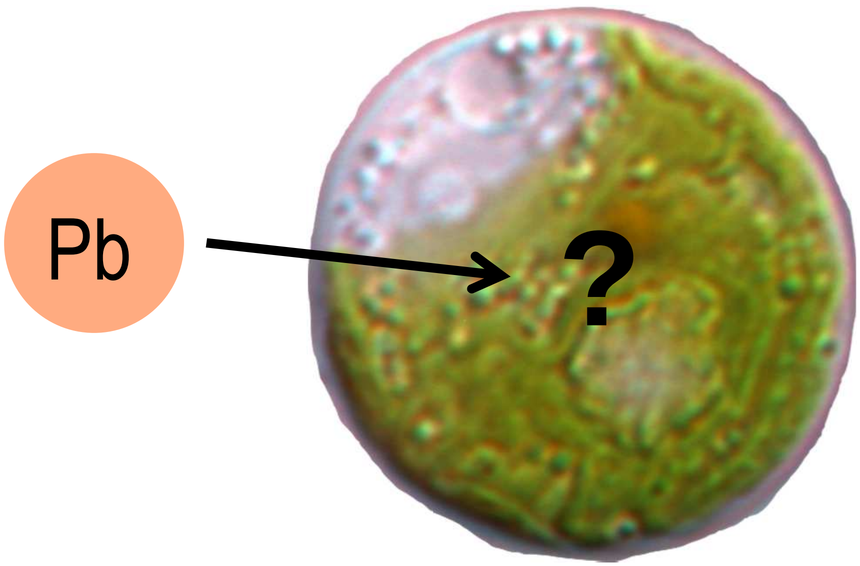


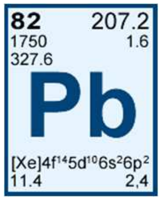
RXES: photon-in photon-out technique, a combination of XAS and XES spectroscopy

XAS = unoccupied density of states

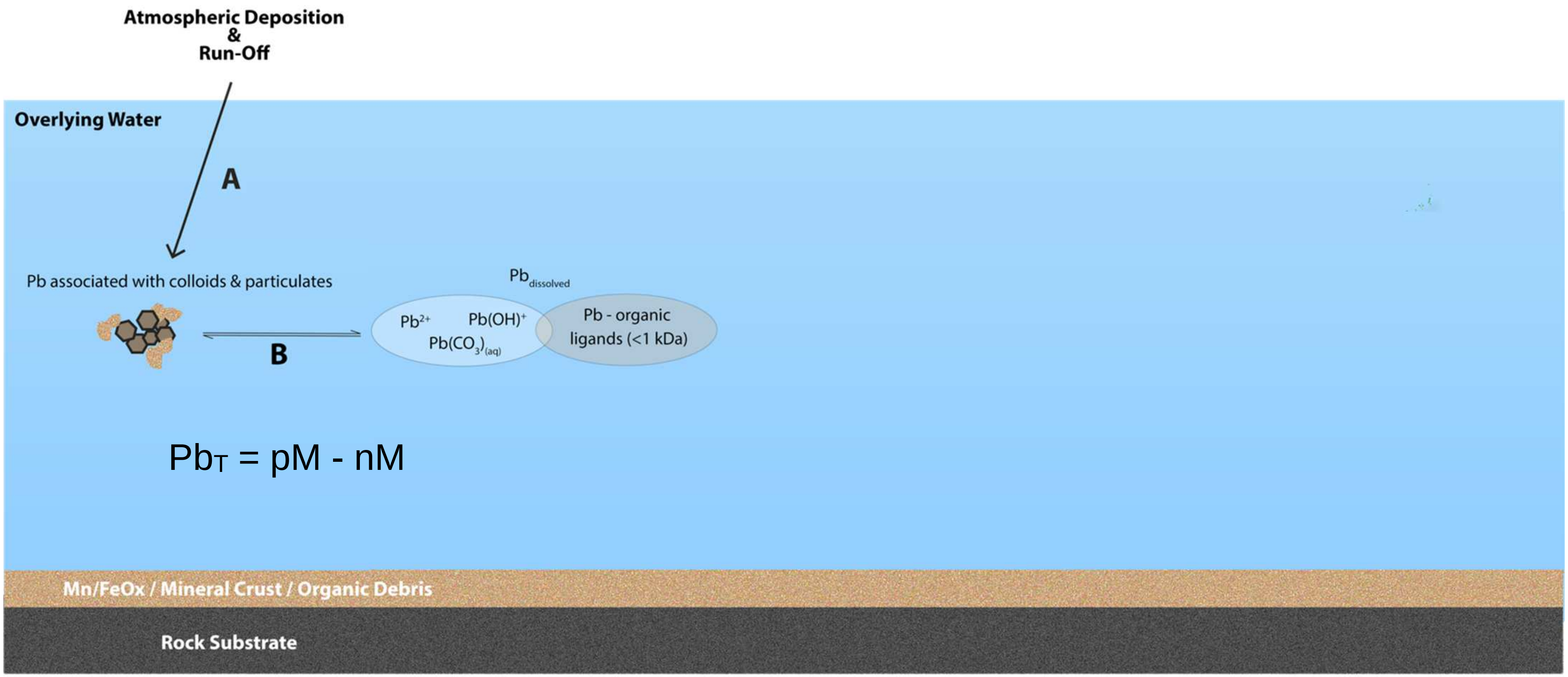
XES = occupied electronic states.

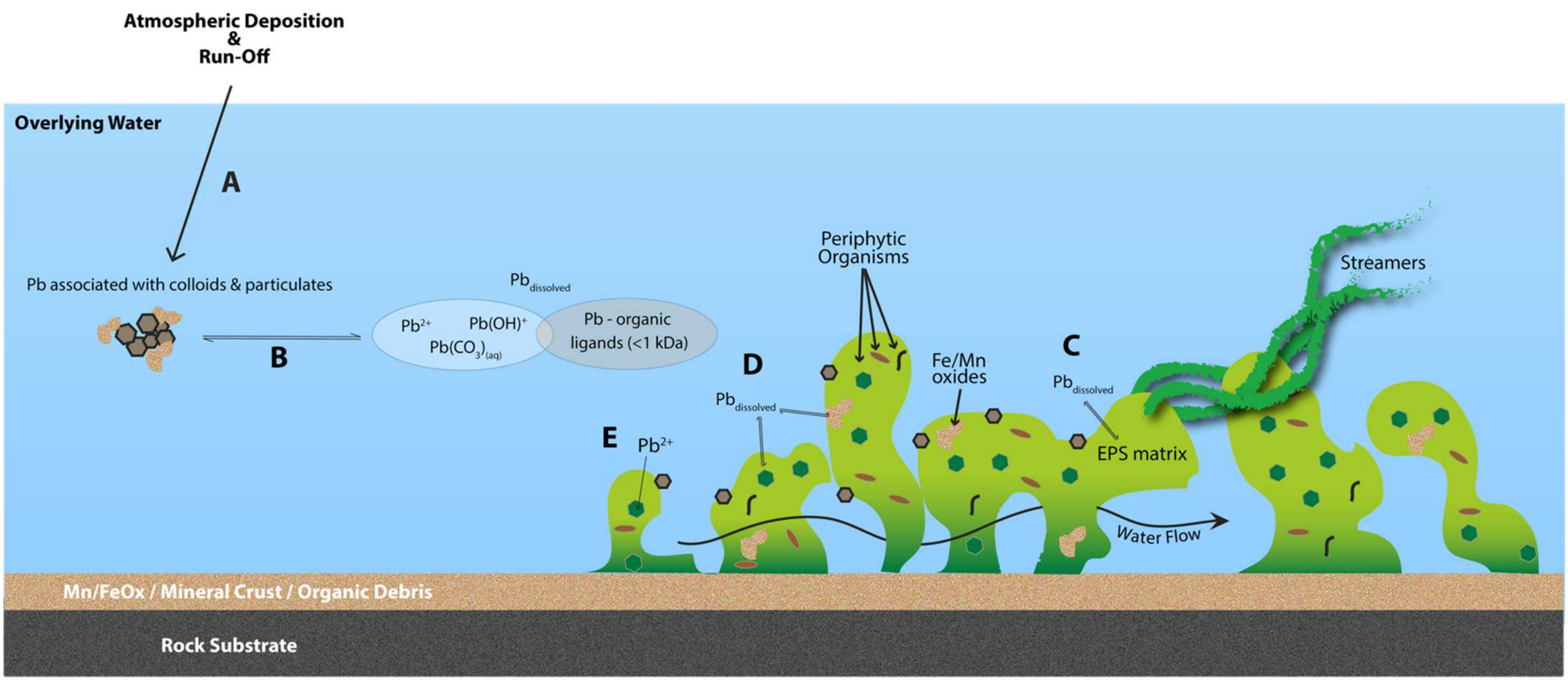
Tracking intracellular Pb speciation dynamics in the green alga *C. reinhardtii*



