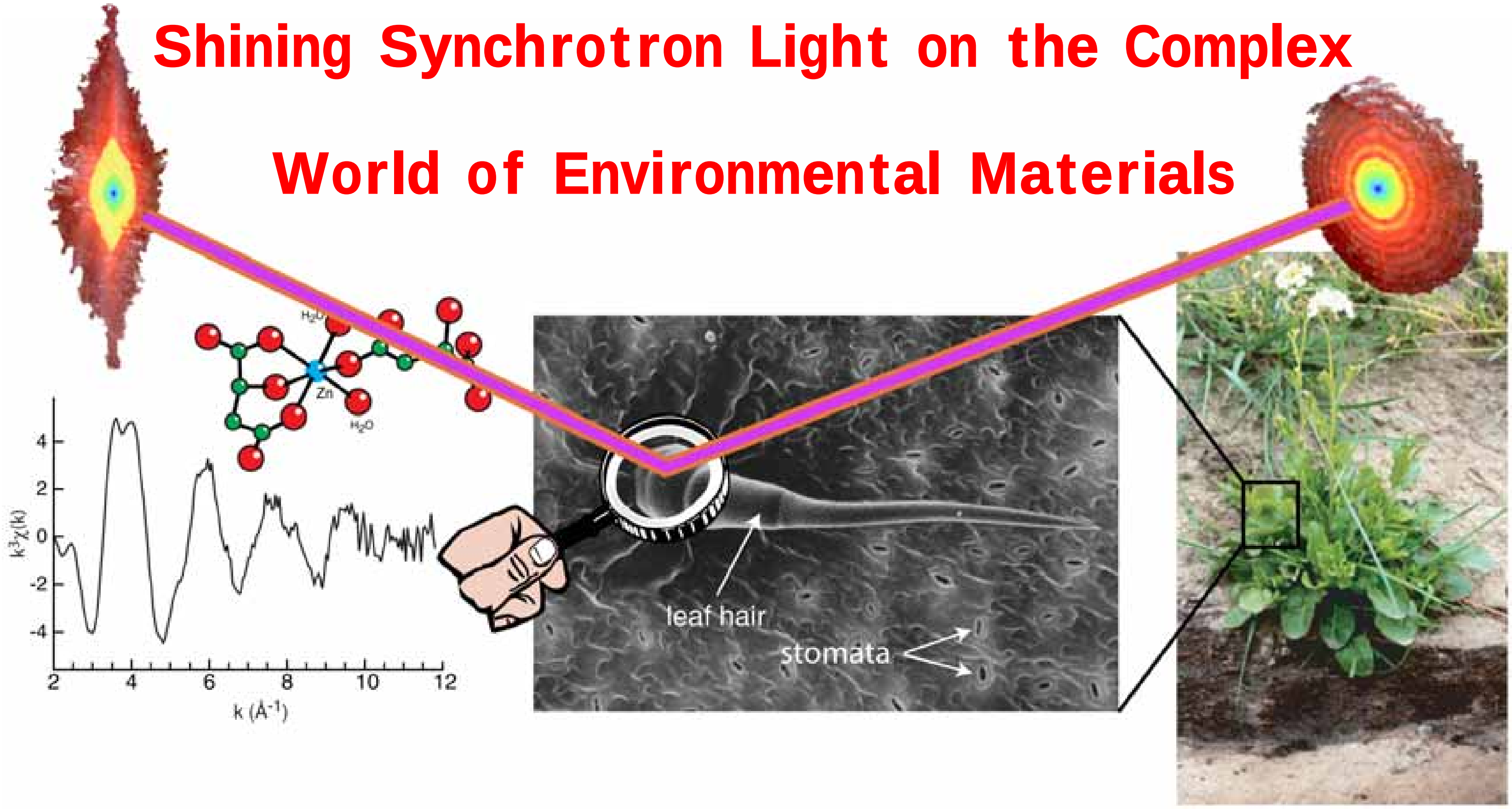
Shining Synchrotron Light on the Complex World of Environmental Materials



1. Societal and Scientific Challenges of Molecular Environmental Science (MES)

2. Some Specificities of Environmental Materials

3. The State of the Art in Speciation Science with SR

4. Technical Difficulties, Present Instrumental Limitations, and Next Instrumental Challenge

1. Societal and Scientific Challenges of MES

- The major goal of Environmental Science is to seek ways to improve the human condition and global environment. ‘Sustainable development is about the very destiny of our planet’ (Jean Chrétien, Prime Minister of Canada).

- Five key areas are the focus of WSSD (world summit on sustainable development; Kofi Annan, Secretary General of the United Nations): Water, Energy, Health, Agriculture, and Biodiversity (WEHAB).

For the first four focus areas, chemical speciation at the molecular scale is a key issue

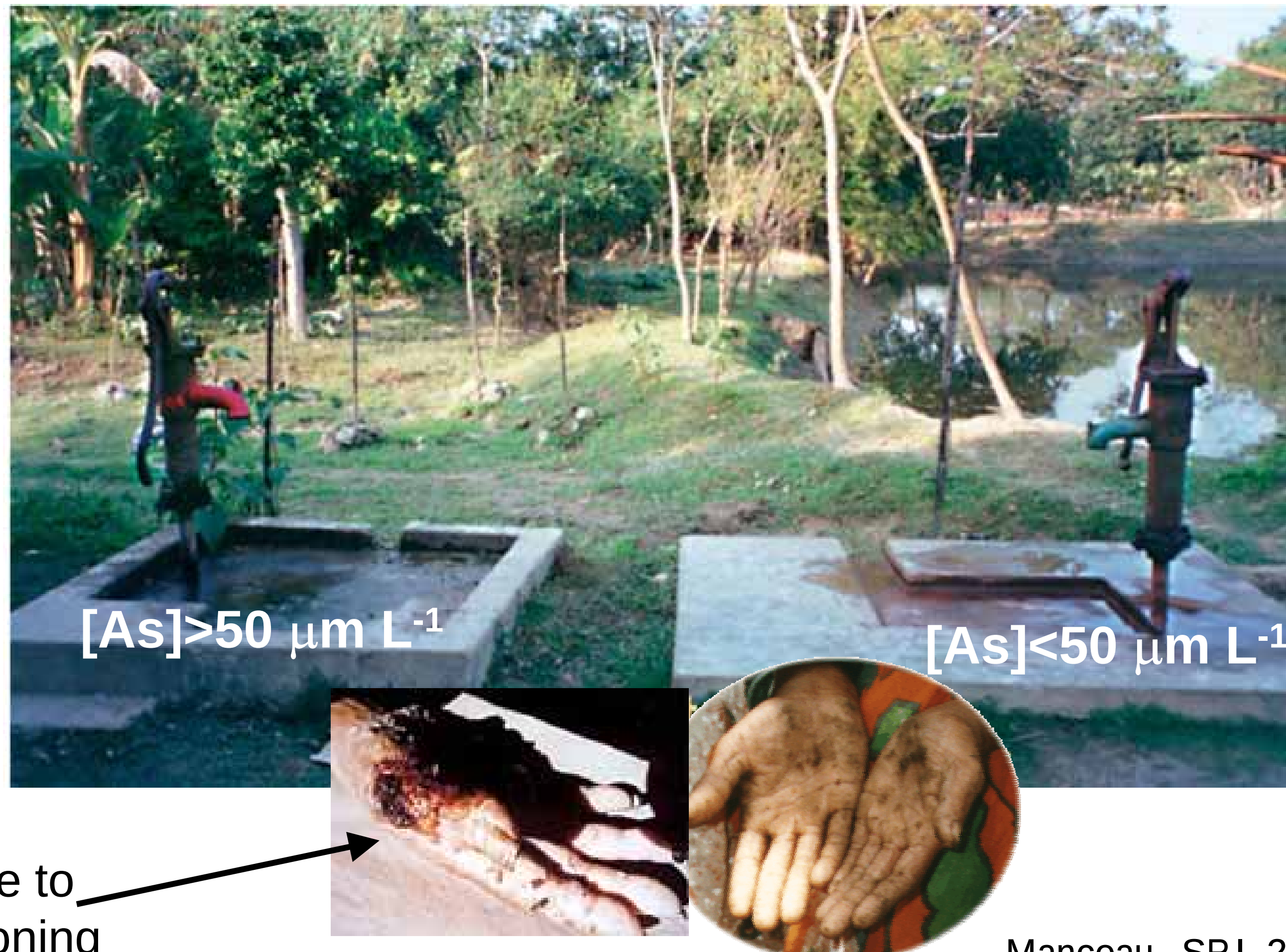
Toxicity ↔ Solubility ↔ Chemical Form

As a rule, the less soluble a chemical species, the less mobile and less toxic; the more soluble it is, the more mobile and more toxic.

Water

- 1.2 billion people don’t have access to safe drinking water; and millions of people in Bangladesh and West Bengal, India, are still being exposed to high levels of arsenic in their drinking water, despite a million-dollar screening effort to distinguish safe from unsafe wells.

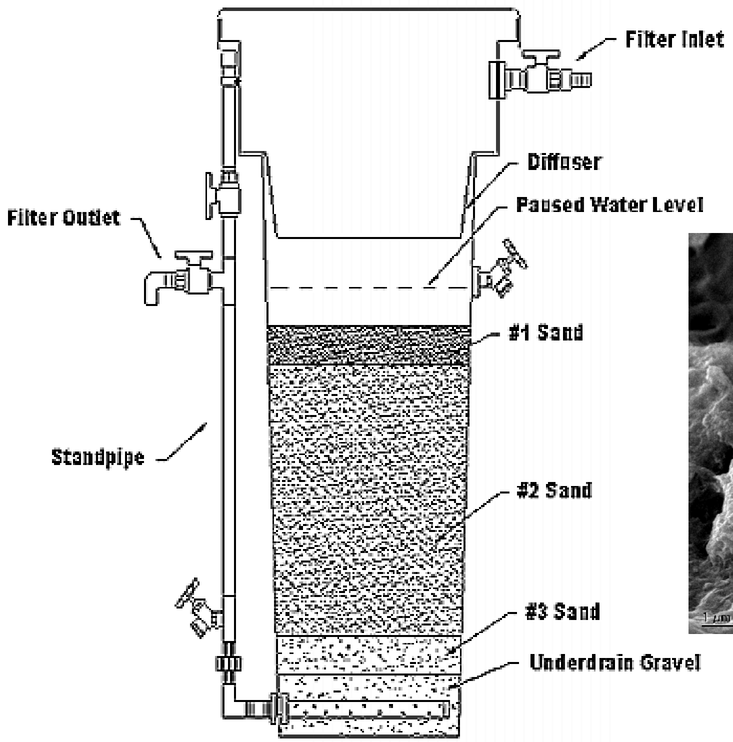
All the wells are not labeled

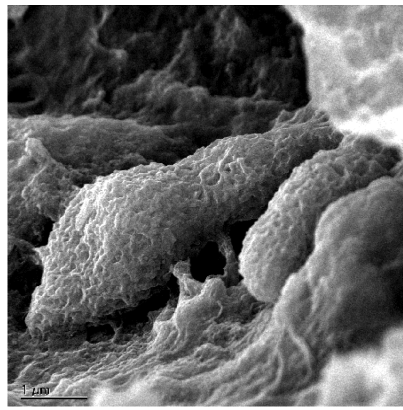


Keratosis due to arsenic poisoning

Bio-sand filter used in Nepal for household water purification

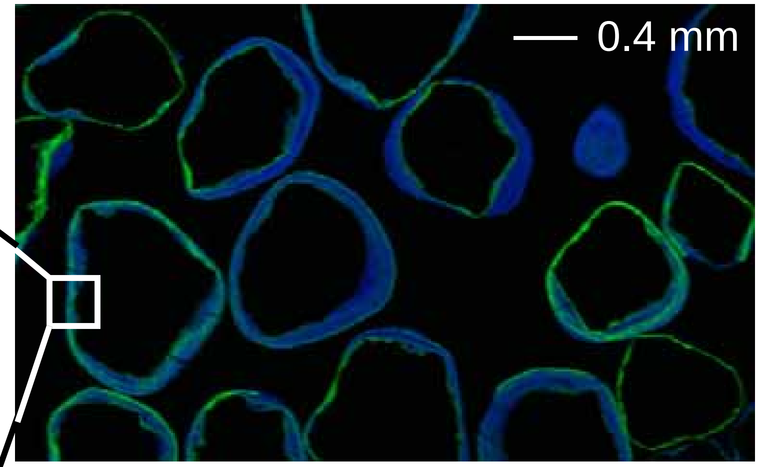
The quartz grains are coated with Fe- and Mn-oxides bio-films



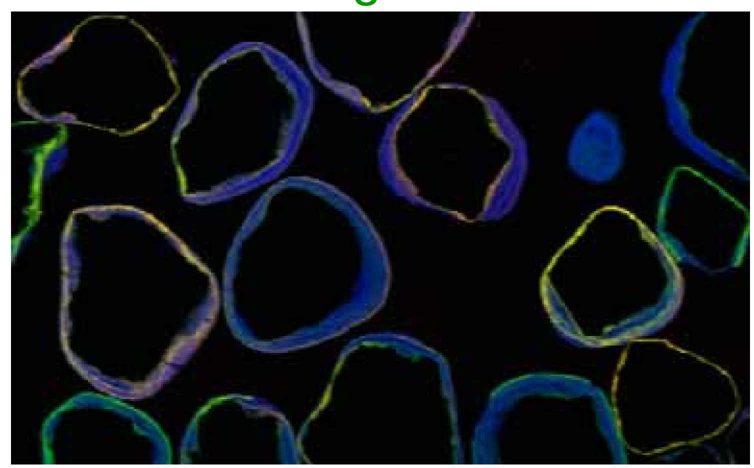


1 μm

gFe bMn



rAs gFe bMn



Benefit:

- Durable
- Effective
- Inexpensive

What is the form of As?

As is specifically bound to Fe oxide layers.

Manceau –SRI-2003

Health

- Lead is neurotoxic. Intellectual development in young children is impaired by long term environmental exposure to lead.
- Source of Pb contamination at Winster (central England): Geological mineralization in veins, Pb has been brought to the surface by mining activities.

Geometric mean of lead concentration at Winster ($\mu g\ g^{-1}$)

	Winster	Birmingham	UK
Garden soil	**7,140**	313	266
Vegetable	**9,580**	Not analyzed	270
House dust	1,560	424	561

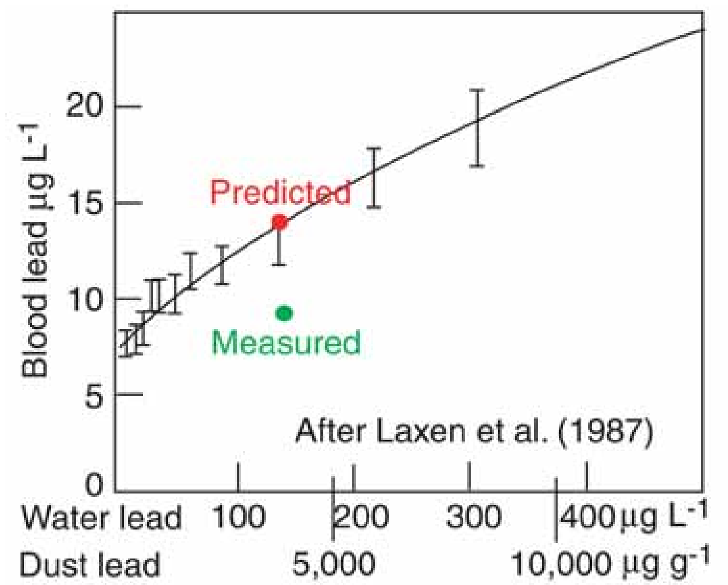
Geometric mean of lead in children's blood ($\mu g\ dL^{-1}$)

Winster	Birmingham	Edinburgh	London
9.4	11.7	10.7	7.4 - 8.3

The blood lead concentration is high for rural areas but is similar to or only slightly higher than in cities. All values fall below the recommended action level of 25 $\mu g\ dL^{-1}$ (DoE and Welsh Officen 1982).

Cotter-Howells, Envir. Geochem. Health, 1991, 13, 127-135

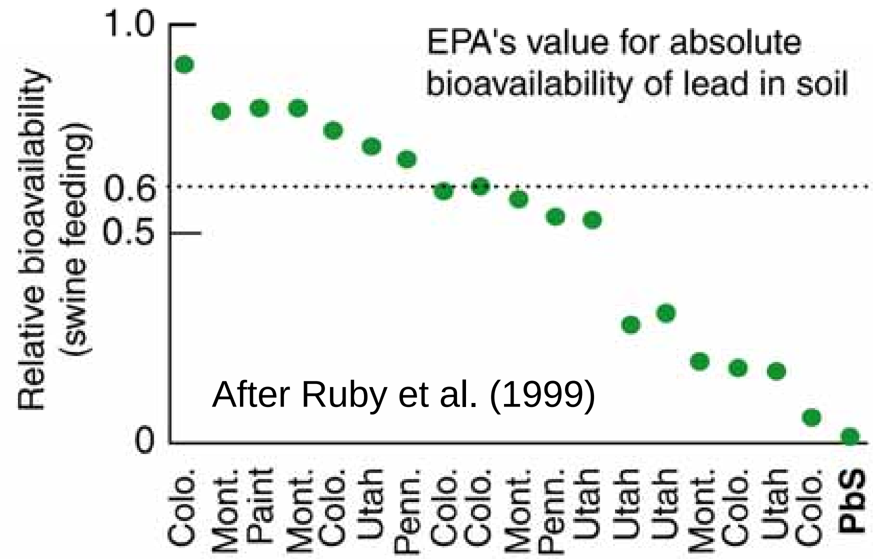
Response-curve blood lead vs. exposure



Why is Pb harmless at Winster?

- Lead is speciated as phosphate, which has a very low solubility; it passes through the digestive tract of animals and humans unchanged.

Relative bioavailability of lead in soil



The bioavailability of a metal contaminant is extremely variable, and so is its toxicity.

Mineral	Solubility (log Ksp)
Anglesite - $PbSO_4$	-7.8
Cerrusite - $PbCO_3$	-12.8
Galena - **PbS**	-27.5
Fluoropyromorphite - $Pb_5(\mathbf{PO_4})_3F$	-76.8
Hydroxypyromorphite - $Pb_5(\mathbf{PO_4})_3OH$	-82.3
Chloropyromorphite - $Pb_5(\mathbf{PO_4})_3Cl$	-84.4
Hinsdalite - $PbAl_3(\mathbf{PO_4})(OH)_6SO_4$	-99.1
Plumbogummite - $PbAl_3(\mathbf{PO_4})_2(OH)_5H_2O$	-99.3
Corkite - $PbFe_3(\mathbf{PO_4})(OH)_6SO_4$	-112.6

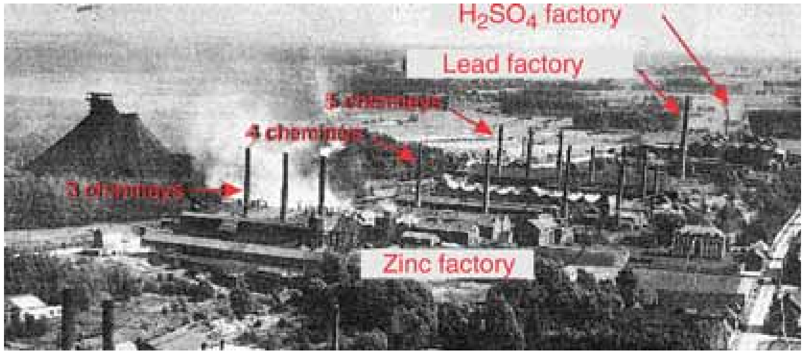
Toxicity ↔ Solubility ↔ Chemical Form

Societal and scientific challenges

Agriculture

- All industrialized countries have countless contaminated sites; e.g., the United States Department of Energy (DOE) is responsible for the environmental management of well over 100 sites that are contaminated with trace elements and organic chemicals.

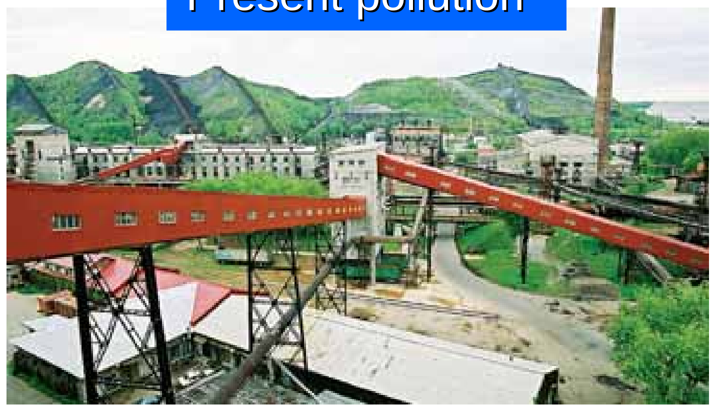
Historic pollution



Industrial complex in 1950

Industrial complex in 1995

Present pollution



Oil shale-fired power plant in Estonia

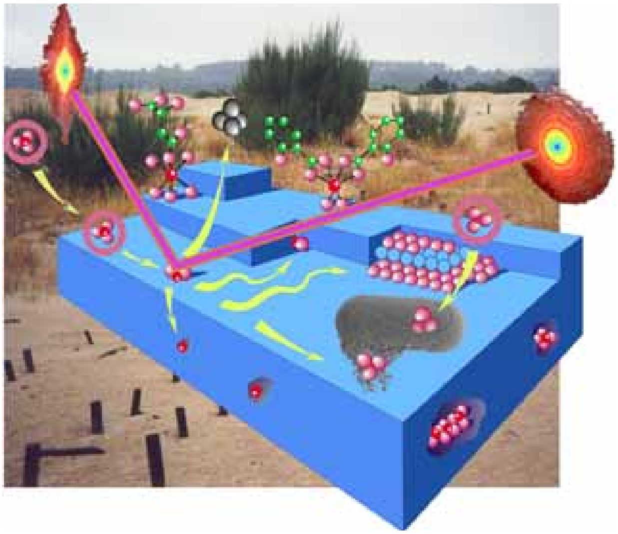
The plant dumps annually 9 million metric tons of ash which contains heavy metals and poly-aromatic organics

Which strategy to use in the cleanup of metal contaminated soils?

In Situ Fixation

Rationale: Addition of mineral amendments to modify the speciation of toxic metals and make them less bioavailable. Metal tolerant or metallophyte plants are then sowed to obtain a well-closed vegetation cover.