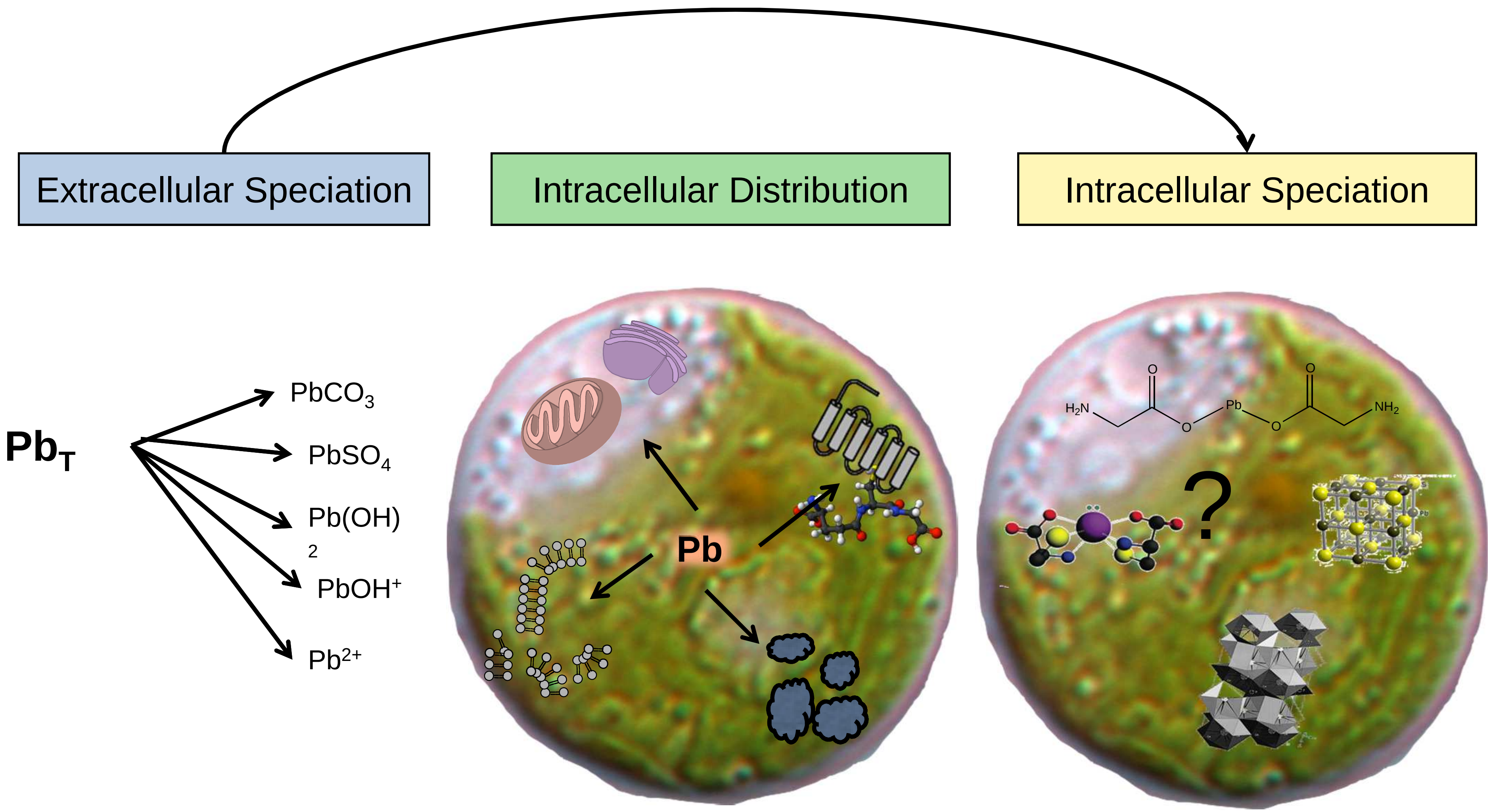


15,000 tons Pb/yr
(UNECE Report, 2006)




Atmospheric Deposition
&
Run-Off
Overlying Water
A
Pb associated with colloids & particulates
B
Pb dissolved
Pb2+
Pb(OH)+
Pb(CO3)(aq)
Pb - organic ligands (<1 kDa)
Periphytic Organisms
D
Pb dissolved
E
Pb2+
Fe/Mn oxides
C
Pb dissolved
EPS matrix
Streamers
Water Flow
Mn/FeOx / Mineral Crust / Organic Debris
Rock Substrate

Biological Effects of Metals



Pb Exposure Conditions

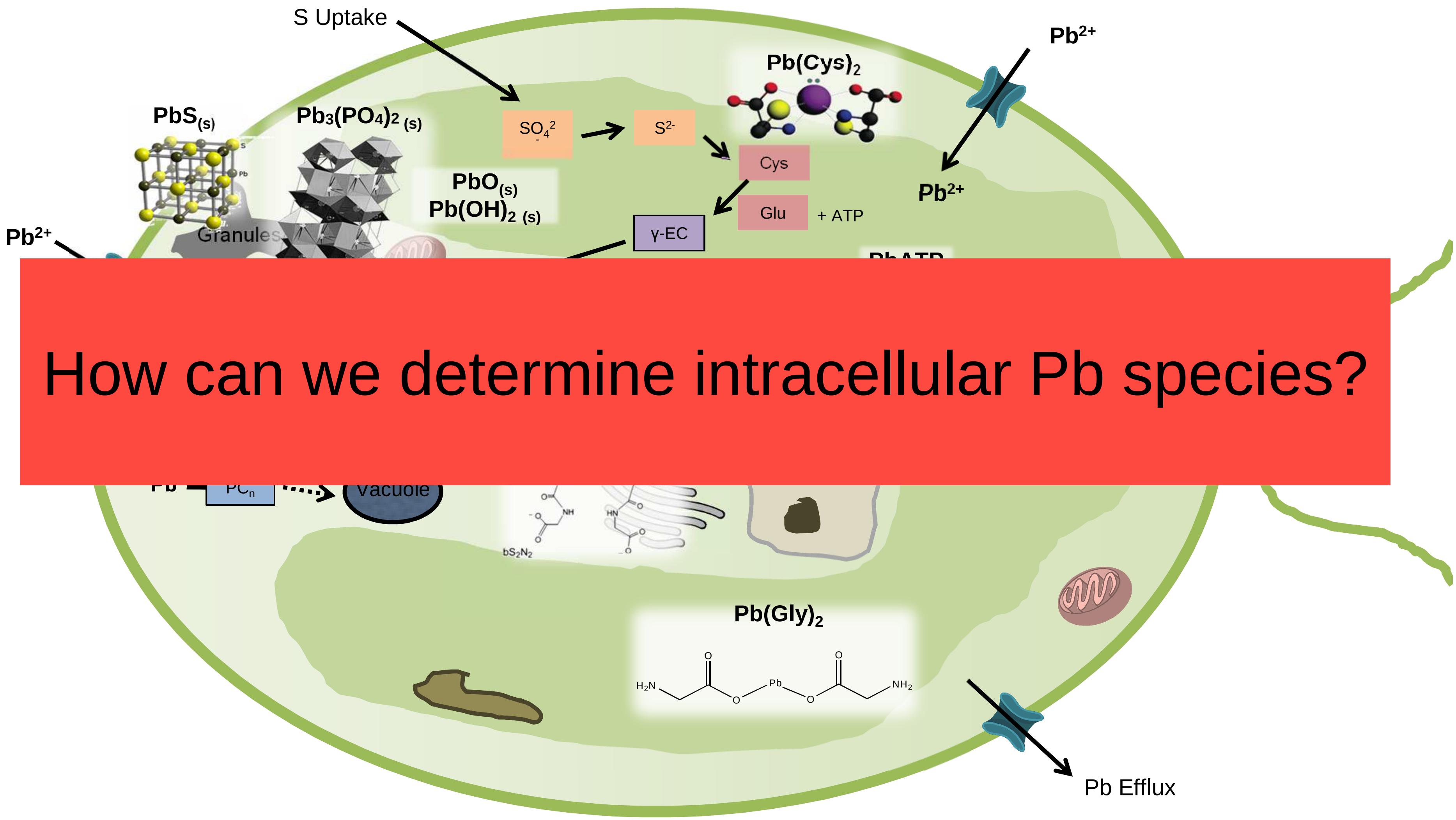
Pb_T = 20 µM
Pb^{2+} = 0.1 nM
Growth medium (+Cl^-)

3, 5, 10, 24 hours
exposure

EDTA
wash

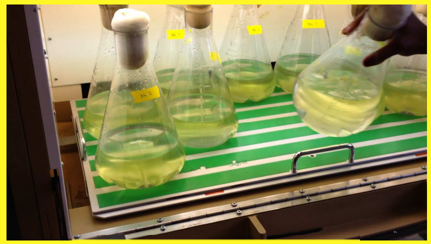
Pb_T = 20 µM
Pb^{2+} = 25 nM
Growth medium (-Cl^-)

Biologically Relevant Pb Complexes

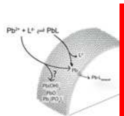


How can we determine intracellular Pb species?

Growth medium (+Cl^-)
pH 7, buffered



Pb_T = 20 µM



What is the intracellular Pb speciation?

Does it change over time?

Does increased Pb^{2+} influence internal Pb speciation?