Benefit : Much less disruptive and expensive than excavation, environmentally friendly.



Before…

Former Zn smelter in Belgium.
Zn is highly mobile (soluble).

After phytostabilization

Zn is still present, but immobile, allowing the reinstallation of vegetation cover and the further development of crops.

One wants to know the forms of metal contaminants, before (risk assessment) and after (purity assessment) remediation.

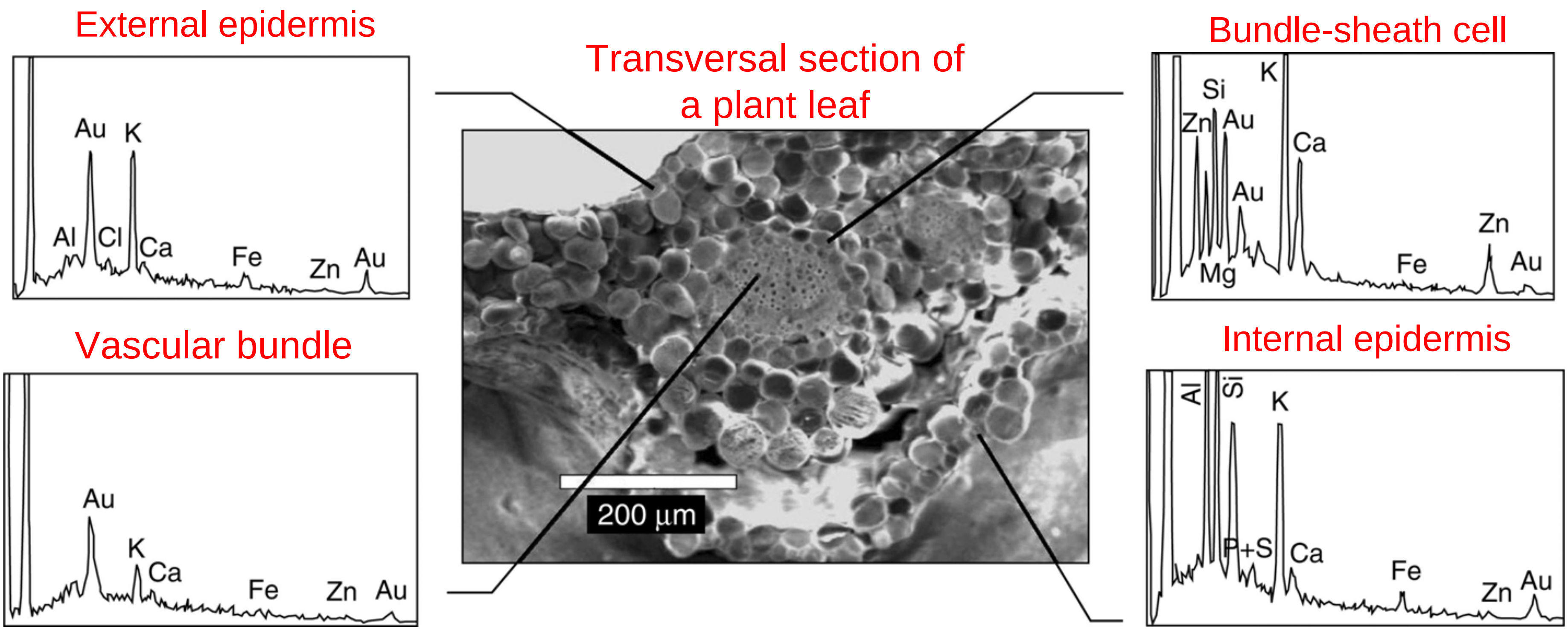
Phytoextraction

Rationale: Accumulation of metals in the areal part of hyperaccumulating plants (typically leaves)

Benefit : Much less disruptive, less expensive, environmentally friendly

Inconvenient : Length of time => increase of the biomass using genetically modified plants

[Zn]=1.95 %; [Pb]=0.89 %; [Cd]=94 ppm

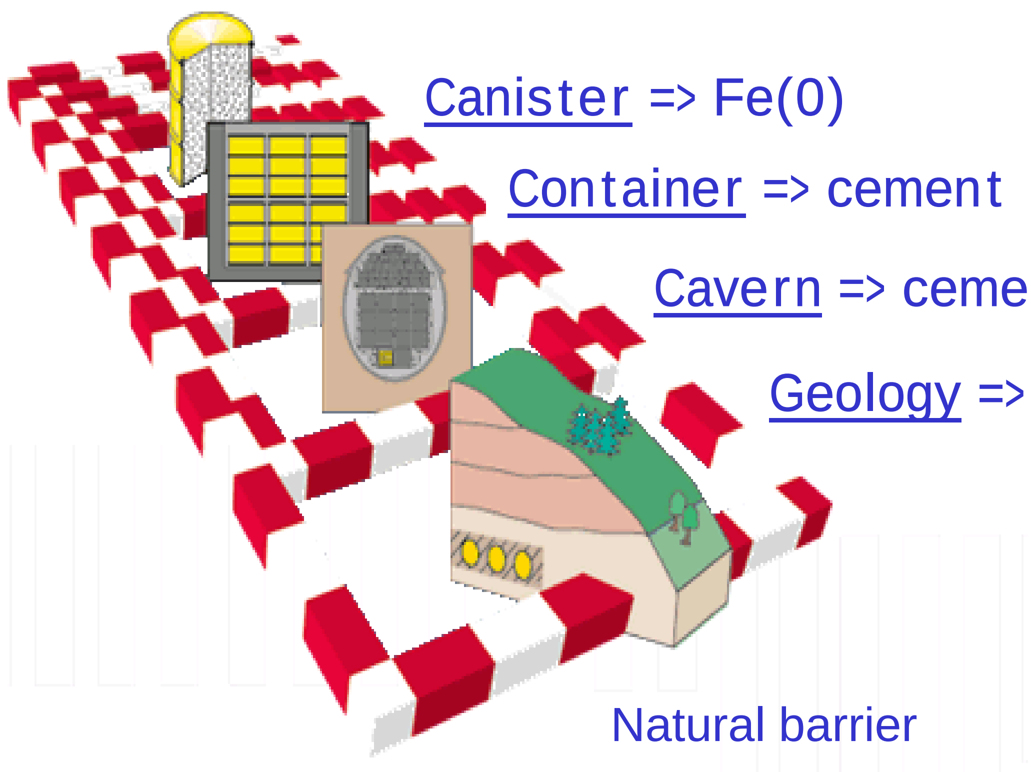


Preparing TEM samples is disruptive. How are the metals stored in living plants?

Energy

- Nuclear waste management. Development and validation of models to decrease the mobility of radionuclides in repositories.
- These goals cannot be met without a fundamental understanding of the molecular mechanisms of contaminant reactions with solid phases in heterogeneous porous media.

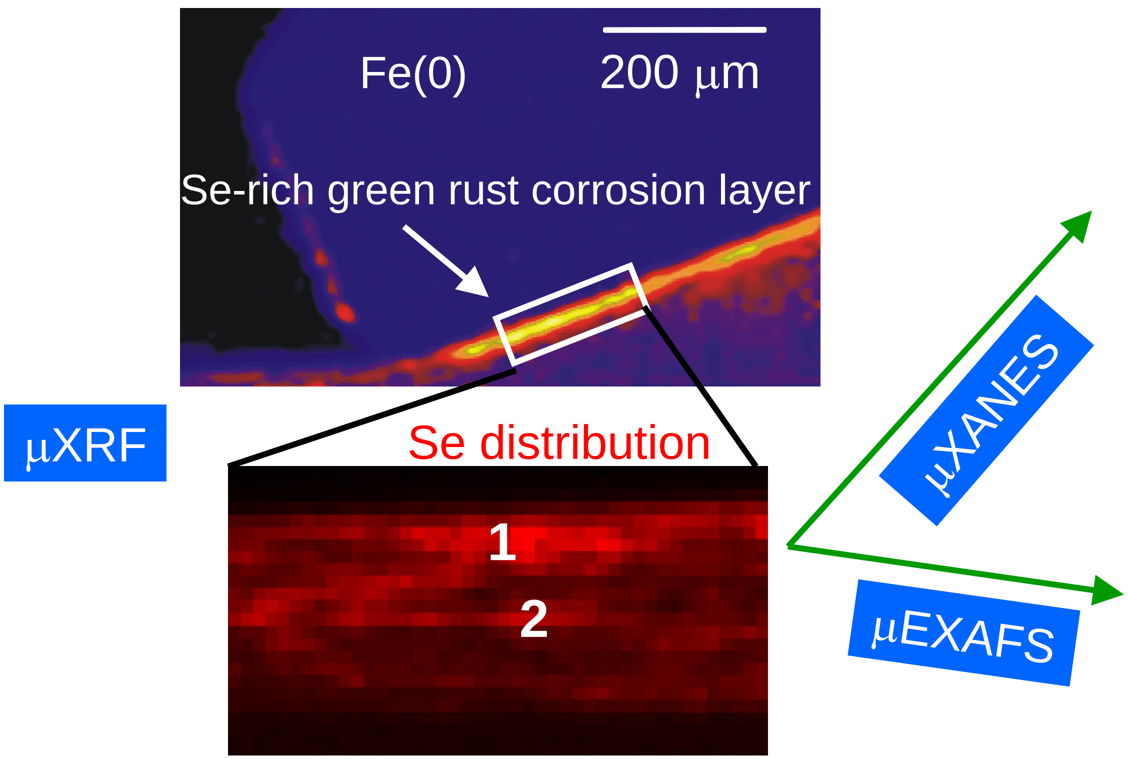
Swiss concept developped @ PSI

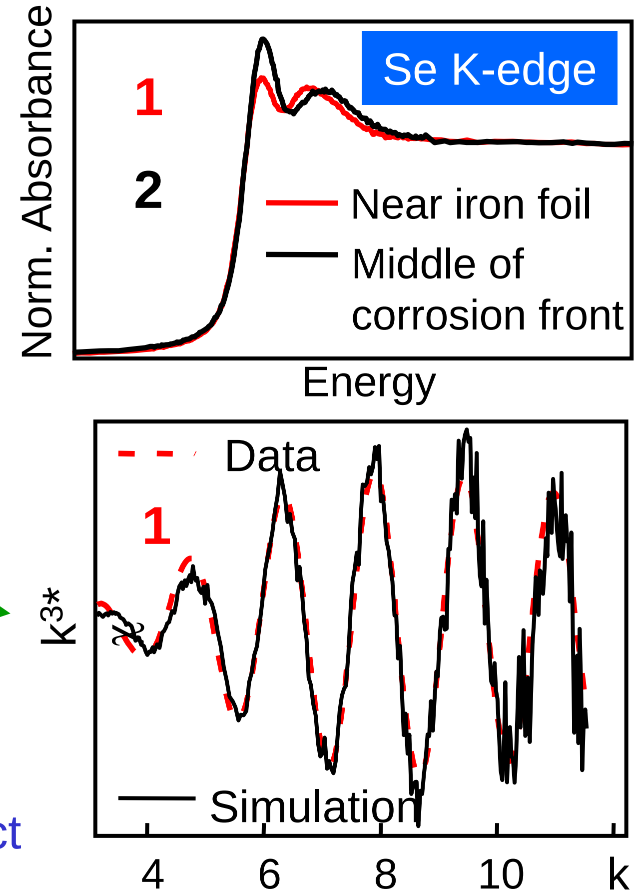


After Scheidegger et al.

Se(IV) uptake on Fe(0) canister

- Interaction with O_2-free groundwater => corrosion of canisters.
- Redox potential: –0.3 V. Formation of green rust layer: $Fe(II)_4Fe(III)_2(OH)_{12}CO_3$





Reduction of Se(IV) by green rust corrosion product and precipitation of an $FeSe_2$ like-phase.

Se forms (VI and IV) present as oxyanions are more soluble and mobile than reduced Se species. Increased Se retardation due to reduction.

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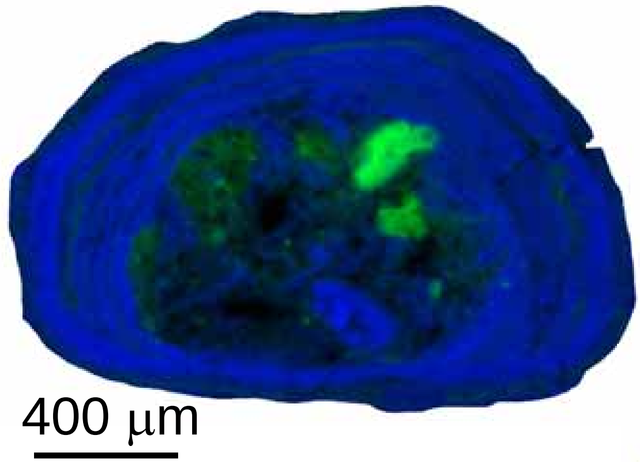
2. Some Specificities of Environmental Materials

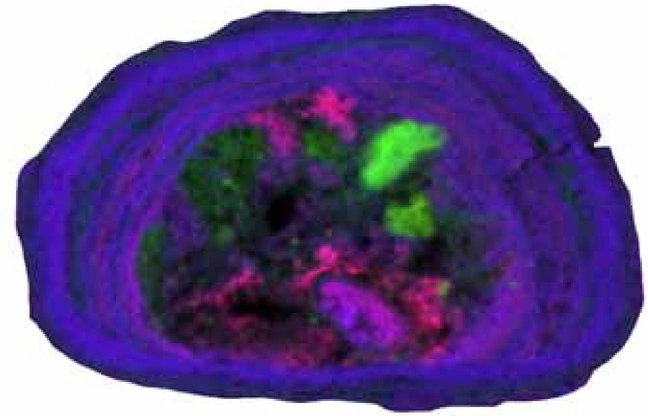
Heterogeneity

gFe bMn



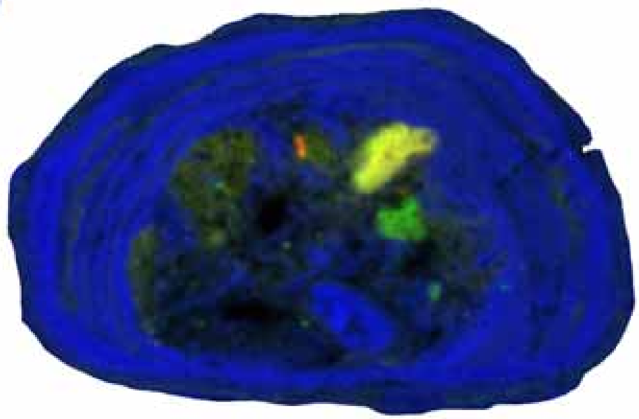
Variability

rNi gFe bMn



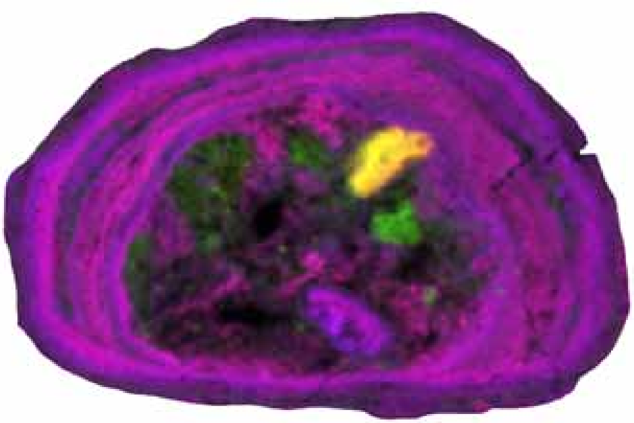
Variability

rAs gFe bMn



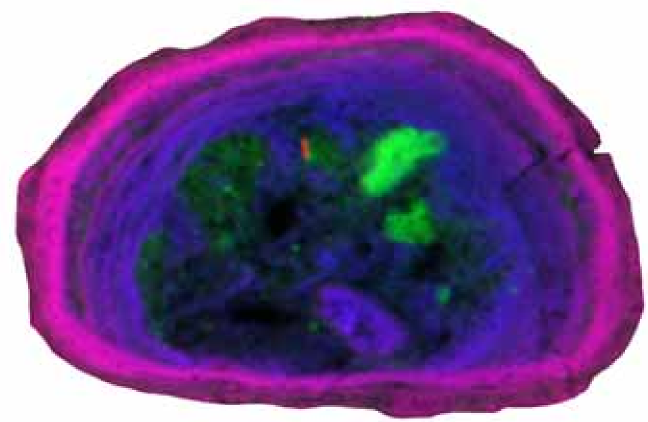
Multiplicity

rZn gFe bMn



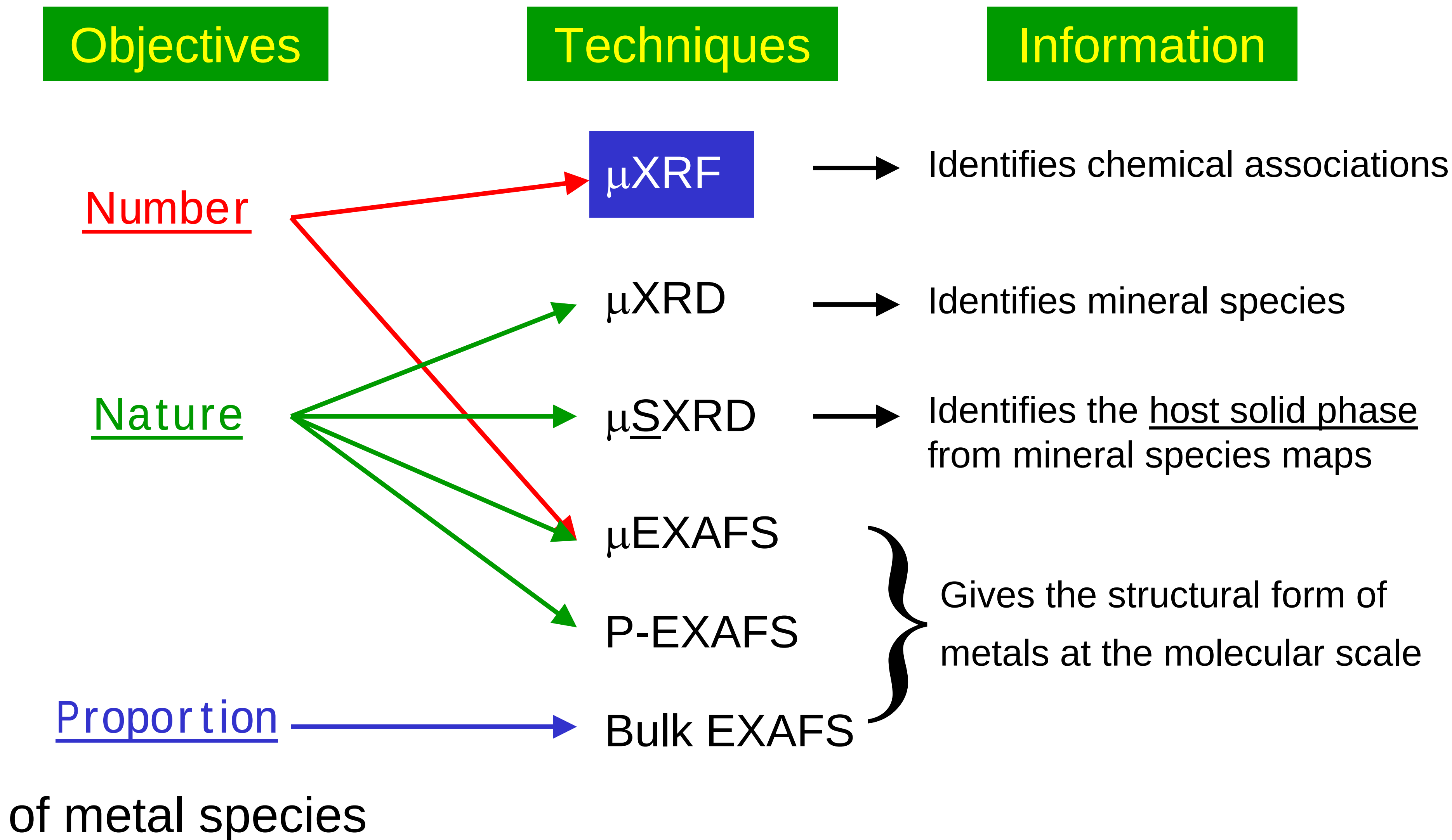
Variability

rPb gFe bMn



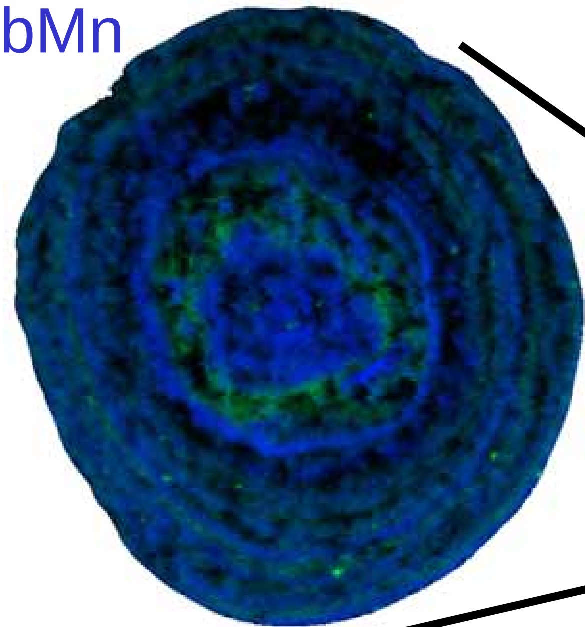
3. The State of the Art in Speciation Science

- How is it possible to rationalize these complex systems?
- Synergistic use of three non-invasive synchrotron-based techniques.