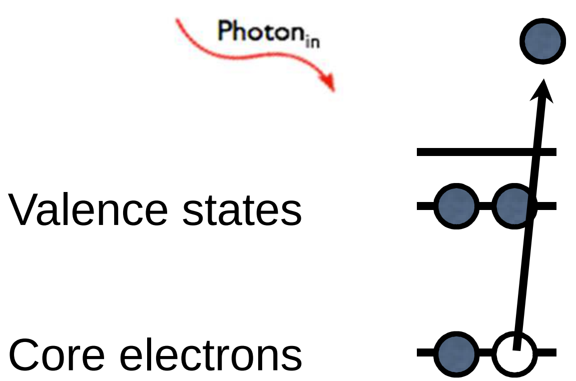
50 L algal culture

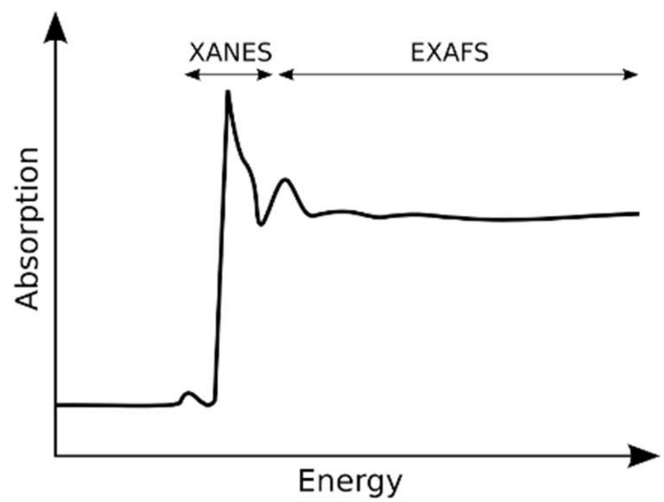
Pb_T = 20 µM
Pb^{2+} = 25 nM

X – ray spectroscopy

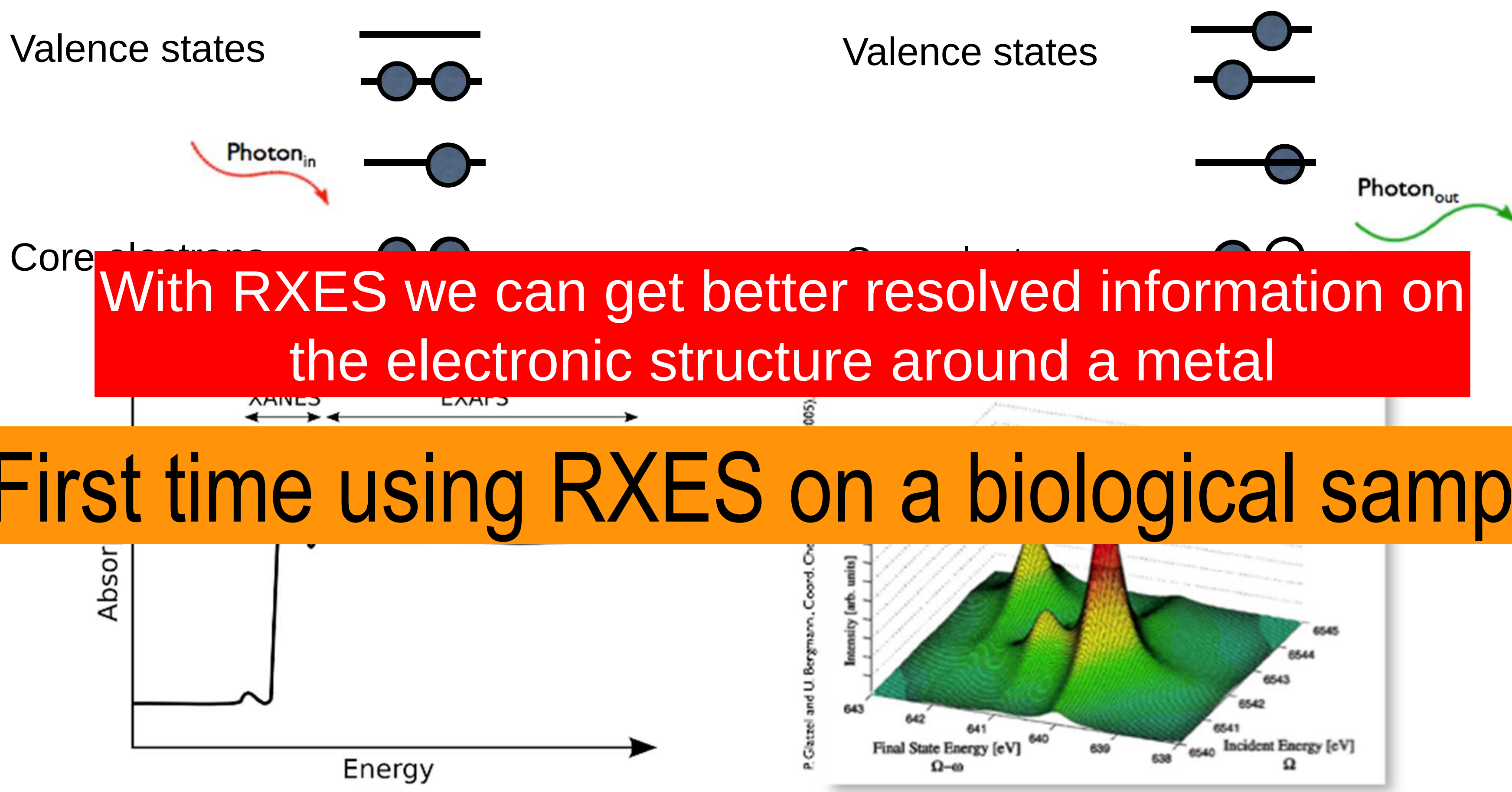
- Element specific, non-crystalline sample
- Obtain information on the *local* chemical environment around Pb
- Relatively non-destructive with low limit of detection

X-Ray Absorption Spectroscopy (XAS)





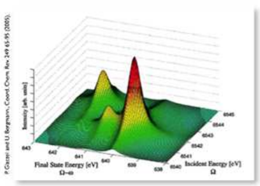
Resonant X - Ray Emission Spectroscopy

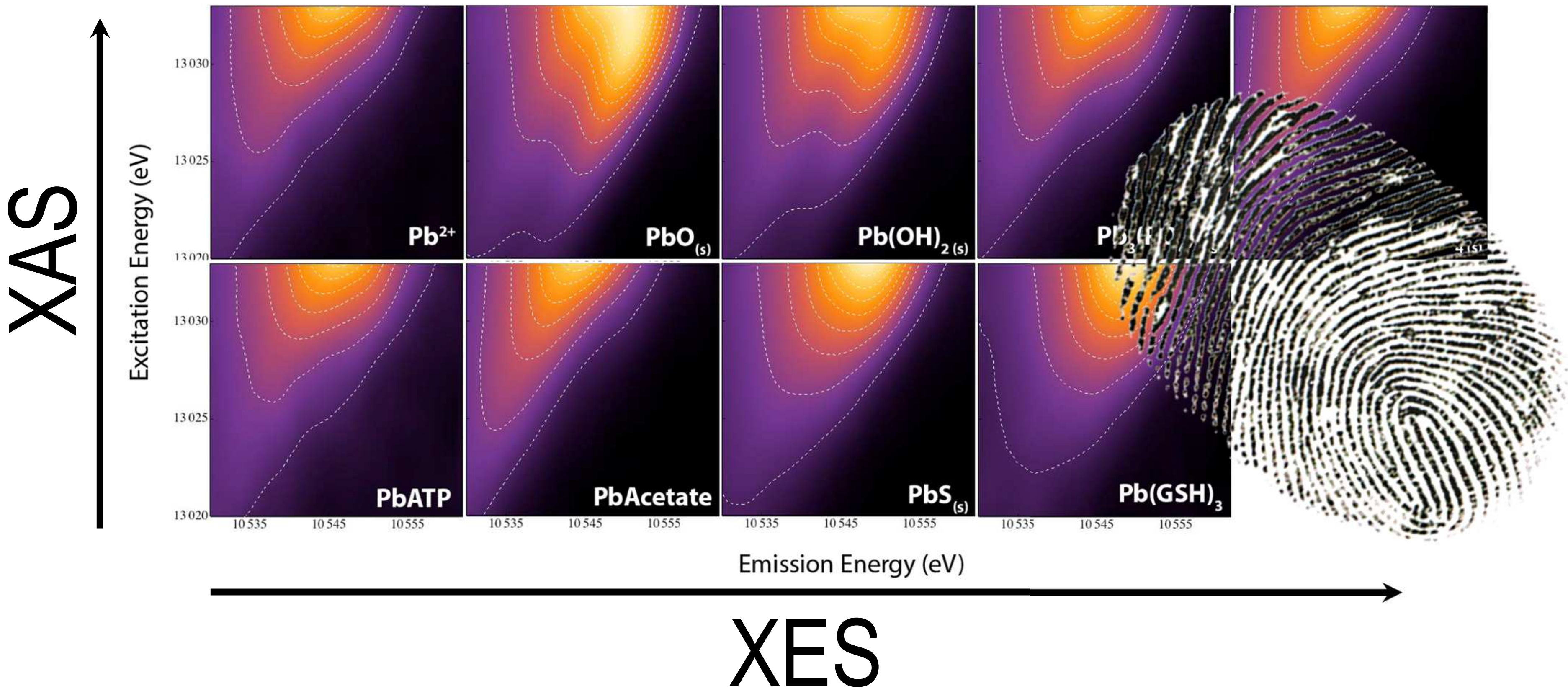


With RXES we can get better resolved information on the electronic structure around a metal

First time using RXES on a biological sample

2D - RXES Maps of Pb Standards





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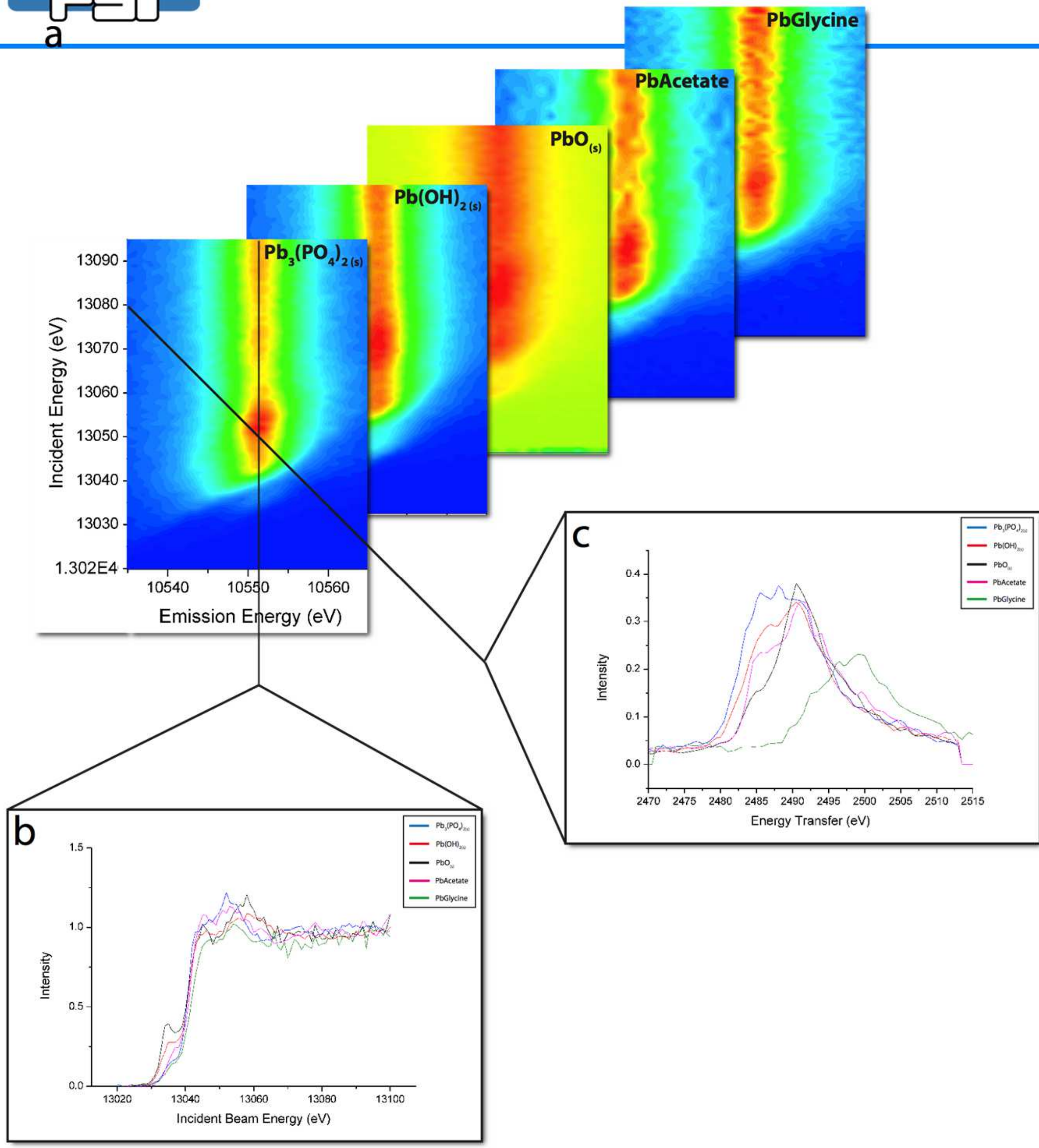
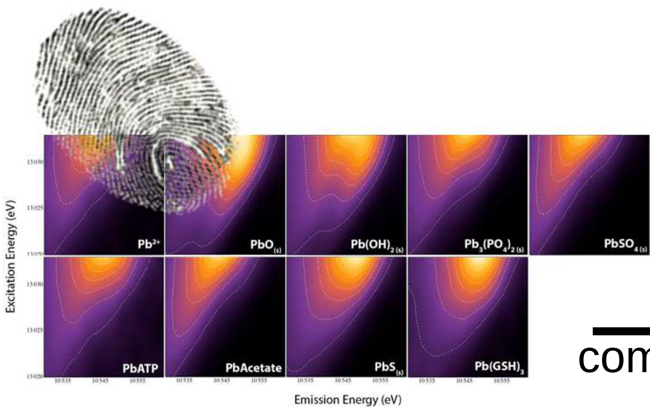
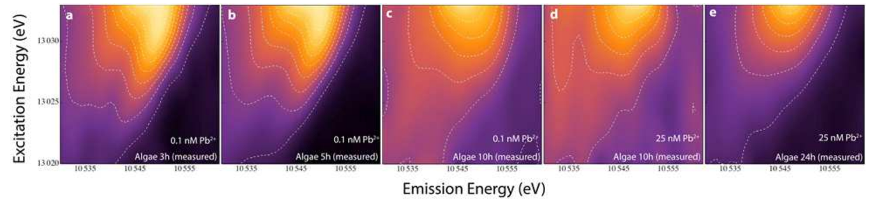


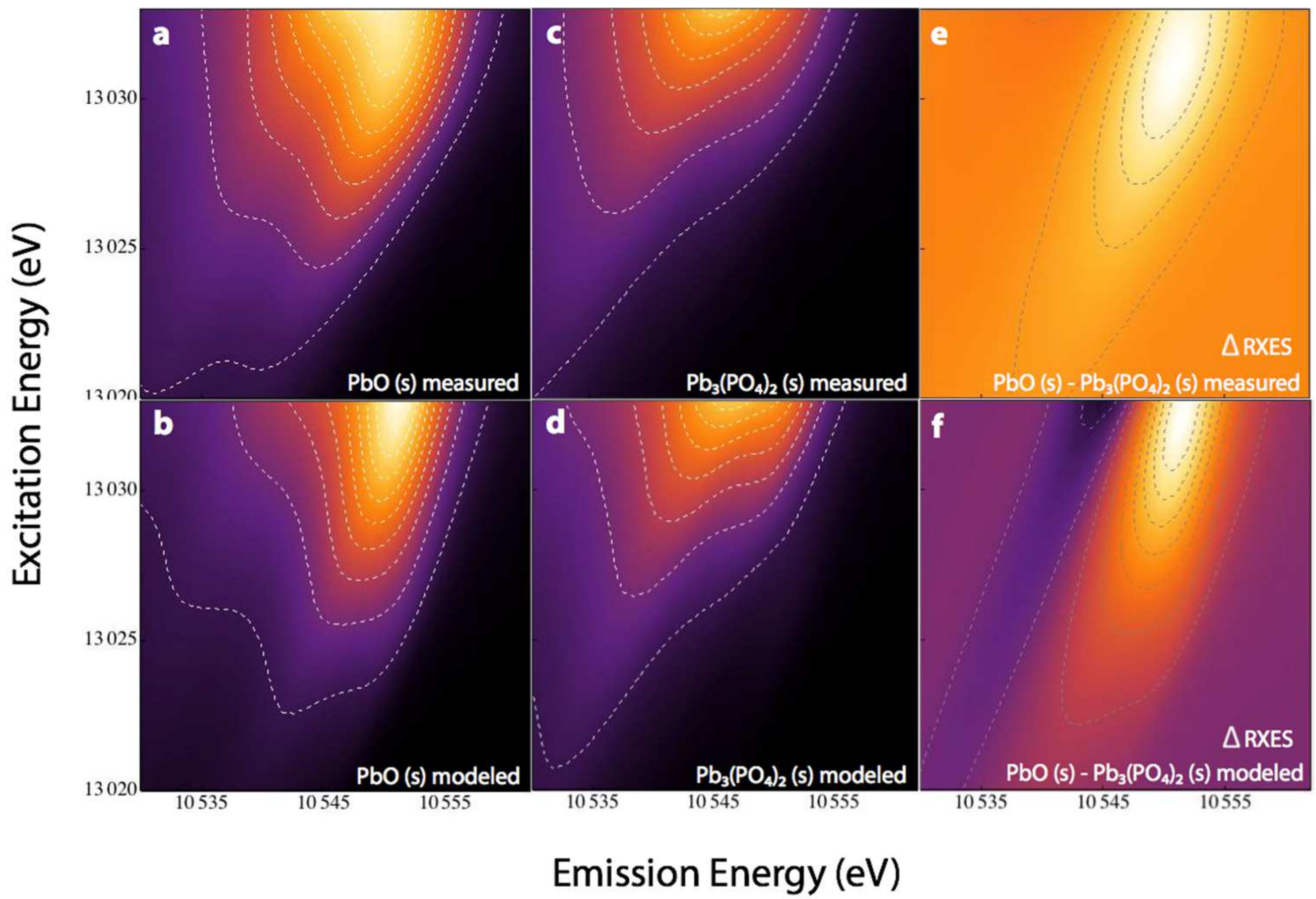
Quantification of Intracellular Pb Speciation