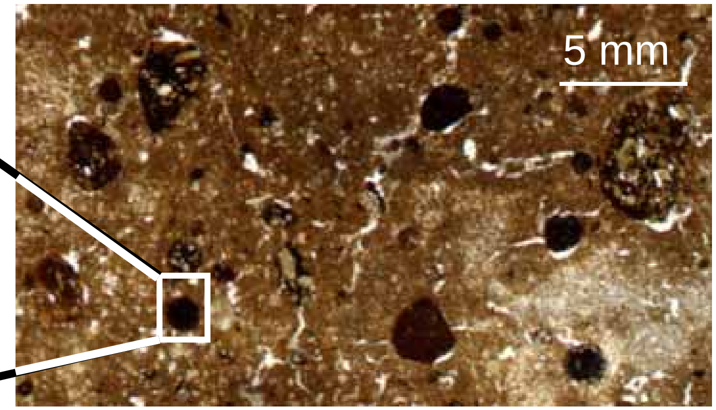


Number of Species

gFe bMn

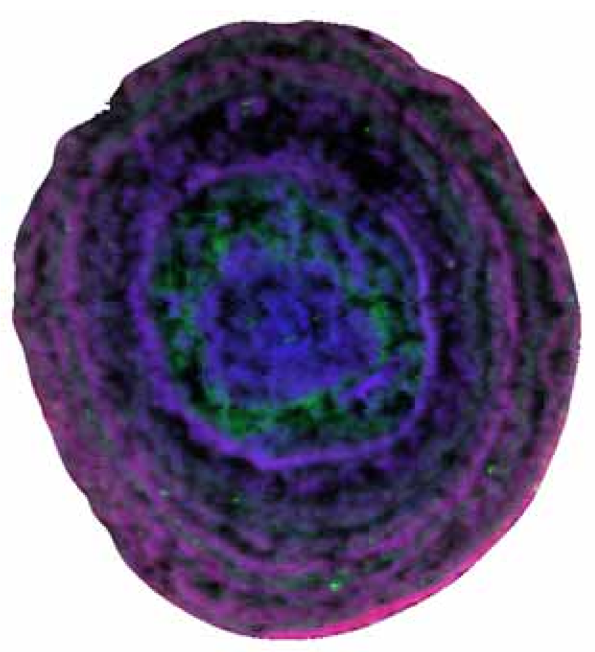


Chemical associations by μXRF

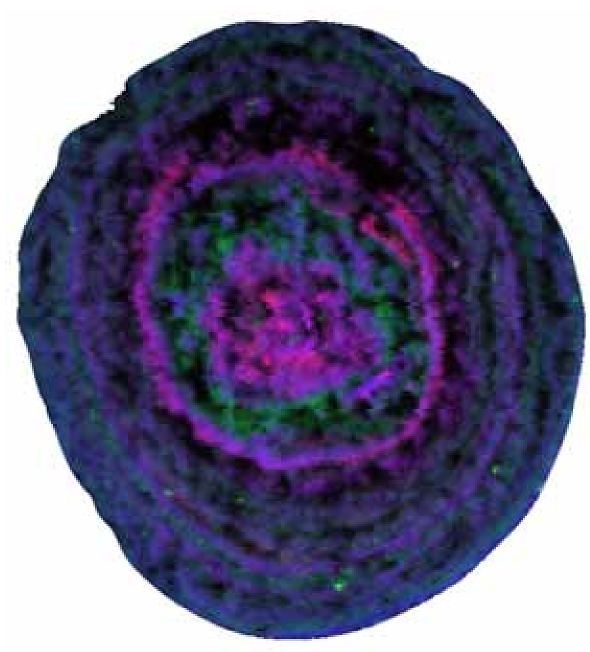


E = 13.2 keV; beam size = 10 μm H x 10 μm V

rPb gFe bMn



rNi gFe bMn



rZn gFe bMn

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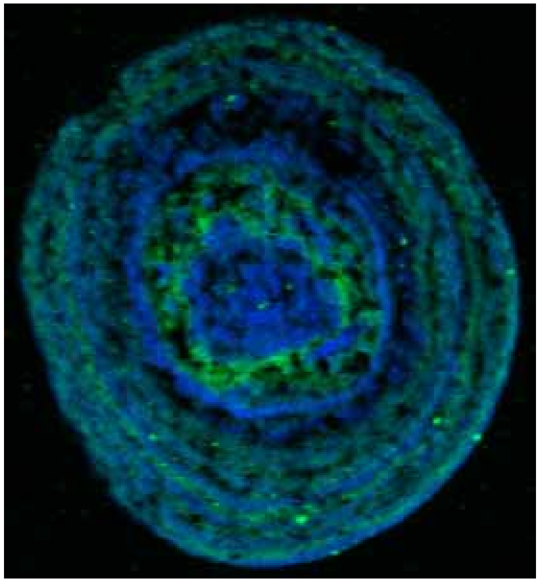
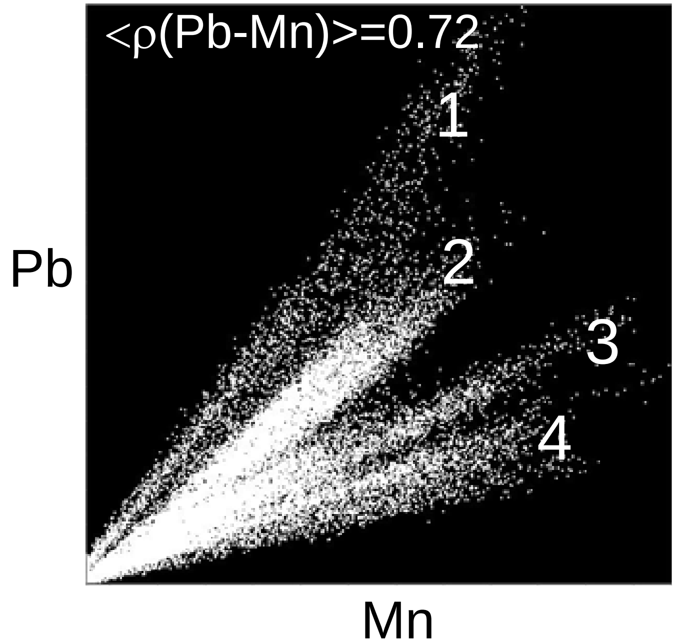
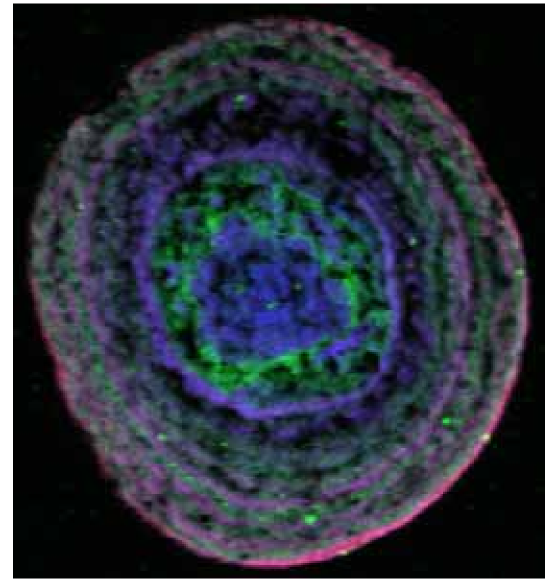
Number of Pb Species

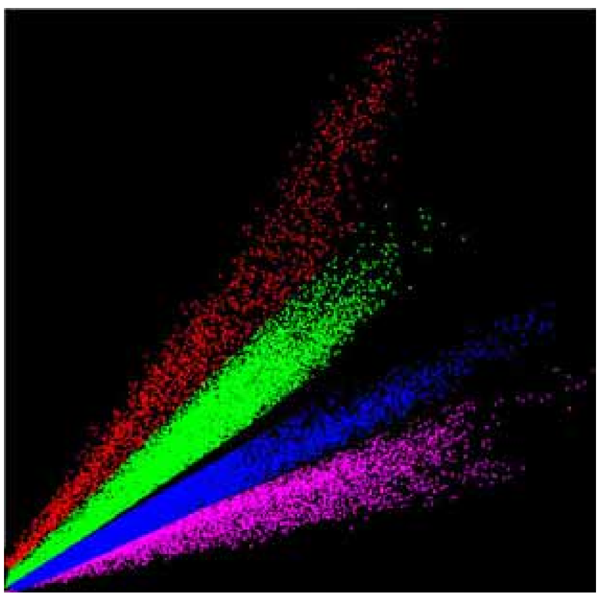
gFe bMn





rPb gFe bMn





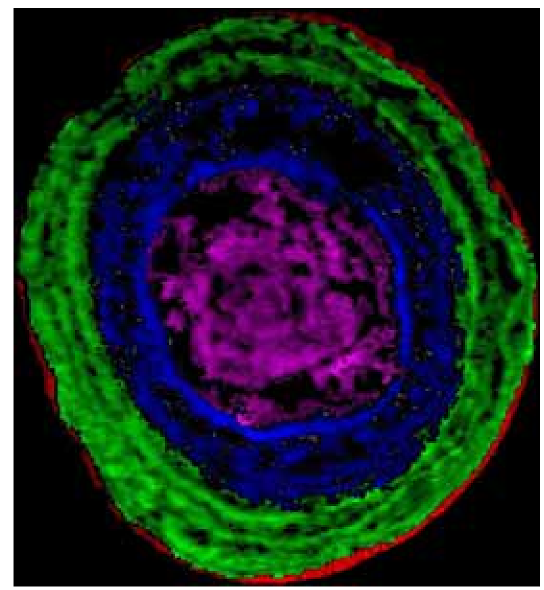
ρ(Pb-Mn)1=0.98

ρ(Pb-Mn)2=0.98

ρ(Pb-Mn)3=0.97

ρ(Pb-Mn)4=0.92

One or four Pb species ?



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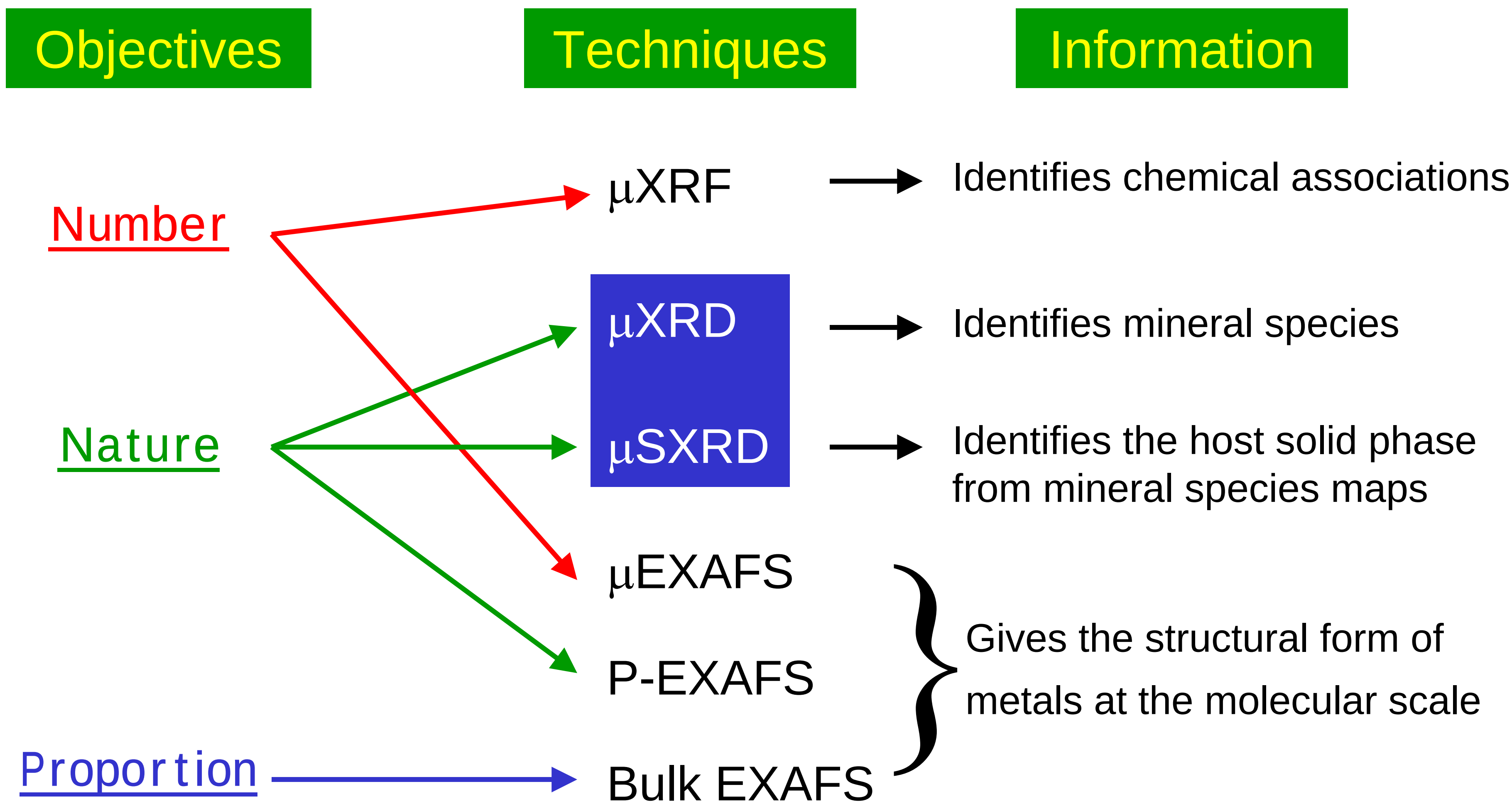
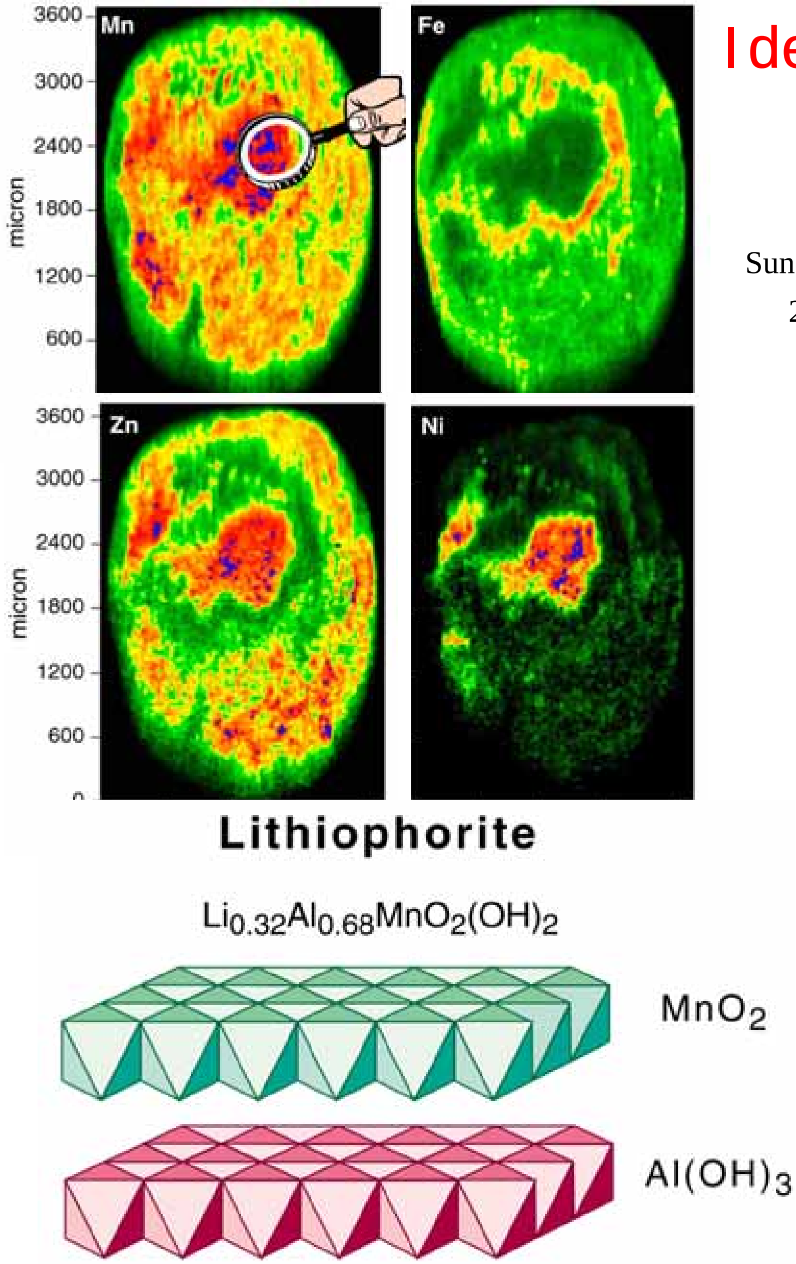
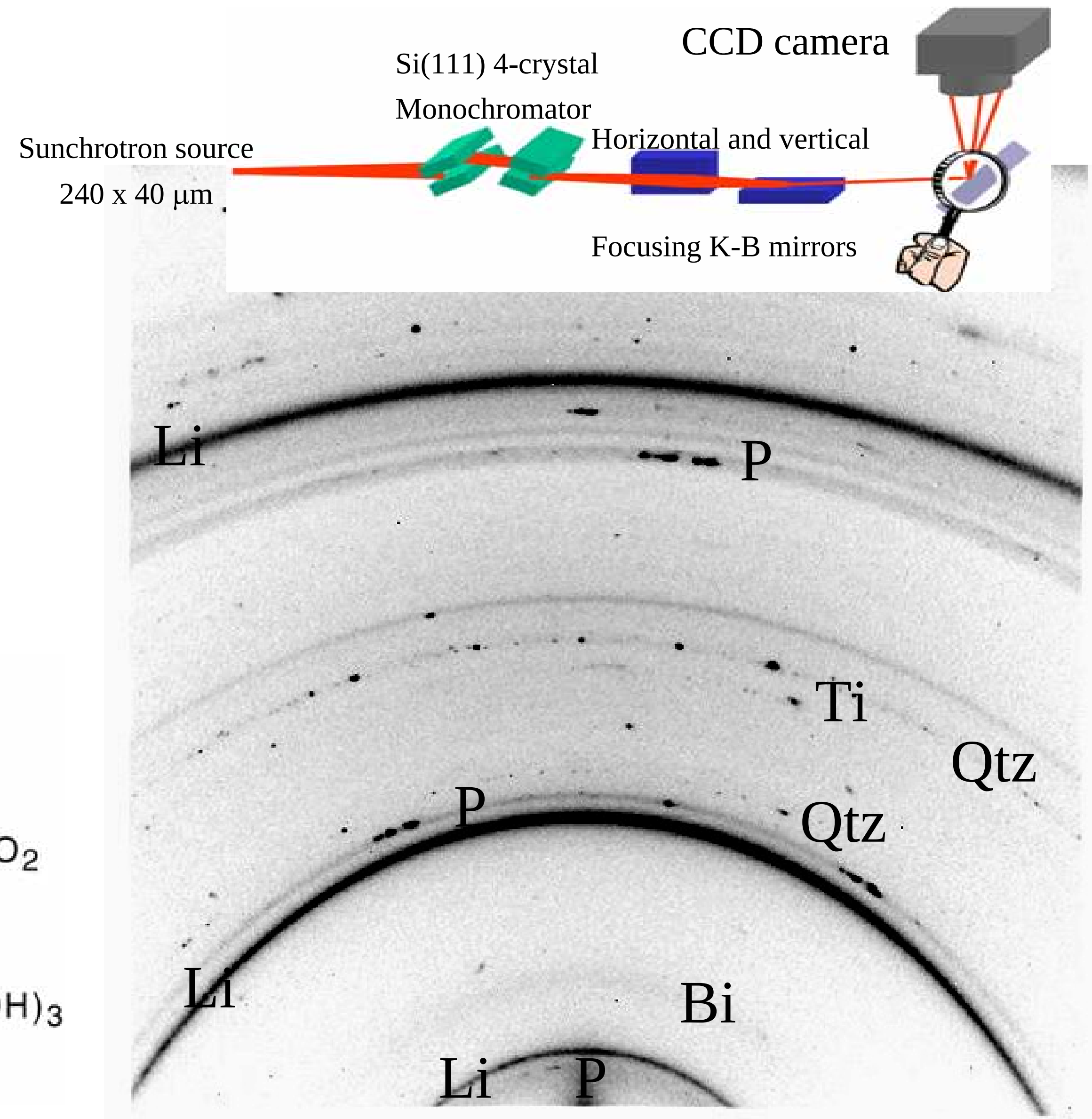


of metal species

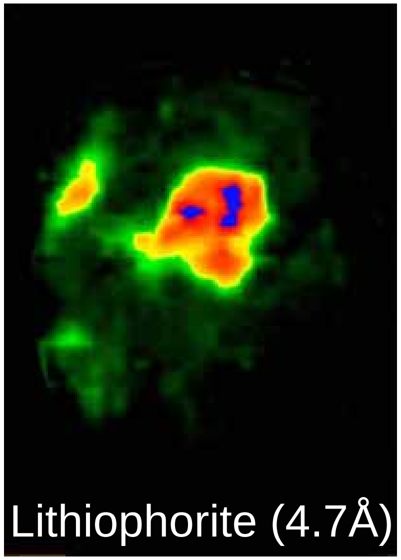
Identification of Mineral Species by µXRD

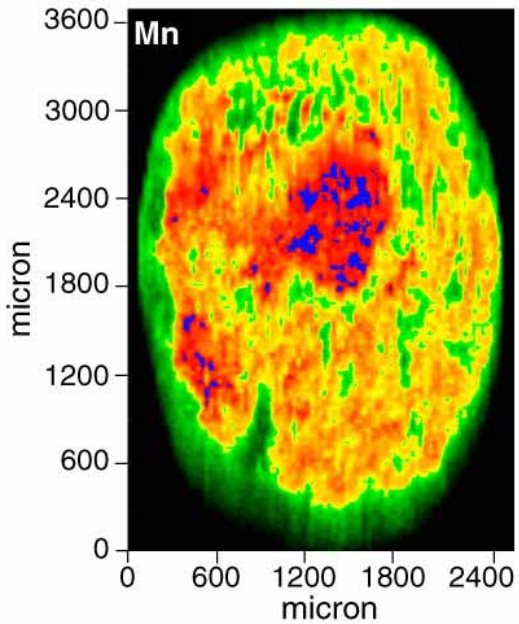


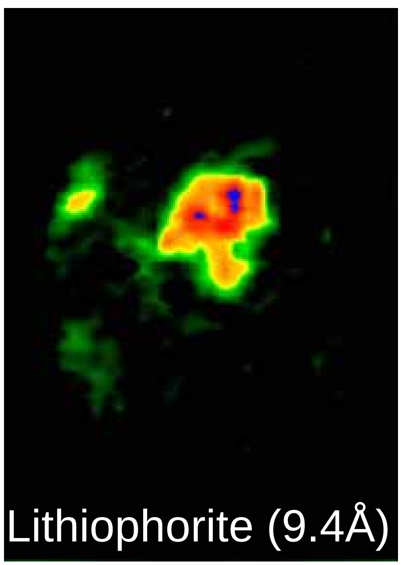


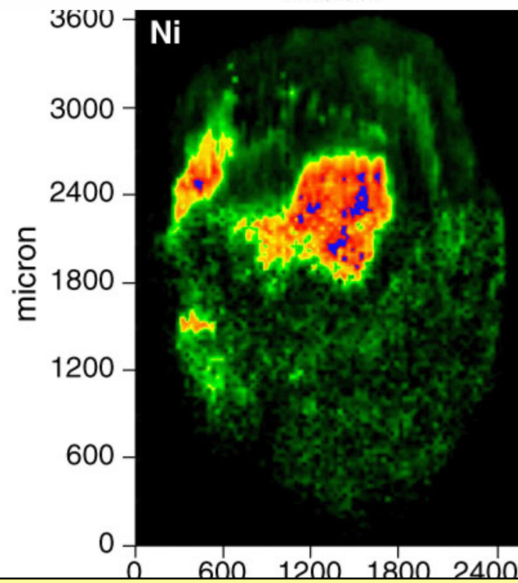
Mn is predominantly speciated as lithiophorite in the Mn-rich regions