Linear combination fitting

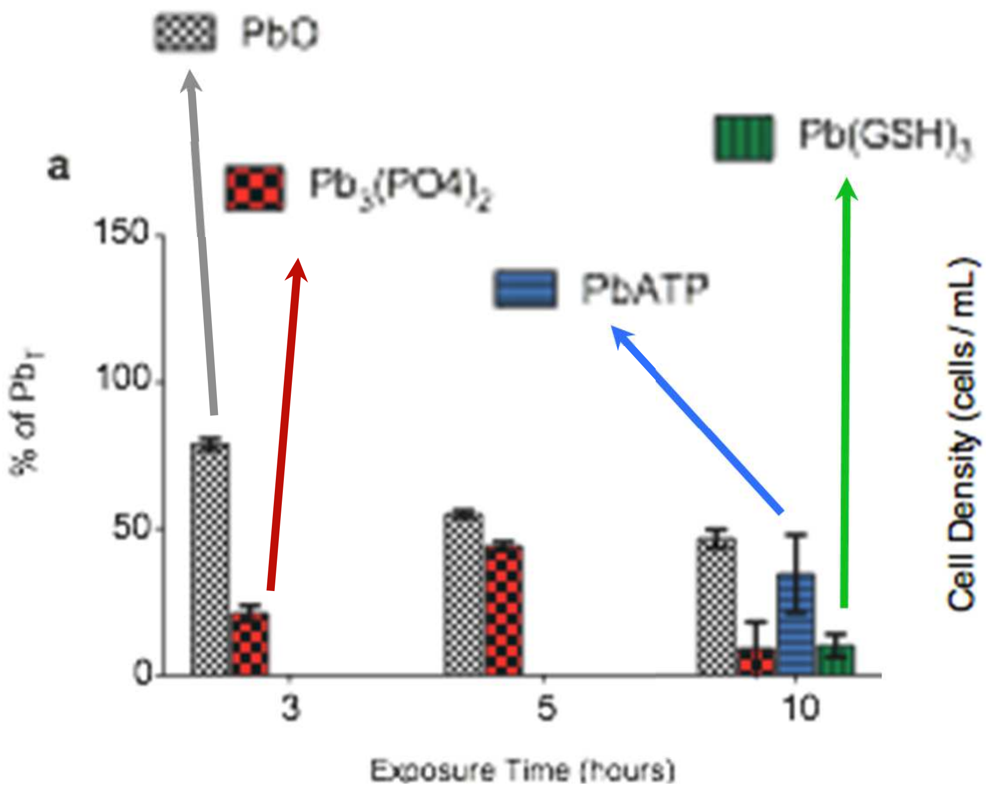
Algae RXES Maps

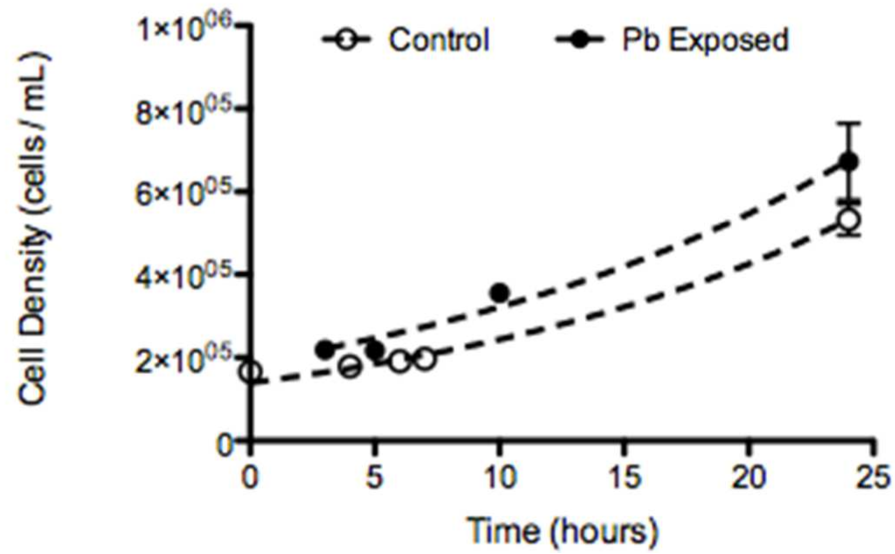



a
PbO (s) measured
b
PbO (s) modeled
c
Pb3(PO4)2 (s) measured
d
Pb3(PO4)2 (s) modeled
e
Δ RXES
PbO (s) - Pb3(PO4)2 (s) measured
f
Δ RXES
PbO (s) - Pb3(PO4)2 (s) modeled
13 030
13 025
13 020
10 535
10 545
10 555
Excitation Energy (eV)
Emission Energy (eV)