Identification of the Host Solid Phase from Mineral Species Maps

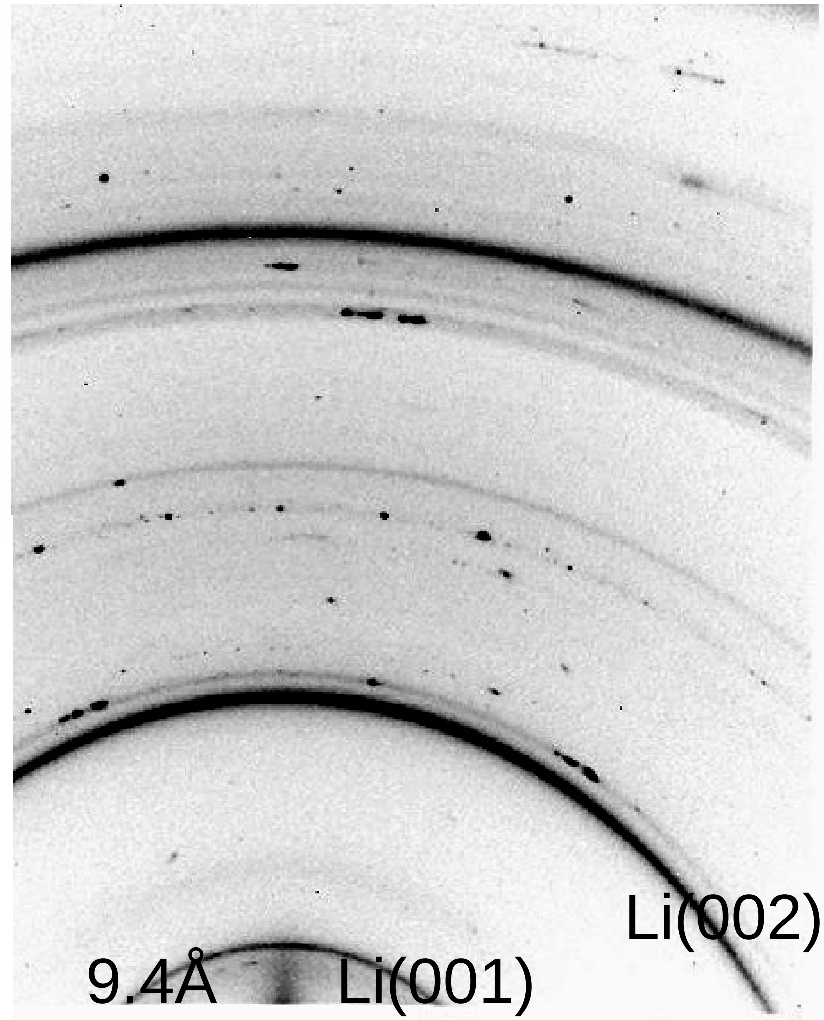






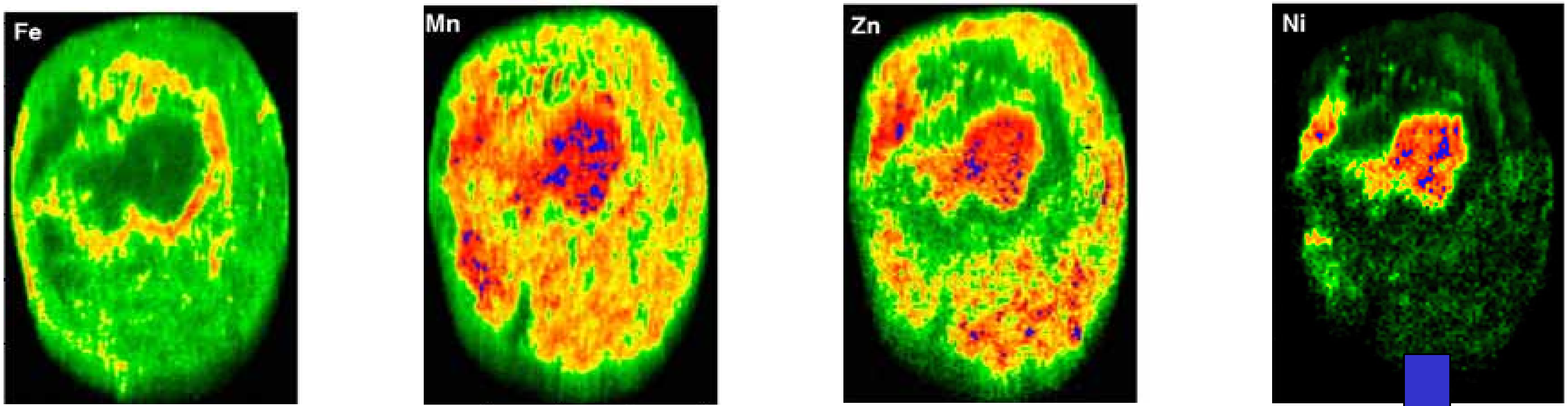


μSXRD

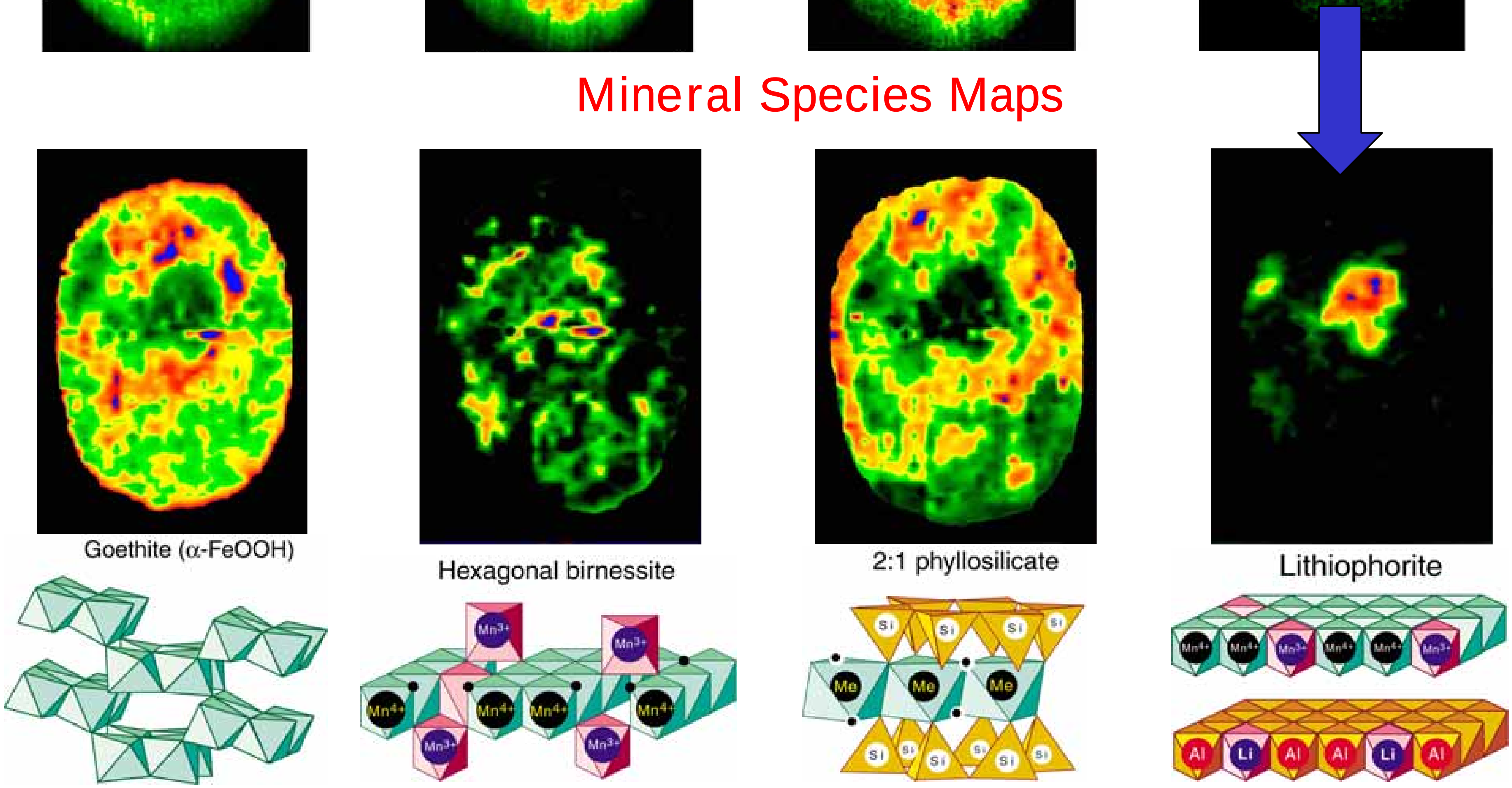


At the μmeter-scale of resolution, the nanometer size of particles becomes an advantage

Elemental Maps

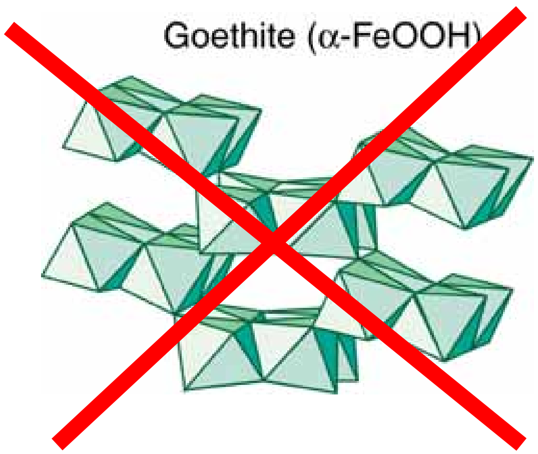


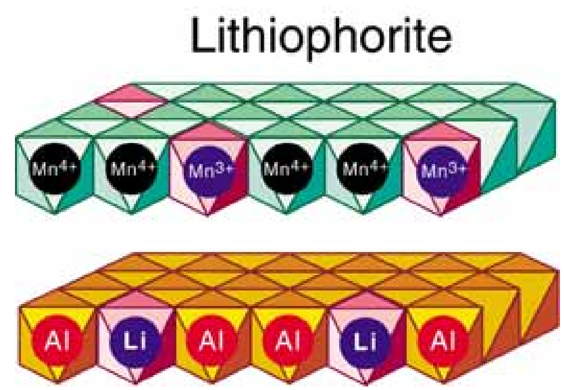
Mineral Species Maps



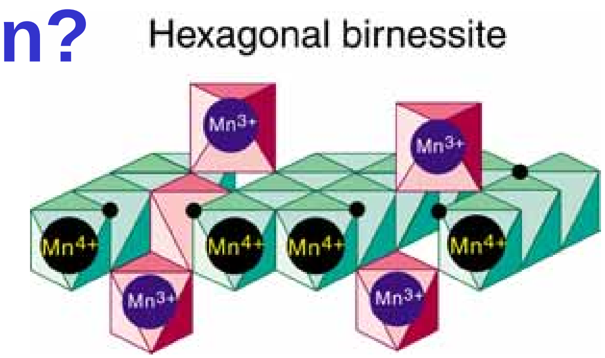
Species Inferred from μXRF + μSXRD

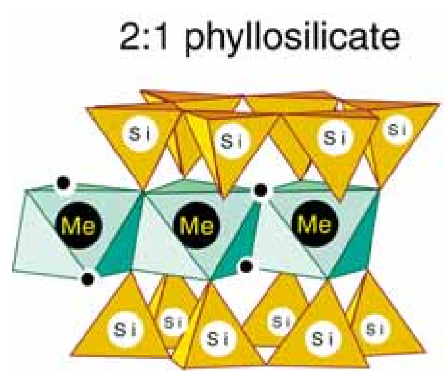
Zn?, Ni

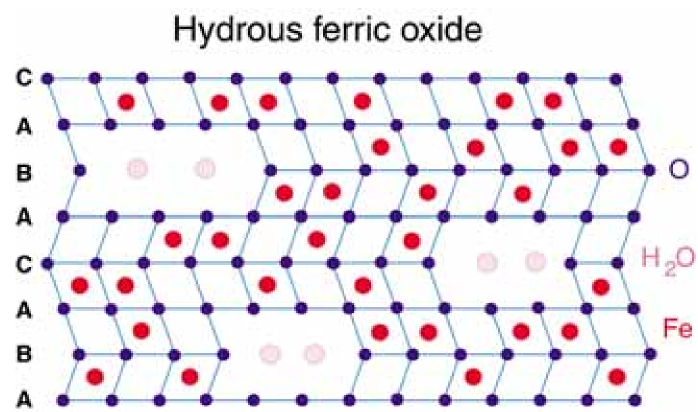




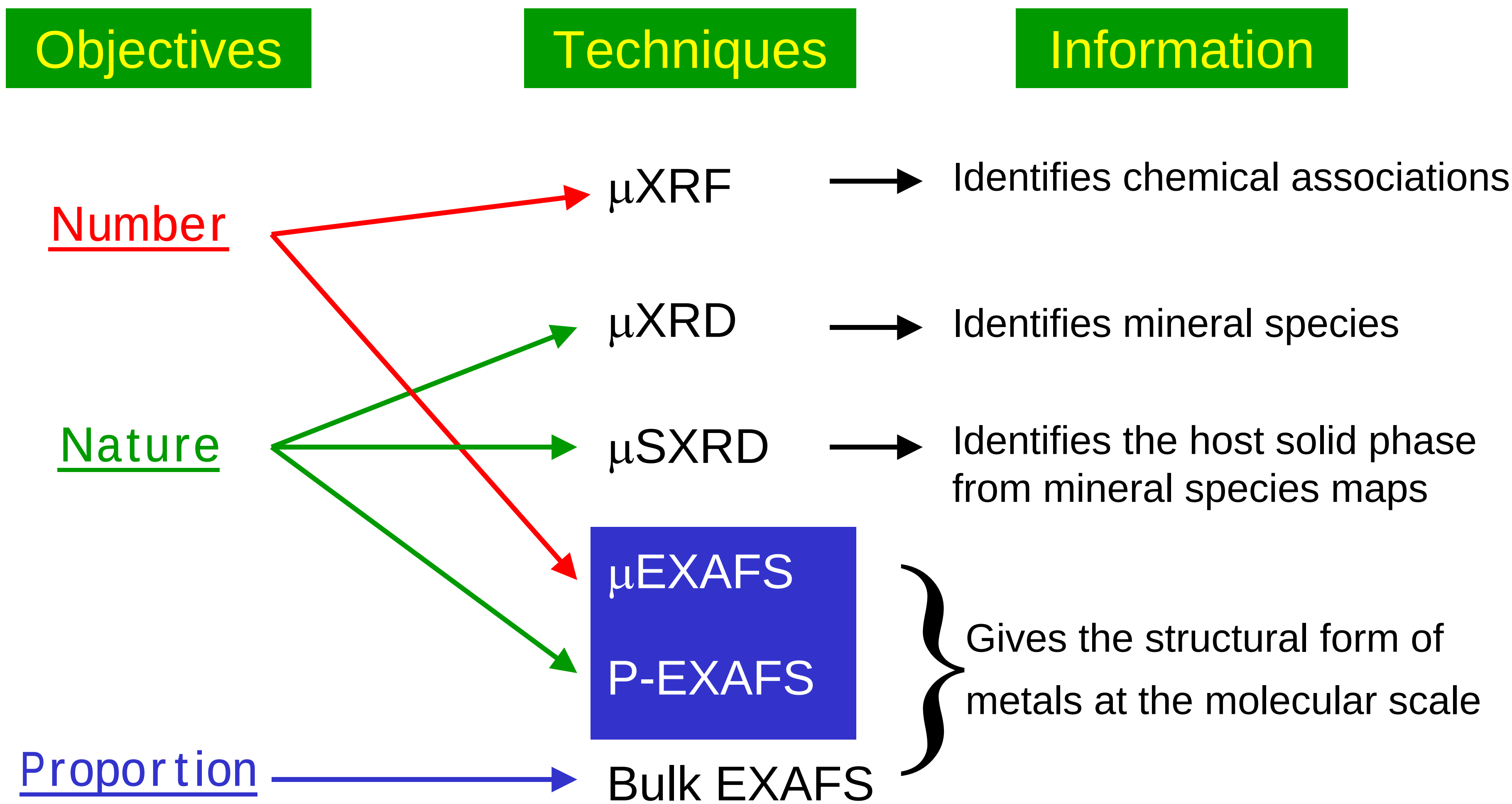
Zn?



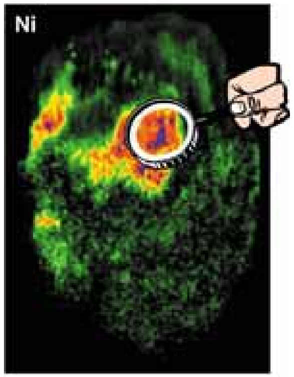




An association between an element E and a mineral M does not necessarily imply that E is chemically bound to or included in the structure of M.



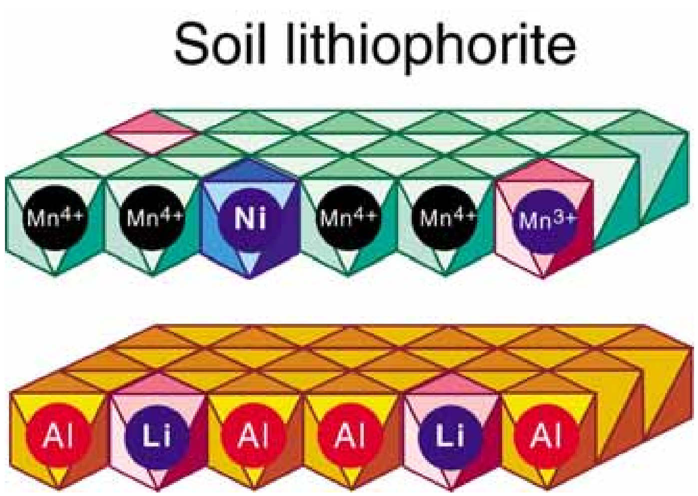
of metal species

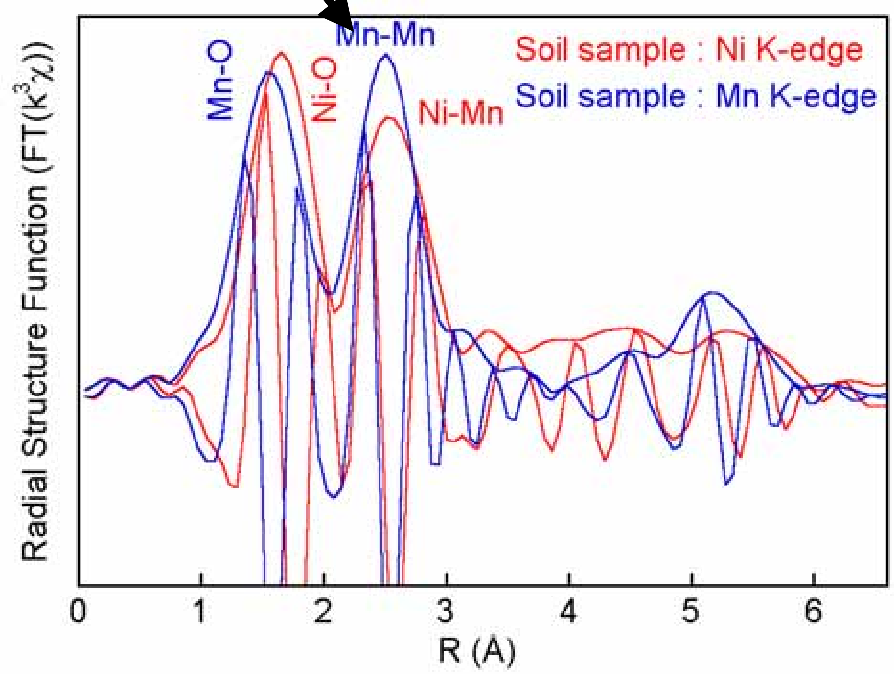


How is Ni bound? → µEXAFS

The answer comes from the comparison of Ni and Mn K-edge measurements

Ni and **Mn** have a similar local structure beyond the first coordination shell





$r(Ni^{2+})$=0.69Å ; $r(Mn^{3+})$=0.65Å

$r(Mn^{4+})$=0.53Å ; $r(Al^{3+})$=0.54Å; $r(Li^{+})$=0.76Å

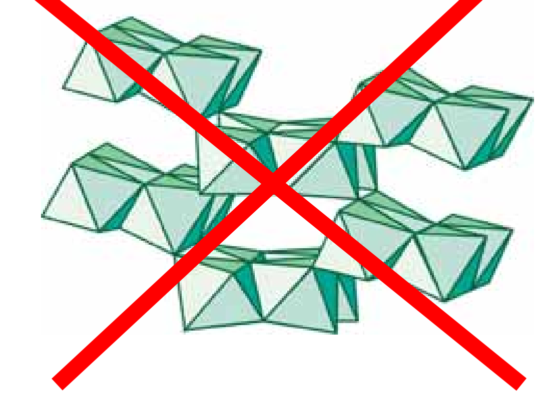
d(Ni-O) = 2.05 Å; d(Ni-Mn) = 2.91 Å

d(Mn-O) = 1.92 Å; d(Mn-Mn) = 2.92 Å

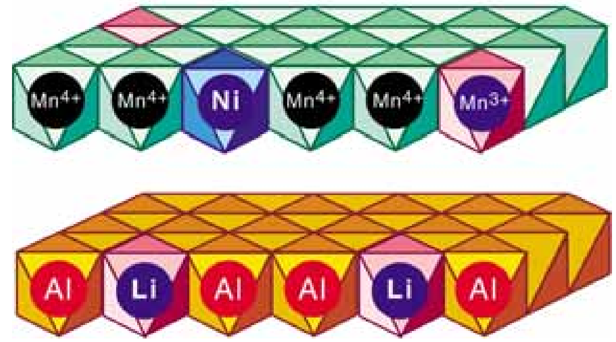
How is Zn bound?