Quantification of Intracellular Pb Speciation

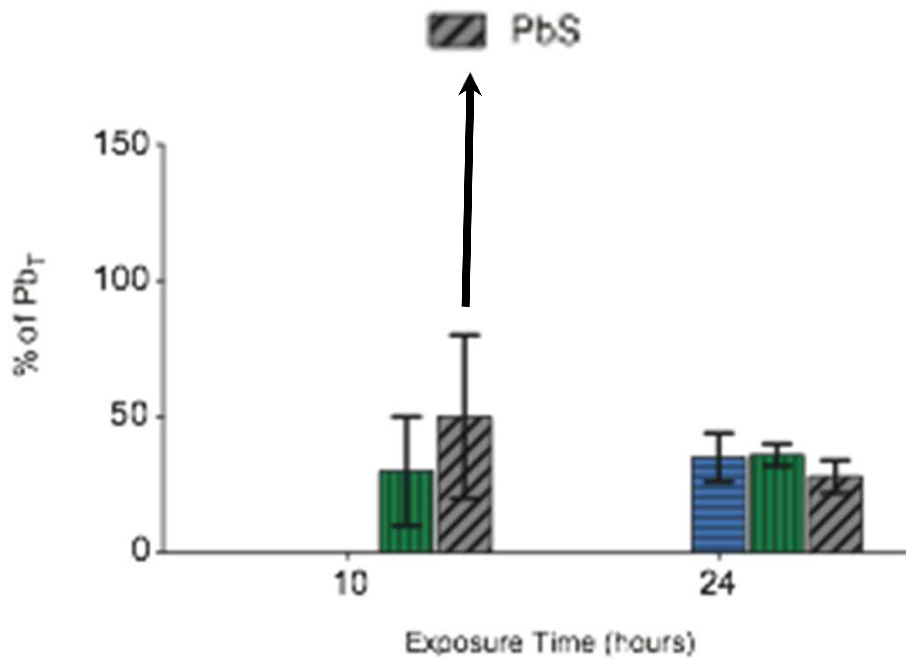
0.1 nM Pb^{2+}

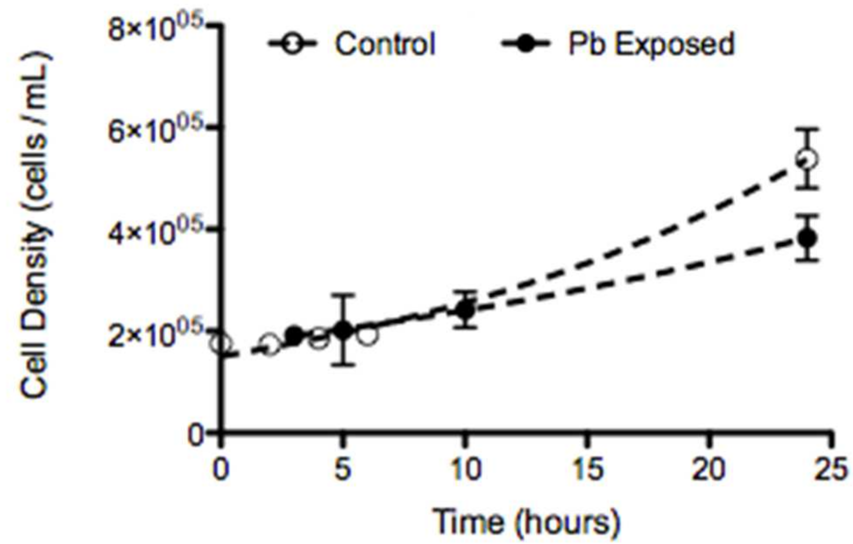




Quantification of Intracellular Pb Speciation

25 nM Pb^{2+}





Conclusions

REXS can be used to identify and quantify biologically important intracellular Pb-complexes at environmentally relevant Pb concentrations

Intracellular Pb speciation is dependent on not only exposure time, but also on exposure solution chemistry

The biological application of REXS (in conjunction with other techniques) can increase our understanding of metal homeostatic mechanisms

Stewart et al. *Submitted*

Shining light on environmental technologies

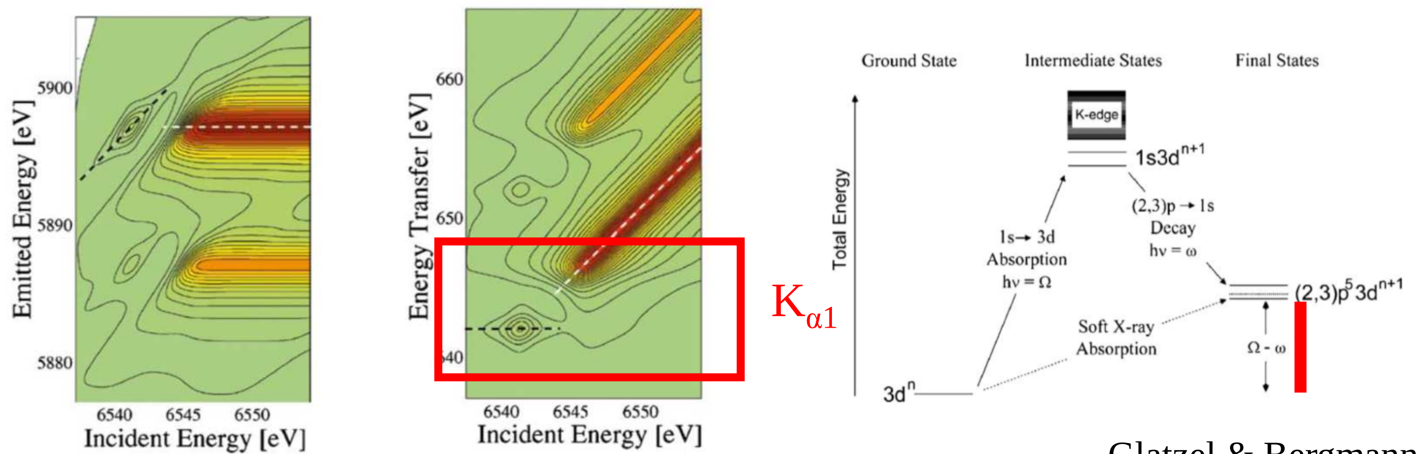
In situ passivation of metals (spatially resolved XAS/XRF)
- metal speciation in a Zn smelter contaminated soil

Permeable reactive barriers to reduce organic and metallic compounds (high resolution XANES)
- Cr speciation in a permeable reactive barrier

Intracellular Pb speciation dynamics (RXES)
- Tracking intracellular Pb speciation dynamics in the green alga *C. reinhardtii*

A bright future for environmental science!

Resonant emission spectroscopy



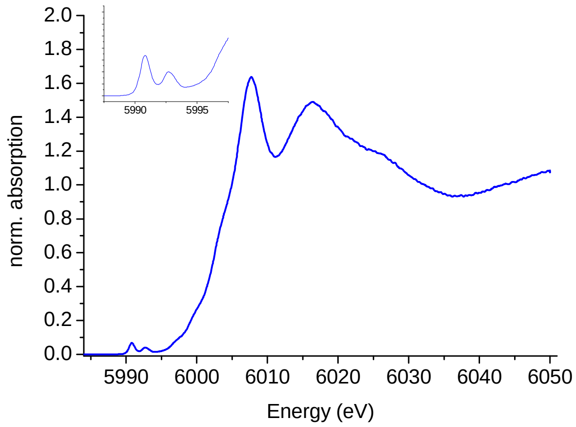
Glatzel & Bergmann, 2005

Two „dispersion patterns“ in the RXES plane (e.g.: de Groot, 2007)

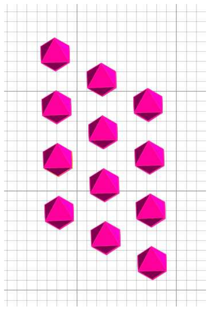
- diagonal; ΔE maintained → above the edge non-local („band“) transitions
- separate resonance → local transitions

Active Cr Hydroxide

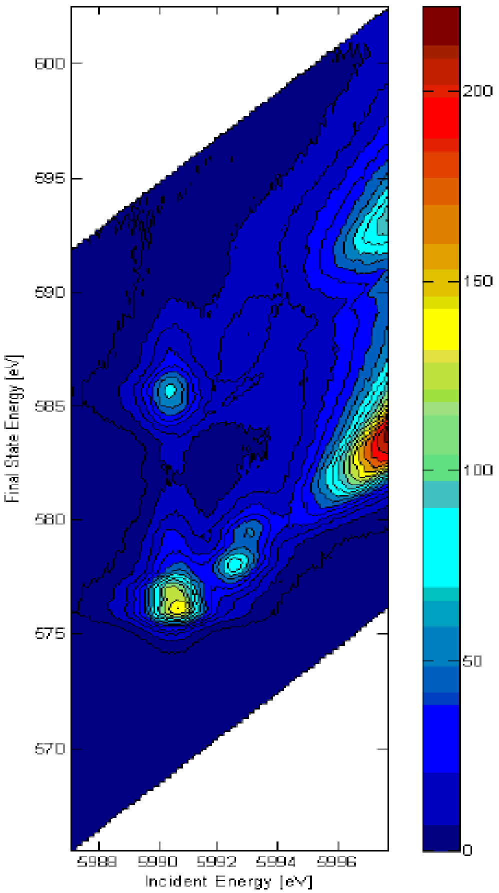
Data

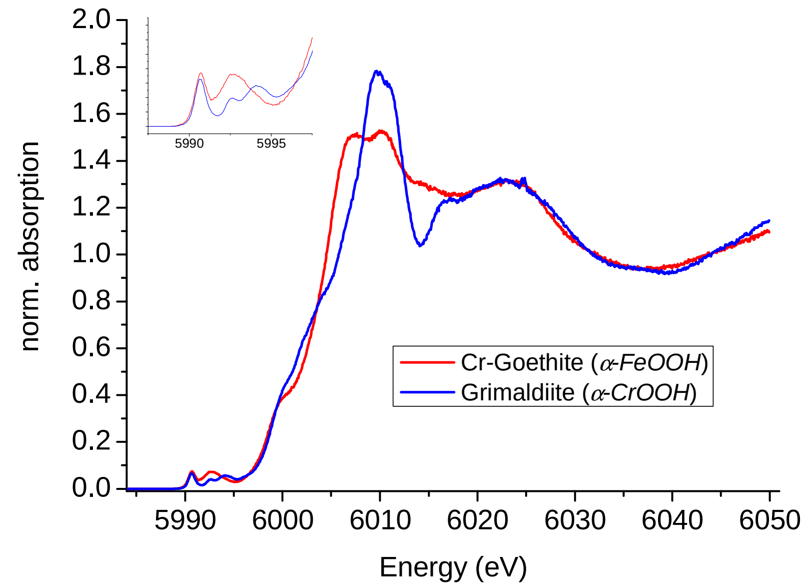


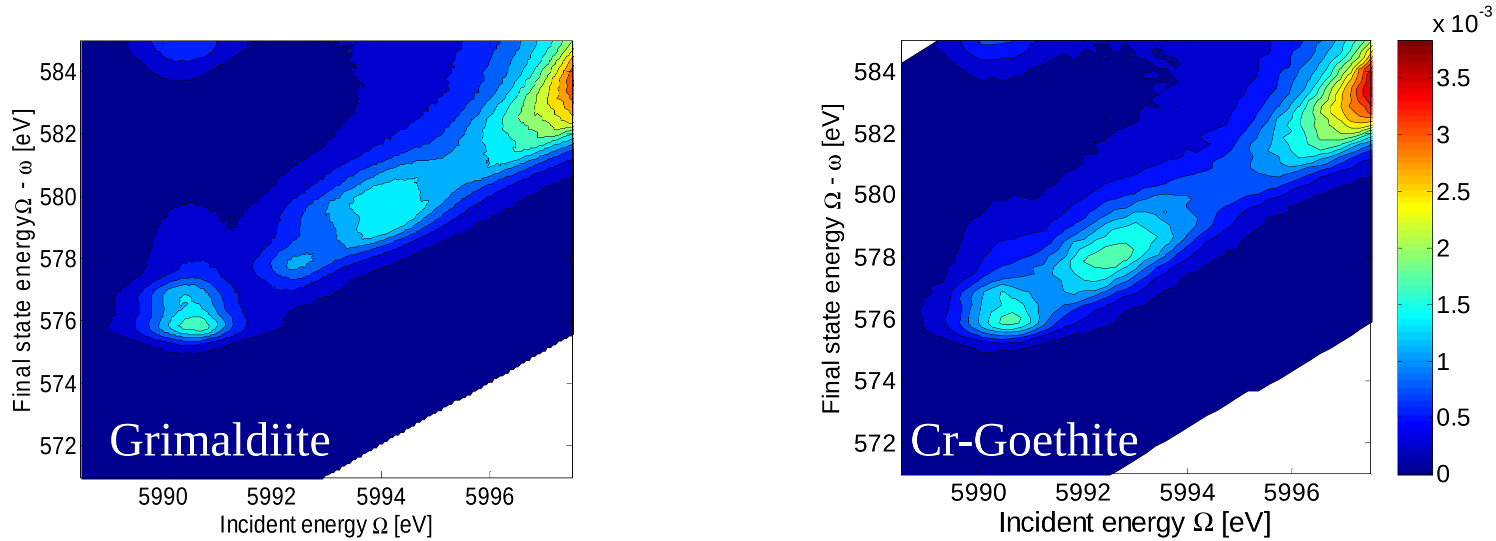
Structure



RXES

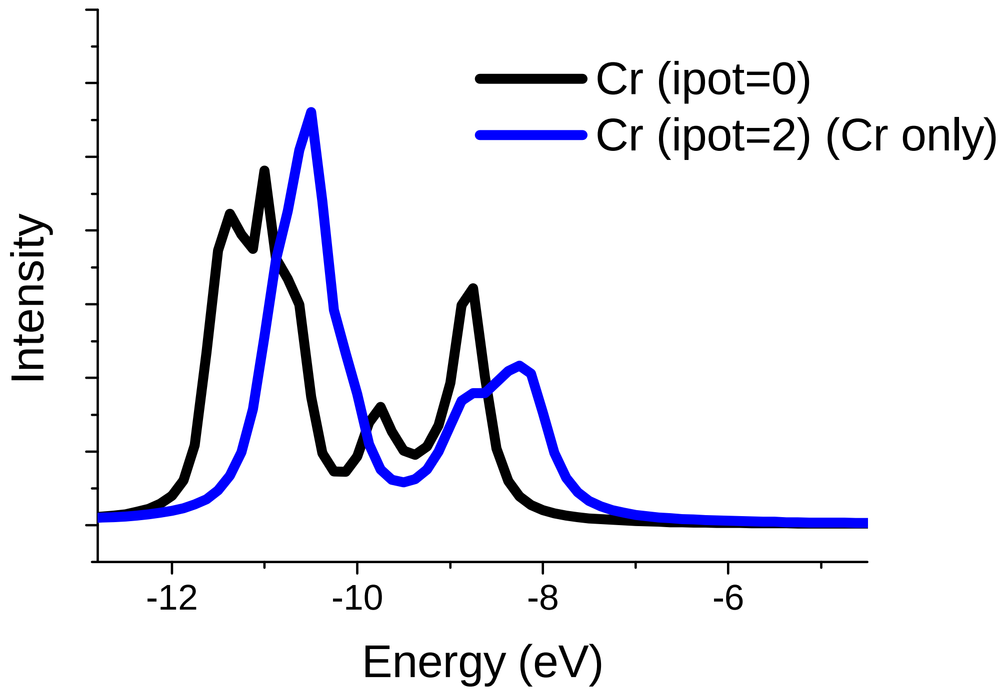



norm. absorption
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
5990
6000
6010
6020
6030
6040
6050
Energy (eV)
5990
5995
Cr-Goethite (α-FeOOH)
Grimaldiite (α-CrOOH)


Final state energyΩ - ω [eV]
584
582
580
578
576
574
572
Grimaldiite
5990
5992
5994
5996
Incident energy Ω [eV]
Final state energy Ω - ω [eV]
Cr-Goethite
Incident energy Ω [eV]
x 10^-3
3.5
3
2.5
2
1.5
1
0.5
0

FEFF assignment

d-DOS



Transition to d-states

Slide 63

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j13 summary
jafromme; 02.10.2008