Zn?, Ni

Goethite (α-FeOOH)

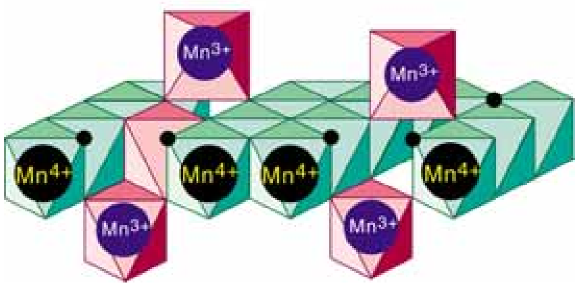


Soil lithiophorite

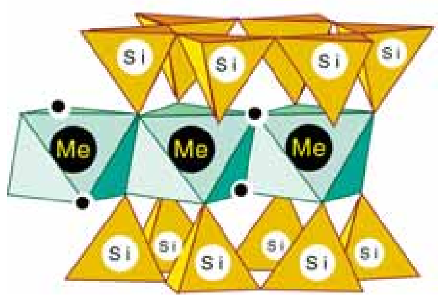


Zn?

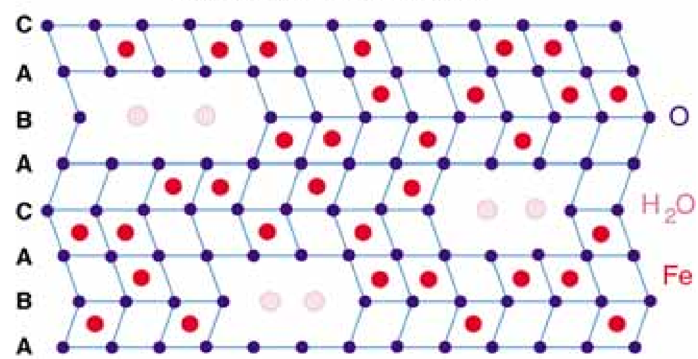
Hexagonal birnessite



2:1 phyllosilicate



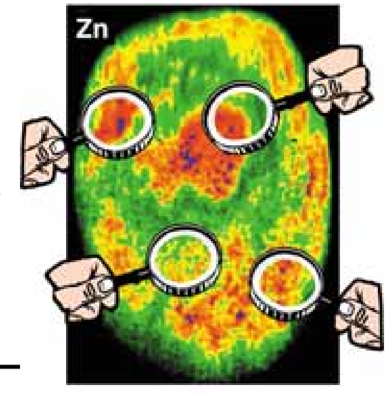
Hydrous ferric oxide



Manceau –SRI-2003

Joseph Fourier (1768-1830)

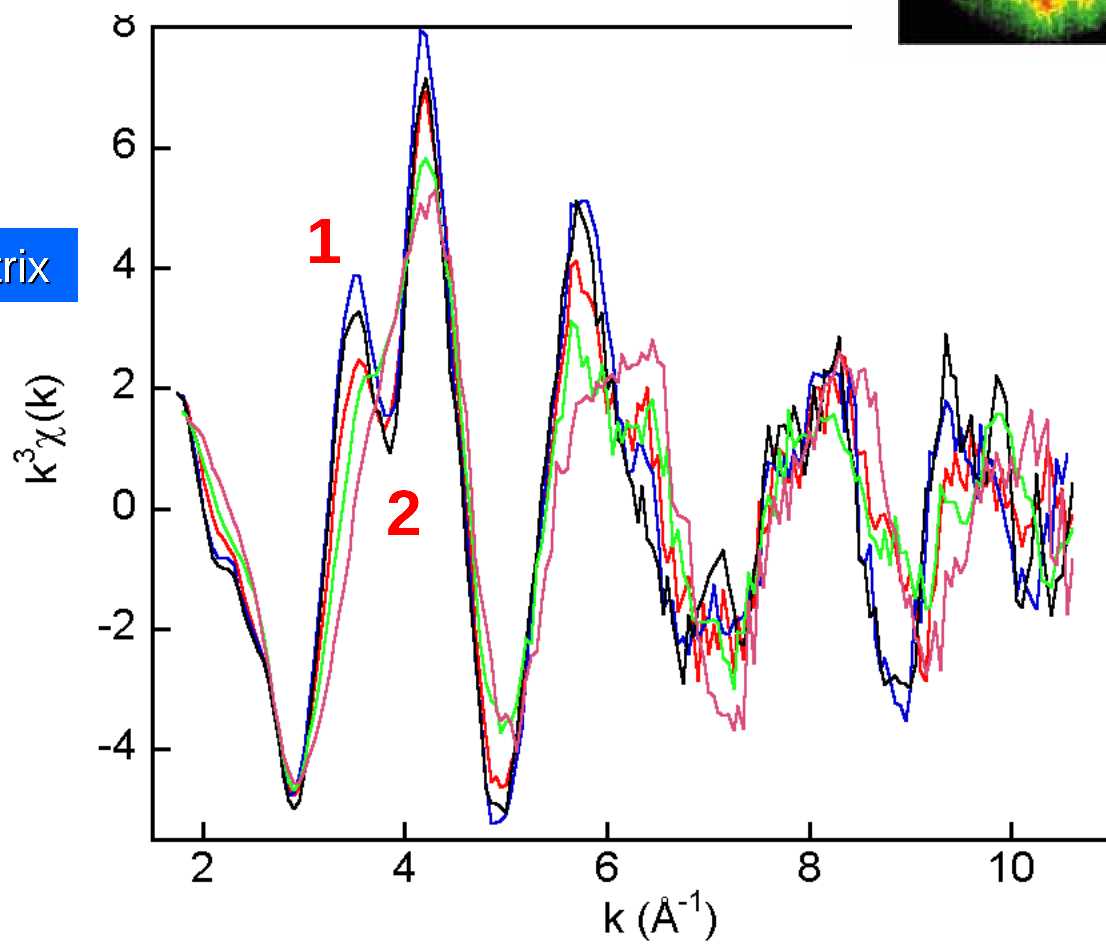
How is Zn bound? → μEXAFS



- **Number** of species => Principal Component Analysis
- **Nature** of species => Target transformation

Calculation of the covariance matrix

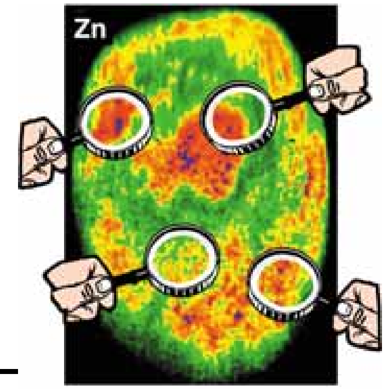
λ	Cumulative % of variance
65	65
19	82
7	89
6	95
5	100



Joseph Fourier (1768-1830)

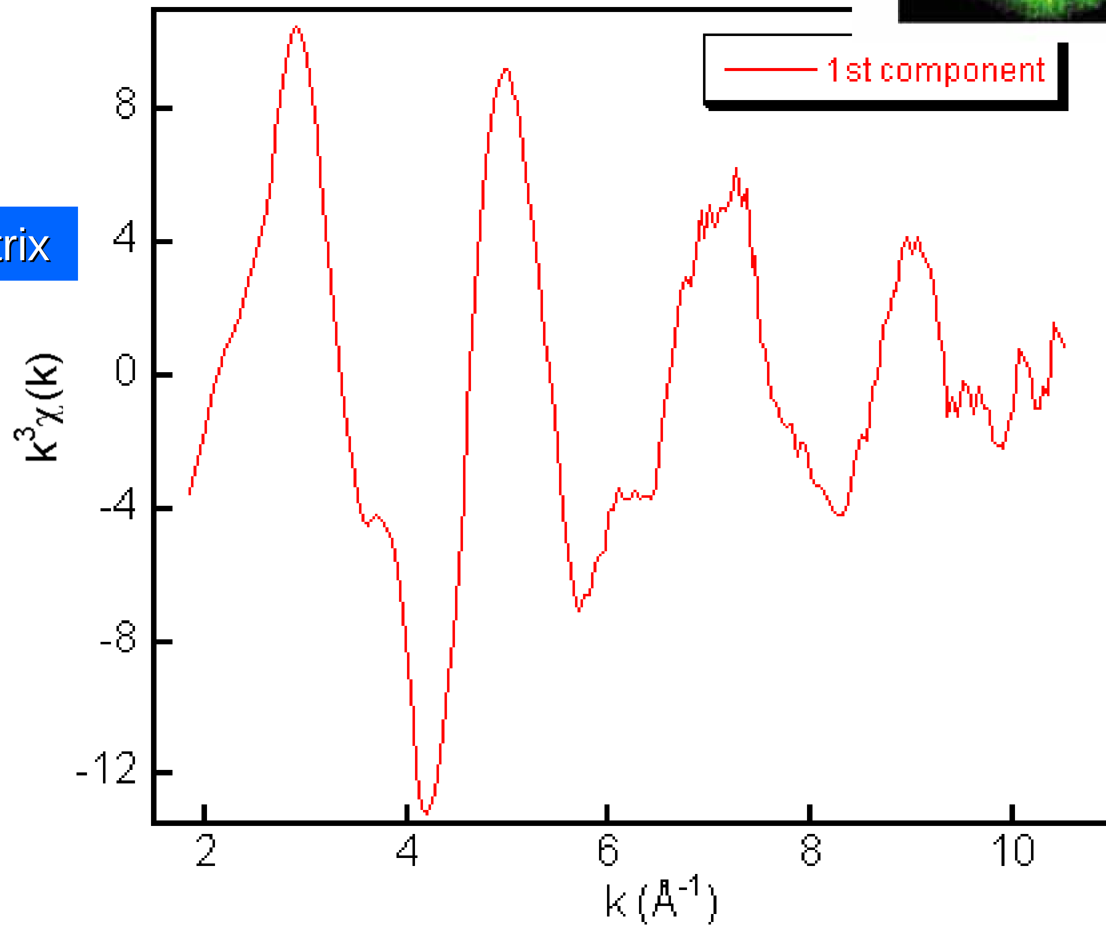
How is Zn bound? ➡ μEXAFS

- **Number** of species => Principal Component Analysis
- **Nature** of species => Target transformation



Calculation of the covariance matrix

λ	Cumulative % of variance
65	65
19	82
7	89
6	95
5	100



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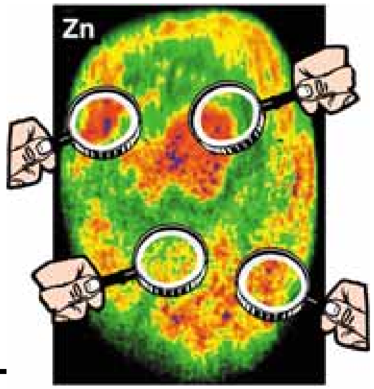

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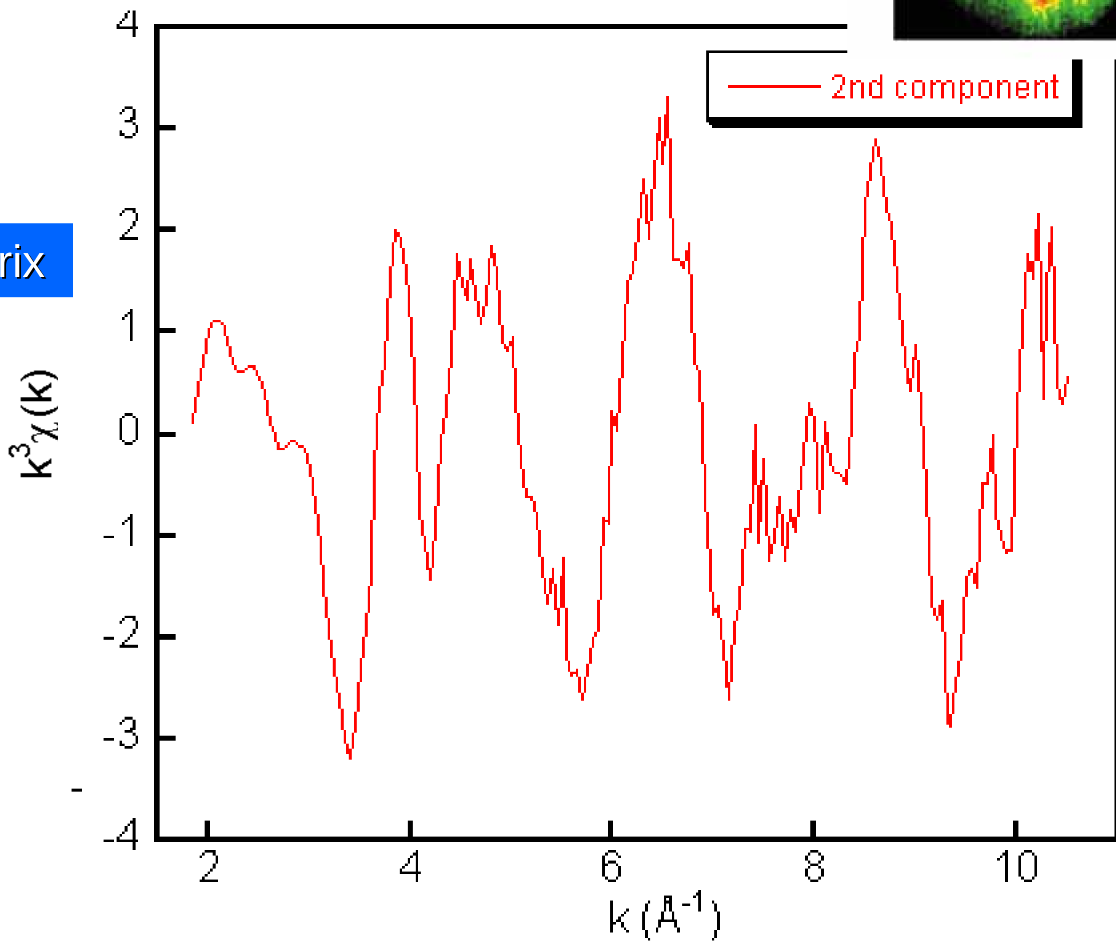

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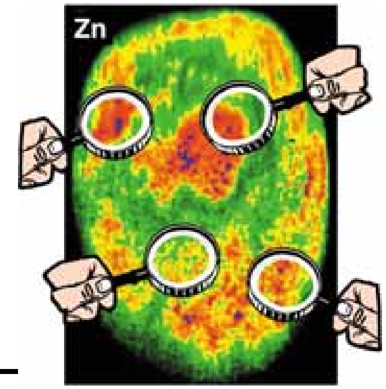

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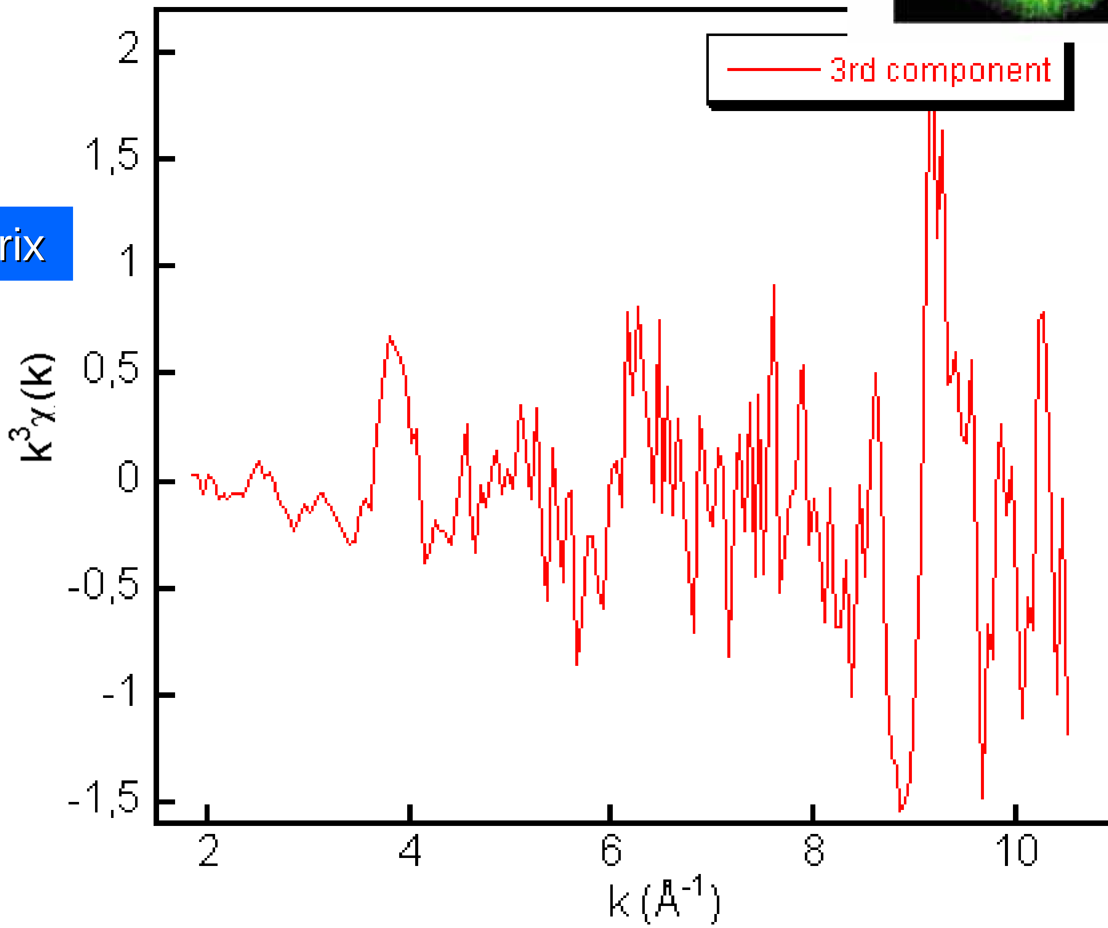
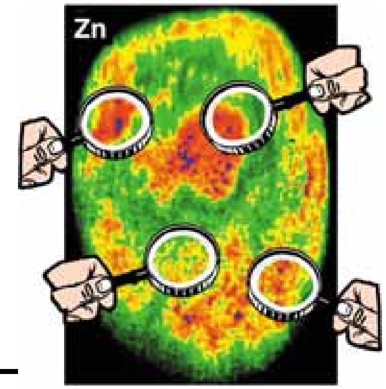


Joseph Fourier (1768-1830)

How is Zn bound? ➡ μEXAFS



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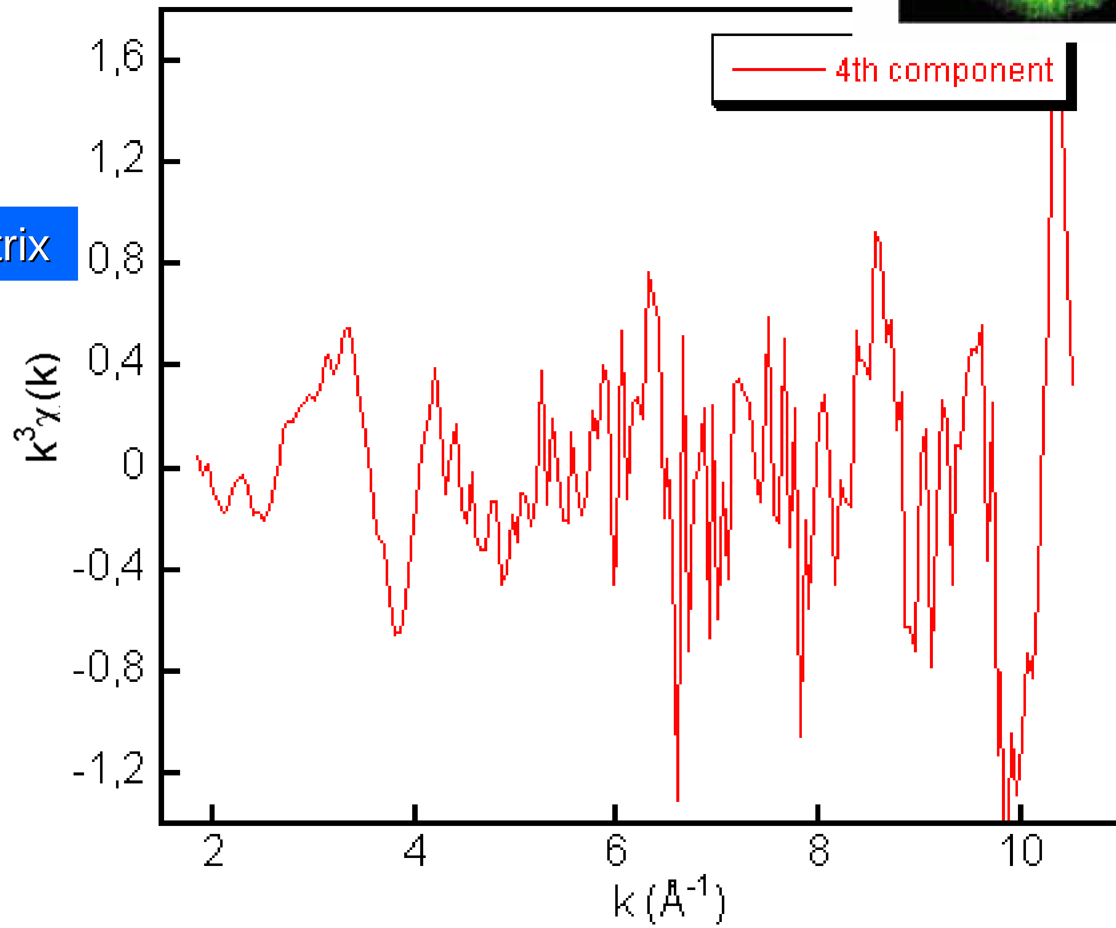
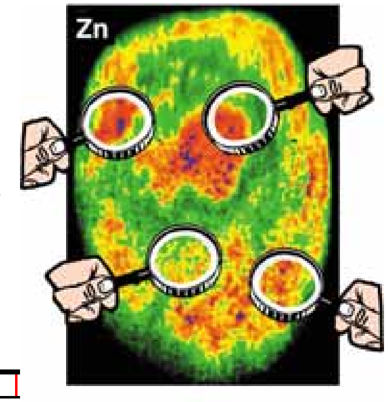


Joseph Fourier (1768-1830)

How is Zn bound? ➡ µEXAFS

- **Number** of species => Principal Component Analysis
- **Nature** of species => Target transformation



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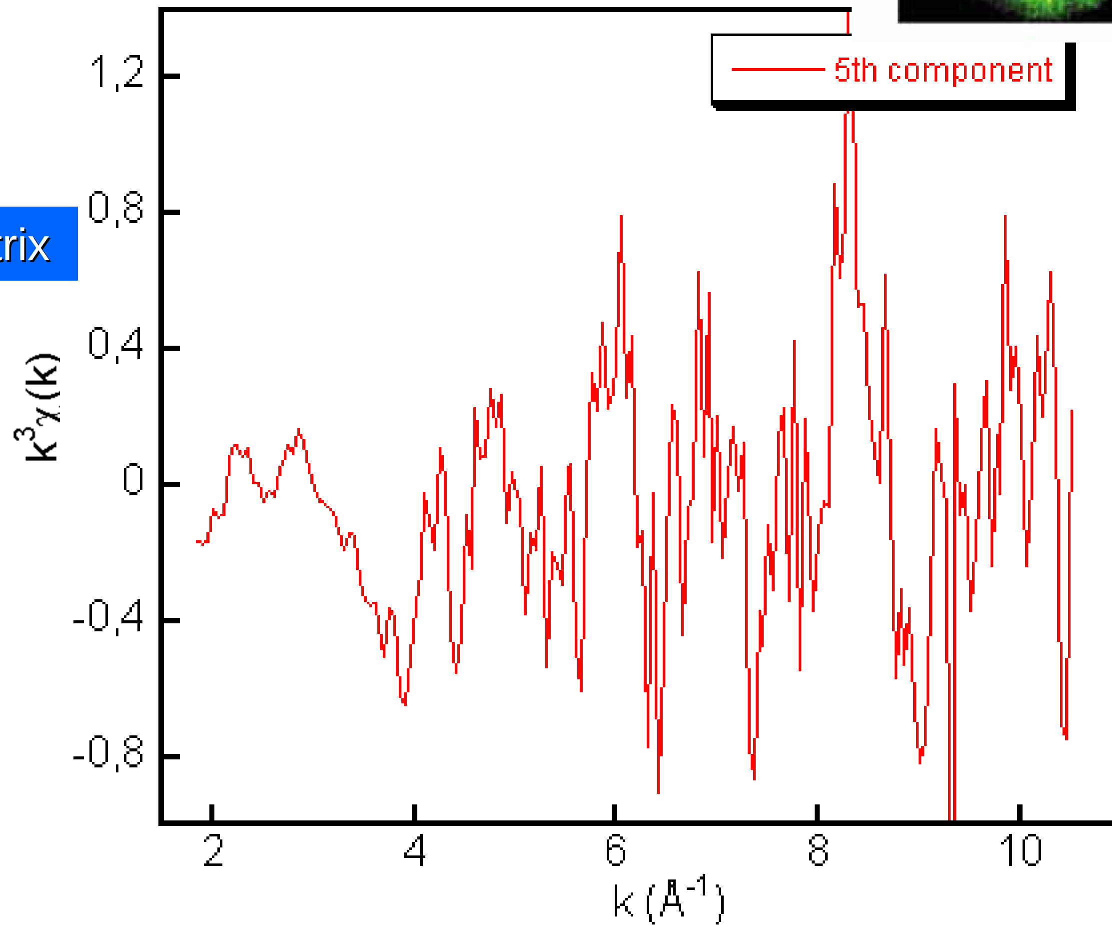
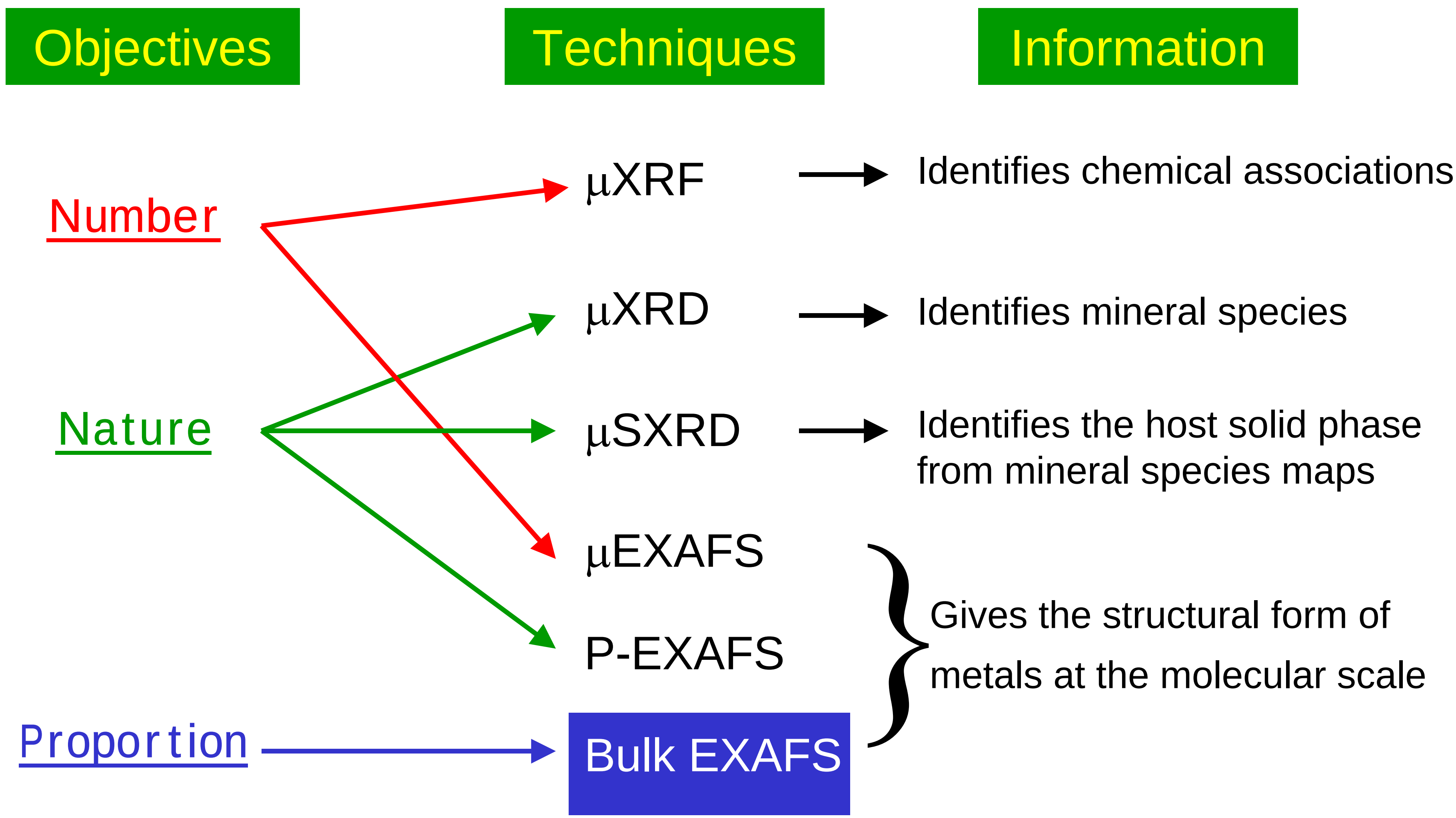


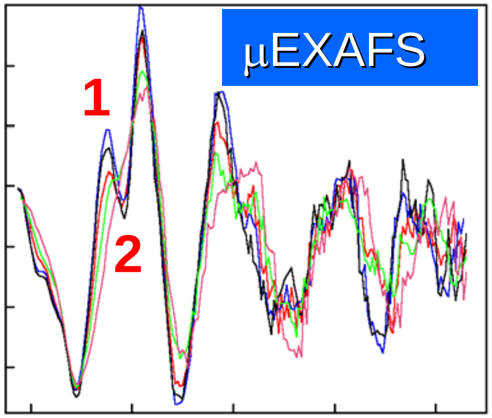
PCA reveals two species

- The drawback in applying the methods is one of sampling. We look at an infinitesimally small portion of a highly complex system. High-resolution techniques cannot avoid the collection of detailed information from vanishingly small amounts of material.

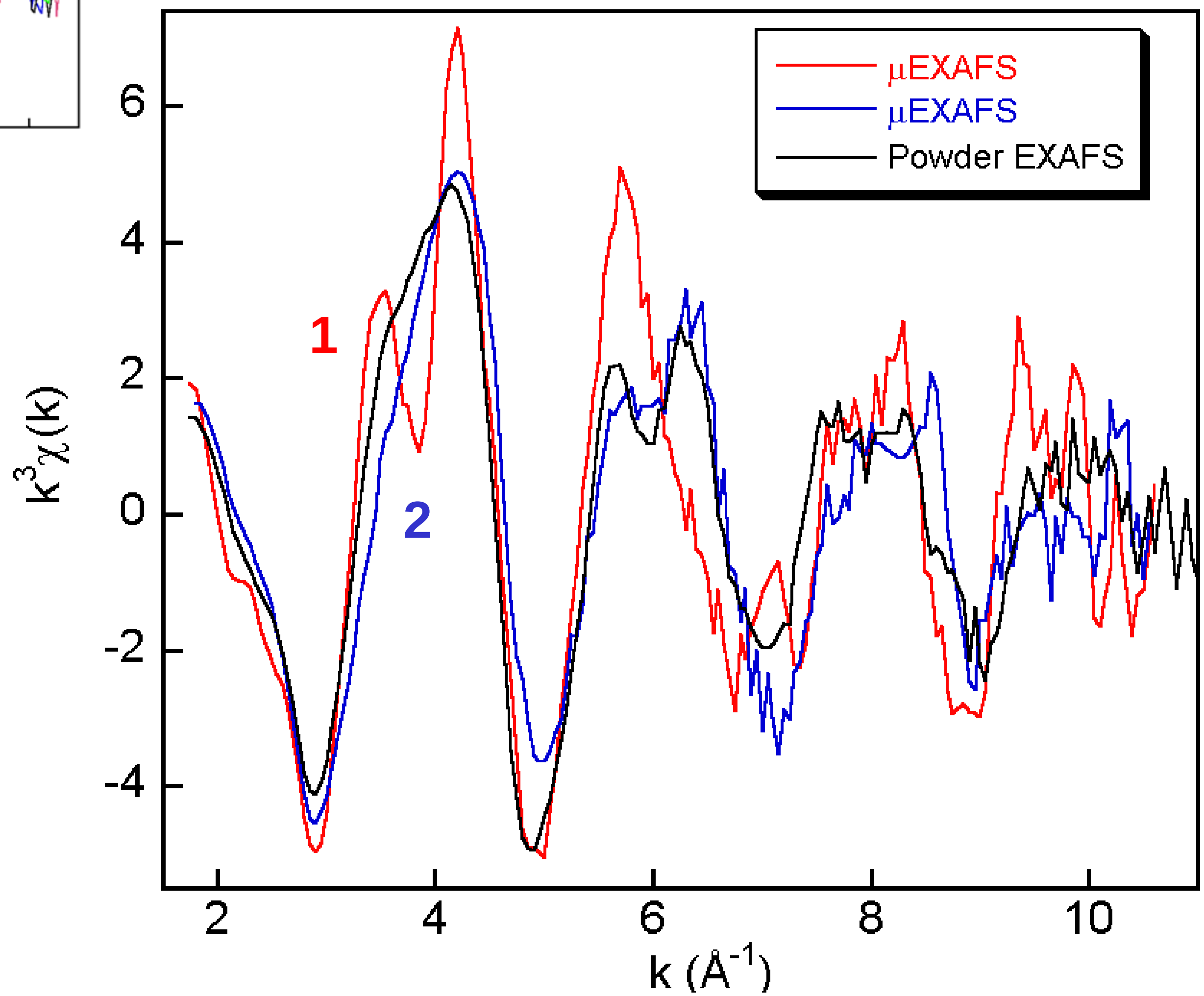
- With synchrotron radiation one can probe a sample over areas from 10 mm^2 to less than one μm^2. X-rays are also advantageous for determining the proportion of metal species in the bulk because they have a much higher penetration depth than electrons.



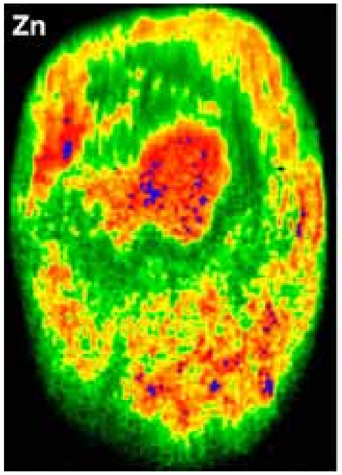
Manceau –SRI-2003



Does Powder EXAFS agree with μEXAFS?



Manceau –SRI-2003



Species identified by:

Micro-EXAFS	Powder EXAFS
	~1/3 Phyllosilicate
Hydrous Ferric Oxide	~1/3 Hydrous Ferric Oxide
Zn-birnessite	~1/3 Zn-birnessite
Lithiophorite	

Why do micro and bulk EXAFS not see the same species?

Twenty individual nodules were analyzed: The σ variability is high

[Fe] = 57526 (σ = 21213); [Mn] = 25592 (σ = 17716)

[Zn] = 76 (σ = 51); [Ni] = 67 (σ = 21) mg/kg.

Because only one nodule was examined by μEXAFS

1. Societal and Scientific Challenges of Molecular Environmental Science (MES)

2. Some Specificities of Environmental Materials

3. The State of the Art in Speciation Science with SR

4. Technical Difficulties, Present Instrumental Limitations, and Next Instrumental Challenge

4. Technical Difficulties, Present Instrumental Limitations, and Future Instrumental Challenges

- Preservation of the moist state of natural samples.

- Sample heterogeneity. Exquisite sensibility to beam motion resulting from putting a small beam on an equally small particle. If the position drifts on a time scale comparable to the length of time required to scan over an EXAFS oscillation => phantom EXAFS.

- Radiation damage. The power density in a microfocus beam is much greater than in a ‘normal’ beamline fed by the same source => photo-reduction, photo-oxidation, amorphization…

- Overwhelming amount of Fe.

Technical difficulties

Examples of Radiation Damage

Photo-reduction

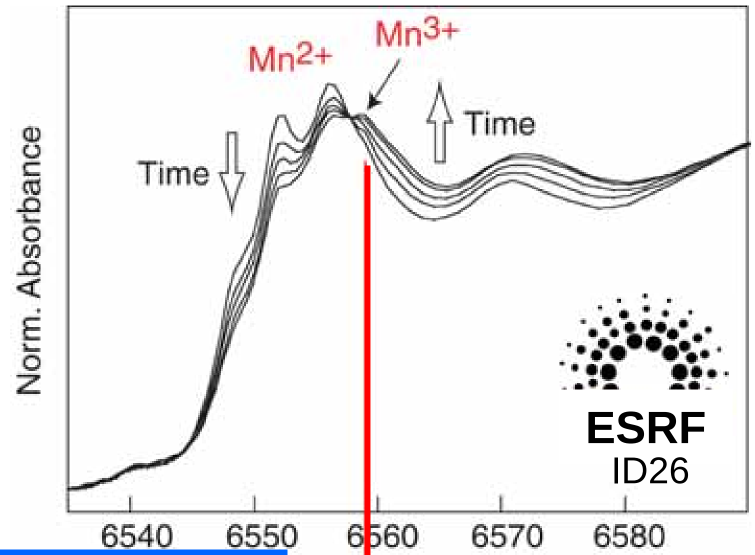
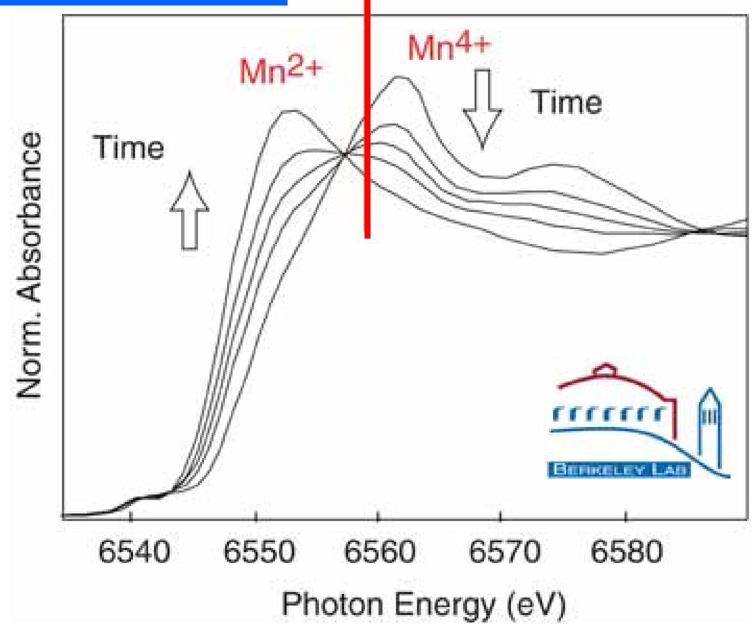
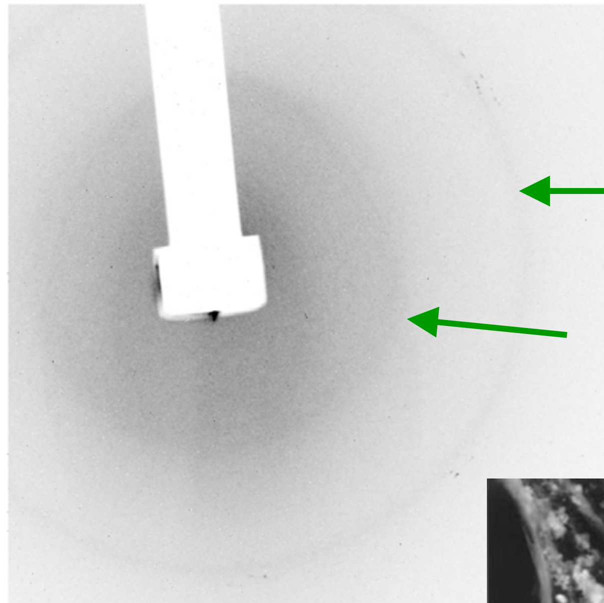
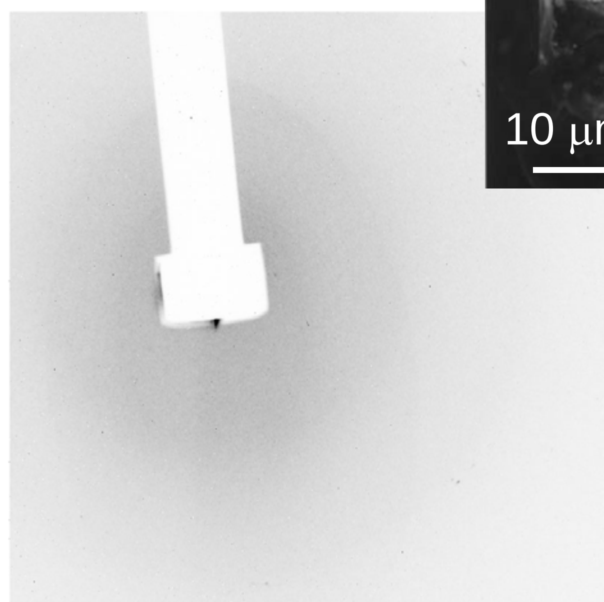


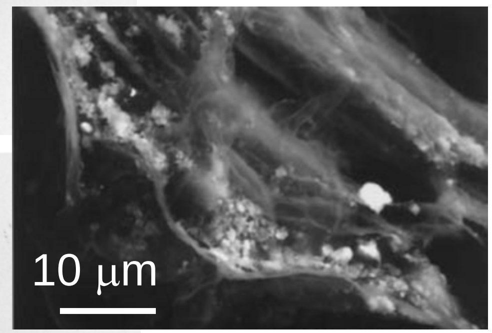
Photo-oxidation



Amorphization



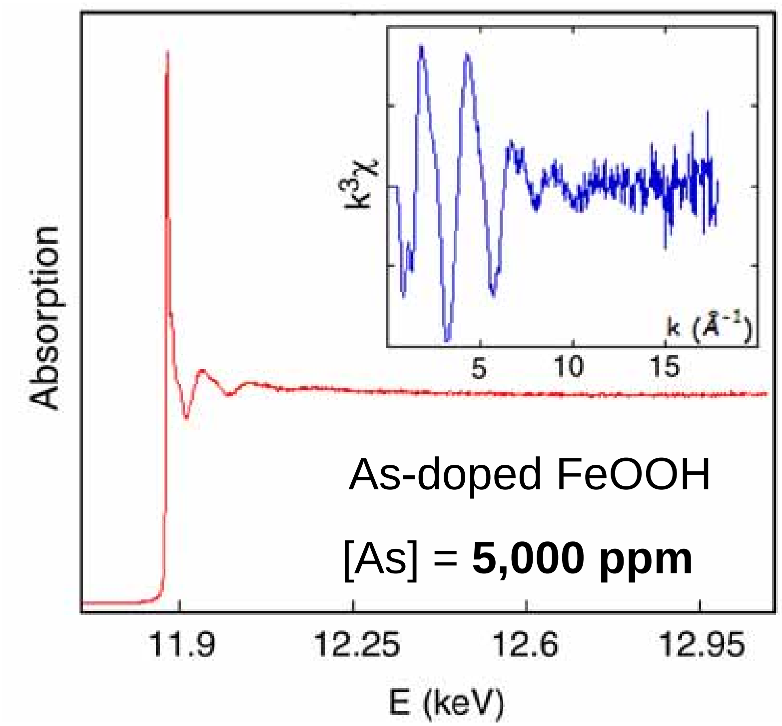




Manceau –SRI-2003

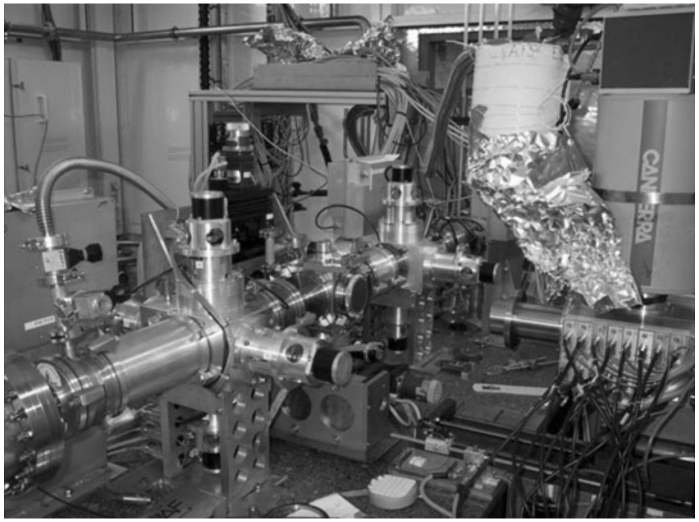
Solution to Radiation Damage

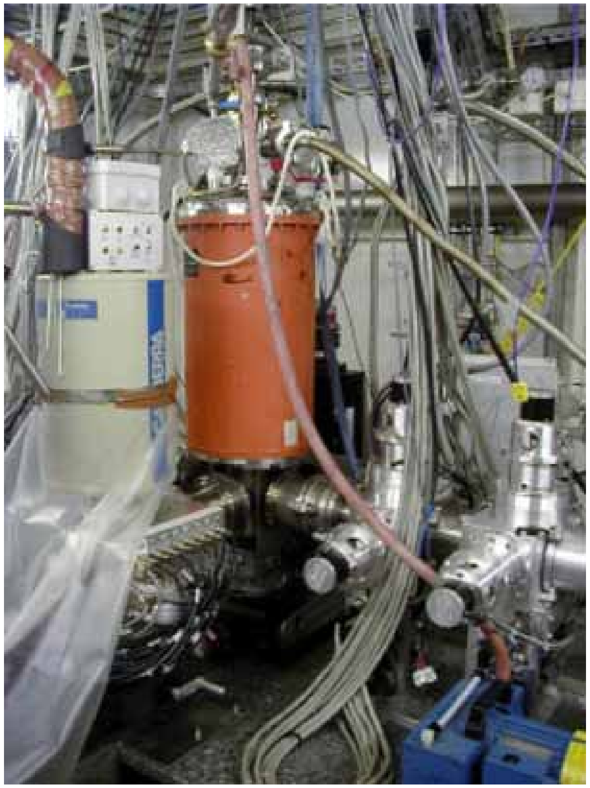
- Quick-EXAFS - cryocooling



Fluorescence detection mode; **0.1s/pt**.

High counting rate detector required



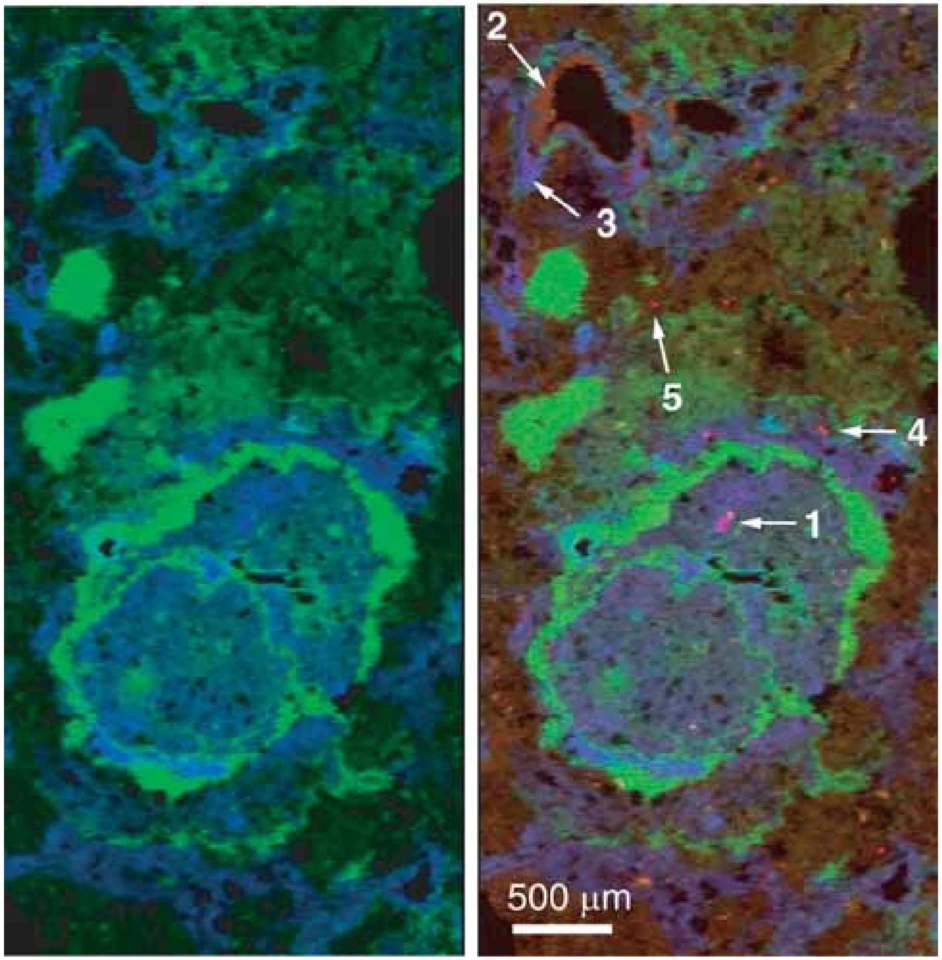


FAME-BM30B-ESRF

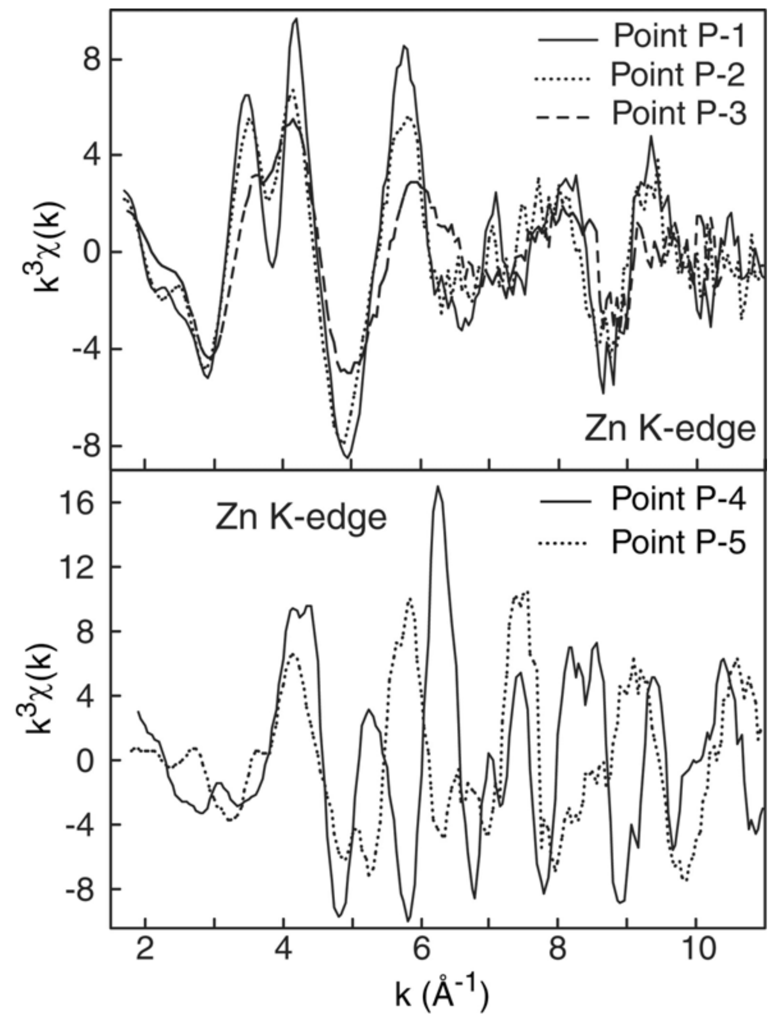
Technical difficulties

Overwhelming Amount of Fe

gFe bMn   rZn gFe bMn



Micro-EXAFS



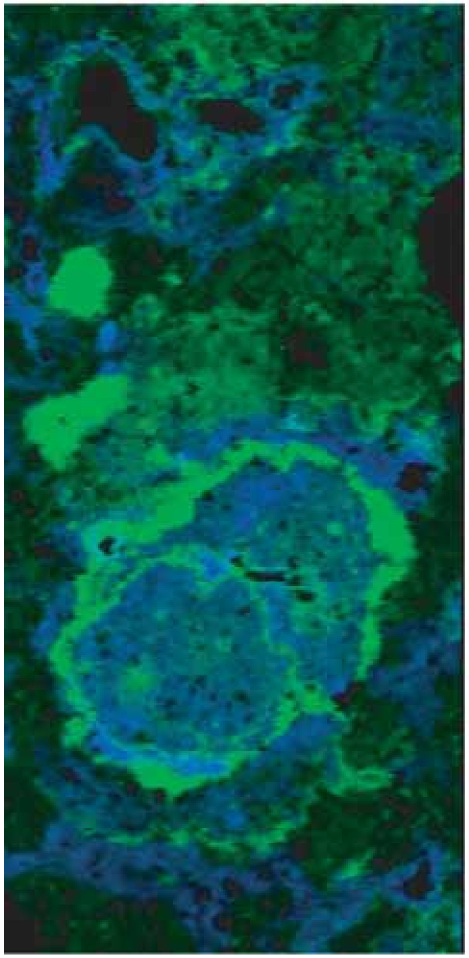
<u>Point</u> EXAFS spectra recorded at 'hot spots' have a <u>high</u> S/N

Manceau –SRI-2003

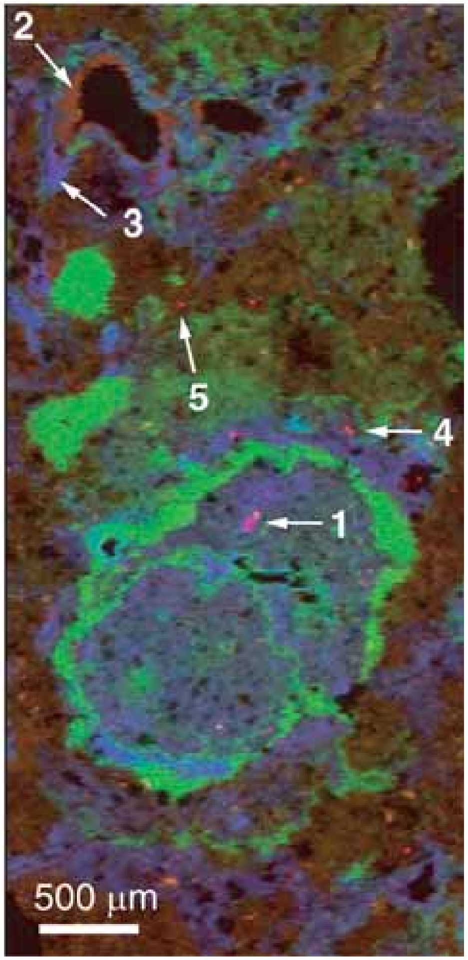
Technical difficulties

Overwhelming Amount of Fe

gFe bMn



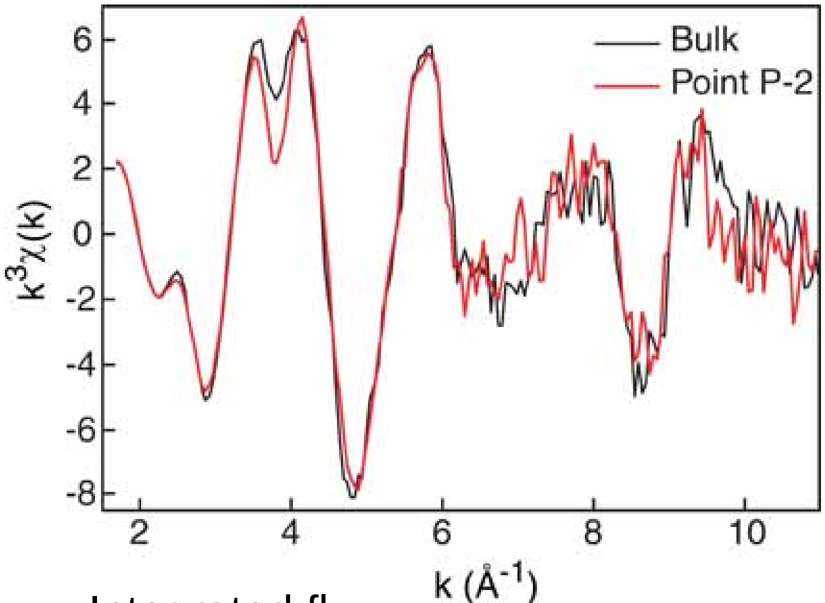
rZn gFe bMn



Bulk EXAFS

ESRF

Micro-EXAFS



<u>Integrated flux</u>

~ 10^{12} photons @ ESRF (FAME)

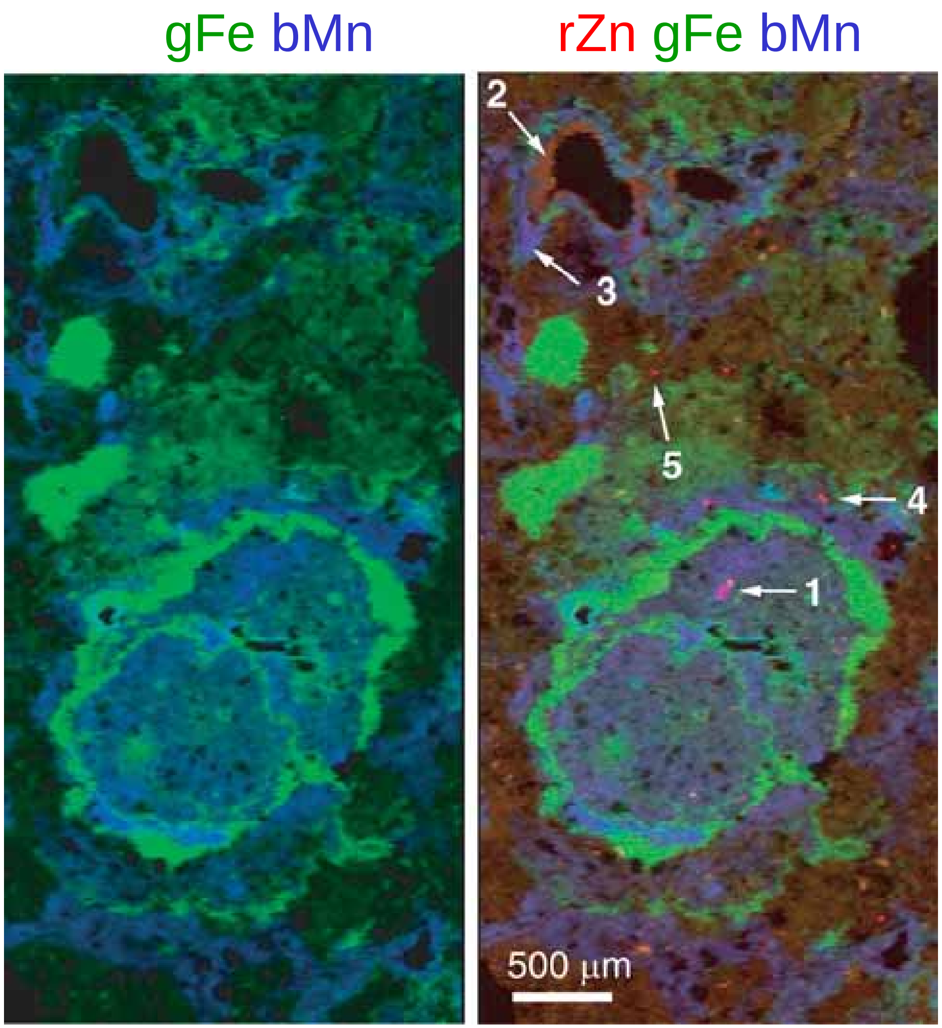
~ 10^{10} photons à ALS (10.3.2)

<u>Bulk</u> EXAFS spectrum has a relatively <u>low</u> S/N

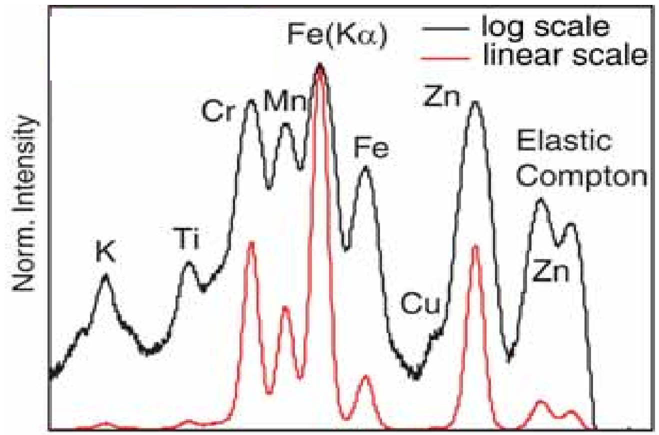
Why?

Technical difficulties

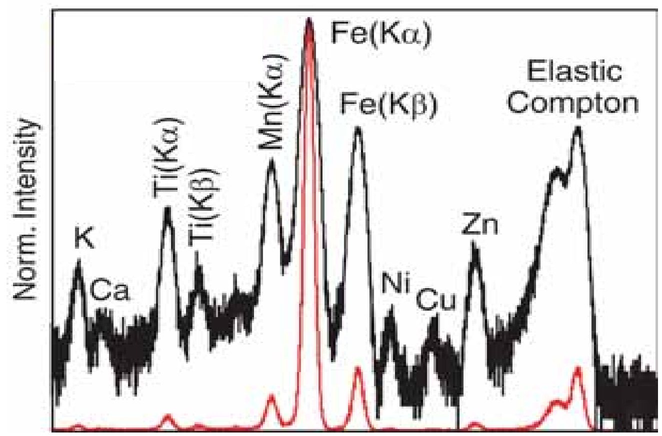
Overwhelming Amount of Fe



EDS @ Micro-EXAFS



EDS @ Bulk EXAFS



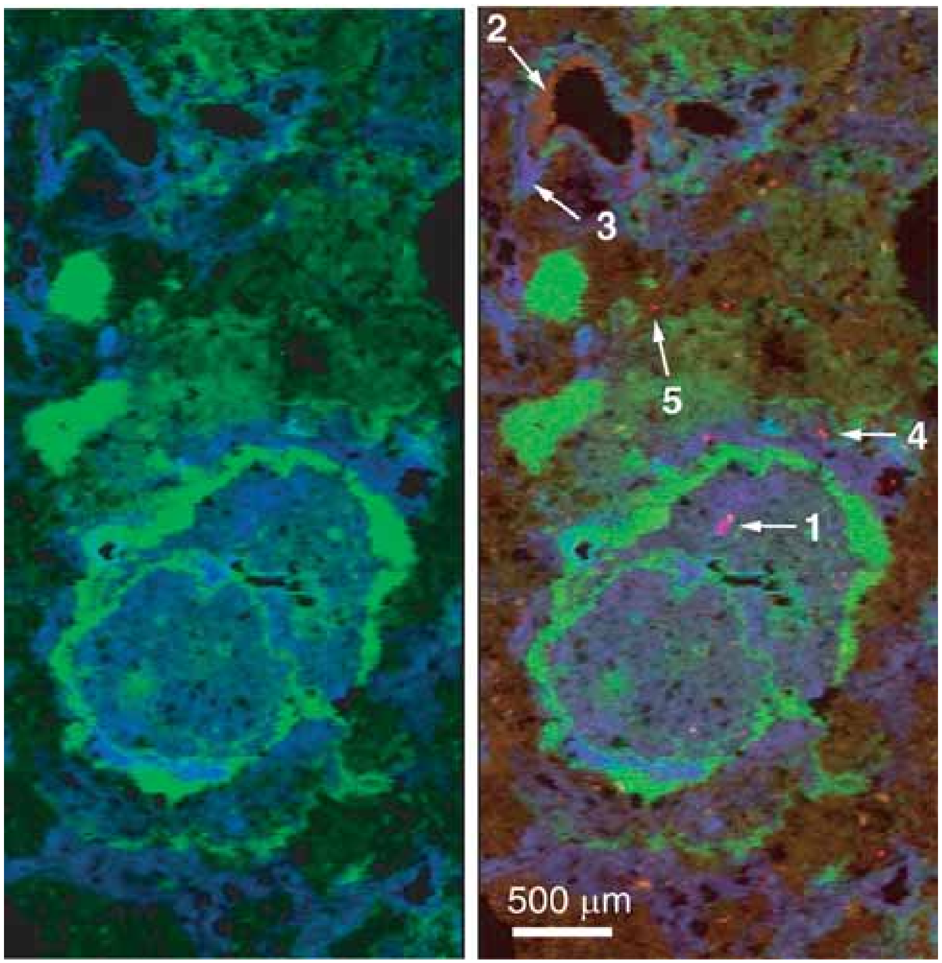
[Fe] = 10.2 %; [Zn] = 128 ppm

Background-to-signal ratio in the <u>bulk</u> higher than 700:1 !

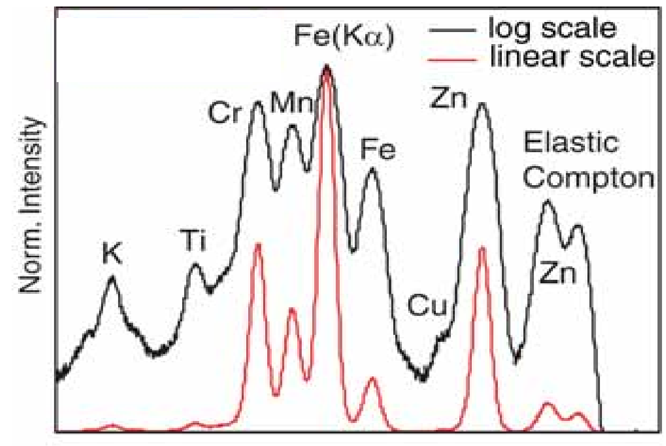
Technical difficulties

Overwhelming Amount of Fe

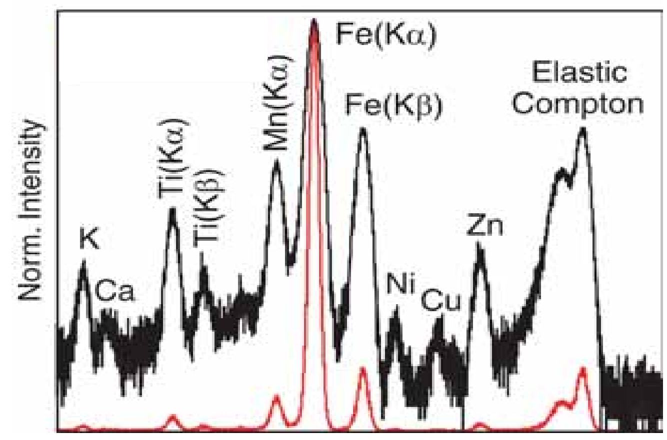
gFe bMn | rZn gFe bMn



EDS @ Micro-EXAFS



EDS @ Bulk EXAFS

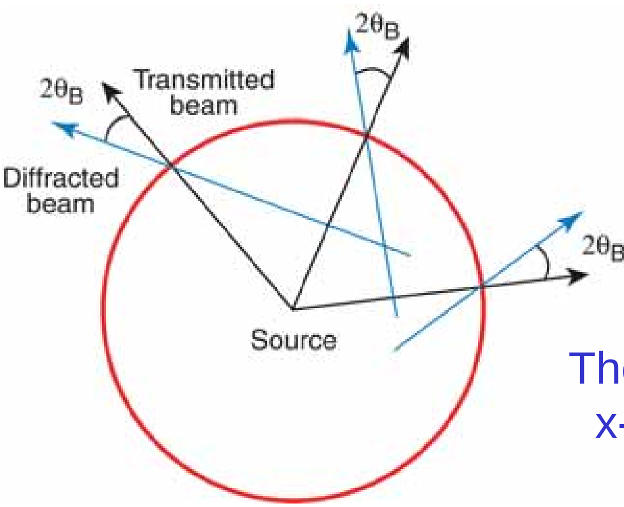


- In highly heterogeneous natural matrices the greatest part of the material is devoid of the element of interest, but still contains Fe => **NOISE**.
- Higher multiplicity of the structural environments of the metal at the centimeter to millimeter than the micrometer scale => **NOISE**.

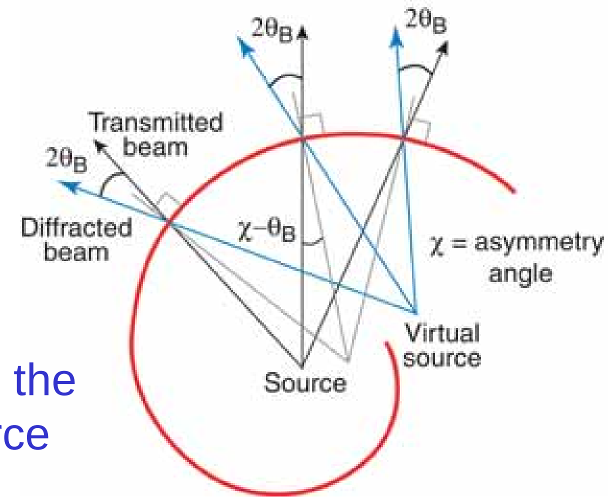
Manceau –SRI-2003

Solution: High throughput detector, such a Log bent Laue analyzer

Crystal bent to cylindrical shape



Crystal bent to log spiral shape



The log spiral diffracts all the x-rays from a point source

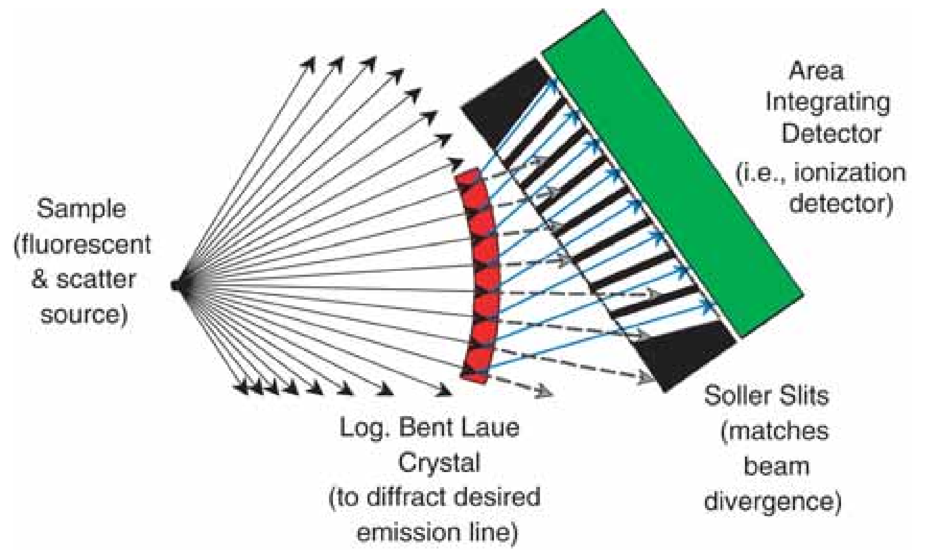
Characteristics

- High reflectivity (20 to 30%) due to the Laue geometry
- Solid angle: 9 to 13% steradian.
- Good resolution (20 to 200 eV)
- High counting rate; Low cost

Inconvenient

- The working range is typically +/- 10% from the design energy

Log bent Laue analyzer

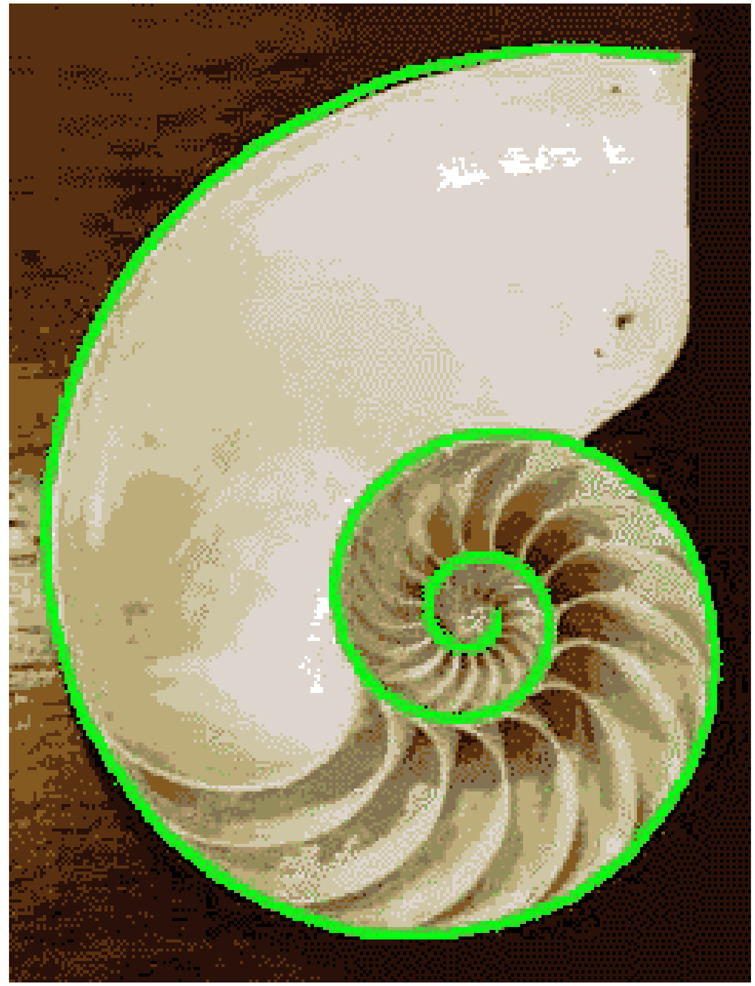


Manceau –SRI-2003

After G. Bunker, Biocat (APS)

This mathematical form is commonly found in nature

The chambered Nautilus



Nautilus shell: A perfect logarithm spiral !

This mathematical shape derives from a simple growth rule: Grow radially outward by an amount in proportion to the present size, turn through a specific angle, repeat.

4. Technical Difficulties, Present Instrumental Limitations, and Future Instrumental Challenges

- Limited number of x-ray microprobes combining SXRF – XRD – XAFS (EXAFS + XANES).

- Quantitative chemical analysis from XRF.

- Analysis of both light and heavy elements.

Quantitative chemical analysis by Integrated Tomographic Techniques (ITT)

ESRF

- Reconstruction by algebraic technique of the distribution in the grain of $\mu(E_0)$, $p_{Comp.}$ and p_{Rayl} from the absorption, Compton and Rayleigh signals.

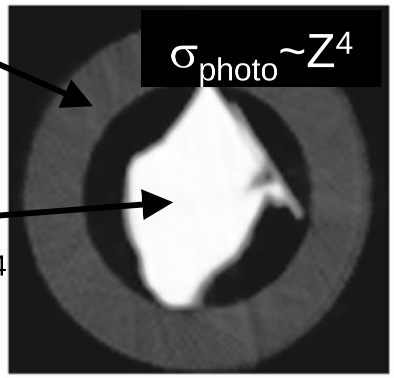
Distribution of $\mu(E0)$

Silica capillary

Olivine

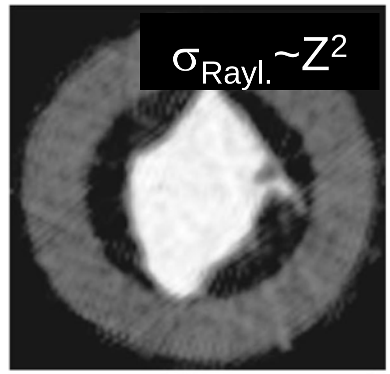
$(Mg,Mn,Fe)_2SiO_4$

$\Phi = 170\ \mu m$



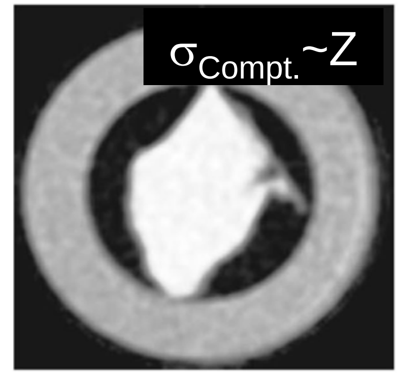
Transmission tomography

Distribution of $p_{Rayl.}$



Rayleigh tomography

Distribution of $p_{Compt.}$

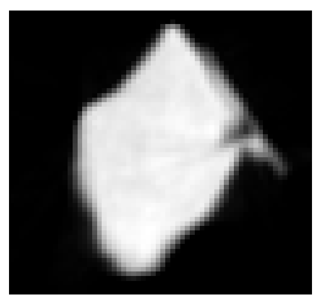


Compton tomography

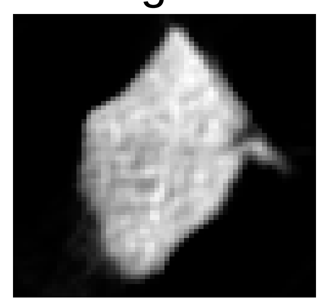
Quantitative spatial distribution of elements

- Fe density 1.45 g/cm^3
- Mn density 0.058 g/cm^3
- Total density 3.89 g/cm^3
- Fe weight fraction 37.2%
- Mn weight fraction 1.50%

Iron



Manganese



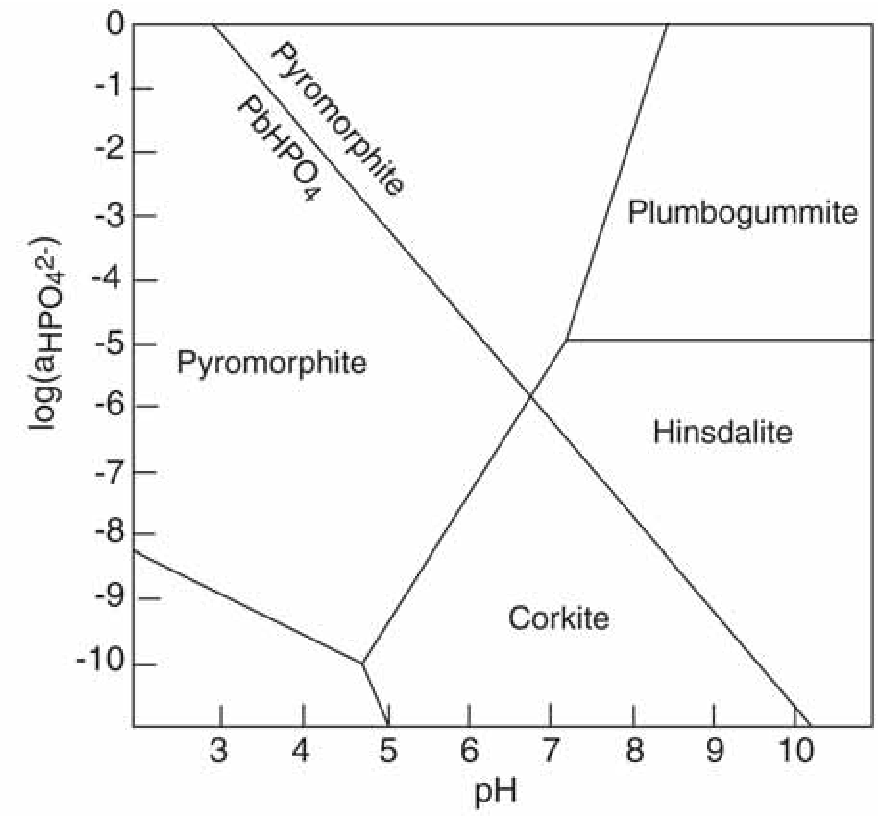
Golosio, Simionovici et al. (2003)

Present instrumental limitations

Analysis of Both Light and Heavy Elements

- Determining ponctual chemical compositions is a pre-requisite to the full identification of metal species and the calculation of structural formulae.

Stabilty diagram Pb phosphates in soils



After Lambert, Pierzynski, Erickson, Schnoor (1997)

Mineral	Solubility (log Ksp)
Anglesite - $PbSO_4$	-7.8
Cerrusite - $PbCO_3$	-12.8
Galena - **PbS**	-27.5
Fluoropyromorphite - $Pb_5(\mathbf{PO_4})_3F$	-76.8
Hydroxypyromorphite - $Pb_5(\mathbf{PO_4})_3OH$	-82.3
Chloropyromorphite - $Pb_5(\mathbf{PO_4})_3Cl$	-84.4
Hinsdalite - $PbAl_3(\mathbf{PO_4})(OH)_6SO_4$	-99.1
Plumbogummite - $PbAl_3(\mathbf{PO_4})_2(OH)_5H_2O$	-99.3
Corkite - $PbFe_3(\mathbf{PO_4})(OH)_6SO_4$	-112.6

One wants to analyze Pb, Fe, Al, P, S, Cl

4. Technical Difficulties, Present Instrumental Limitations, and Next Instrumental Challenge

What next?

To observe, analyze chemically, and probe structurally the long and short range order of environmental samples in their natural state at the **few tenths of nanometer resolution**.

- To observe => X-ray imaging using either scanning or full-field microscopes
- To analyze chemically => XRF, fluo-tomography
- To probe the long range structural order => XRD
- To probe the short range structural order => EXAFS + (XANES)

For which science?

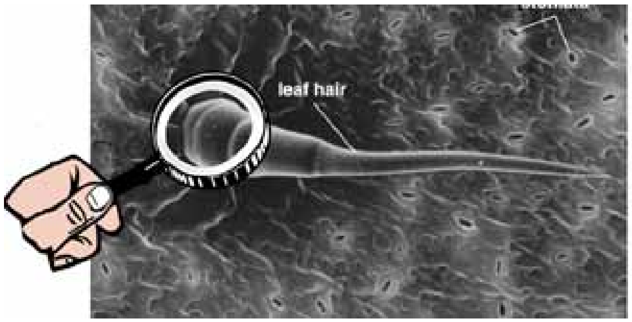
To determine the form of elements within cells

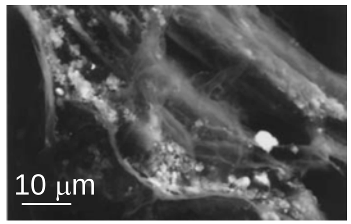
Structural form of elements (metals) @ 1-5 µm resolution

Chemical form of elements @ 0.1 µm resolution

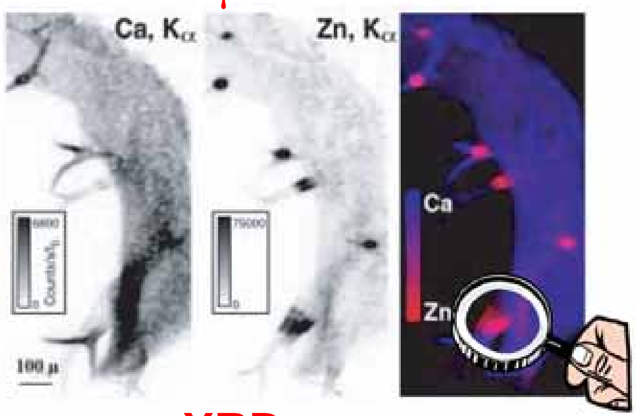
Today with x-rays…..

SEM



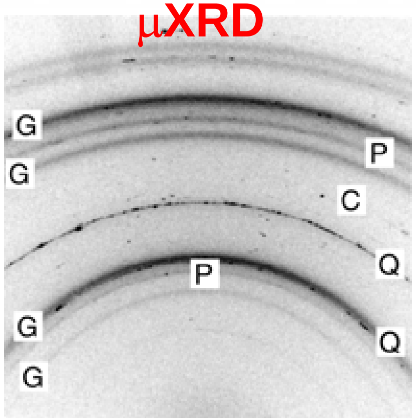


µXRF

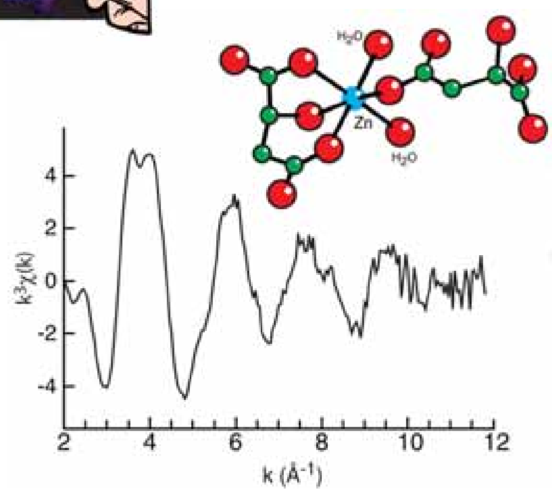


Form of Zn in plant leaf

µXRD



µEXAFS

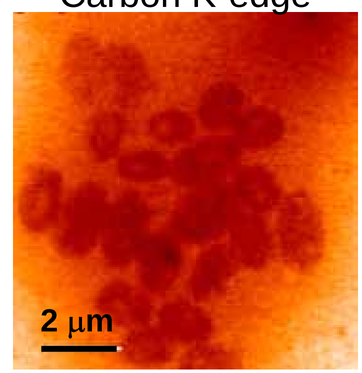


Bio-mineralisation of Mn oxides

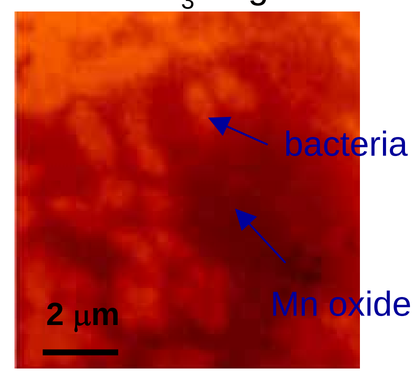
SEM

STXM

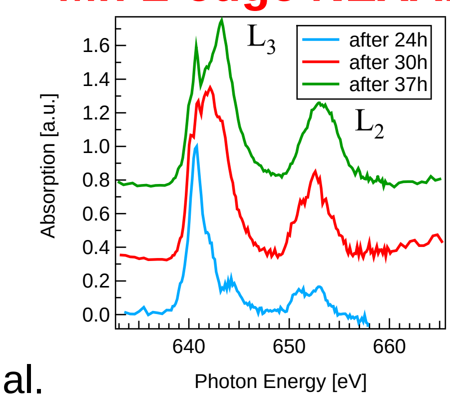
Carbon K-edge



Mn L_3-edge



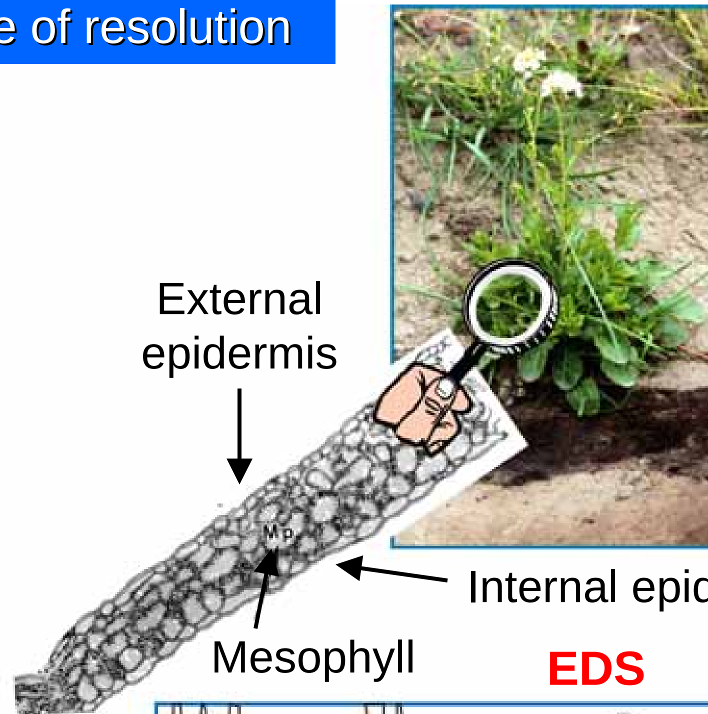
Mn L-edge NEXAFS



Toner et al.

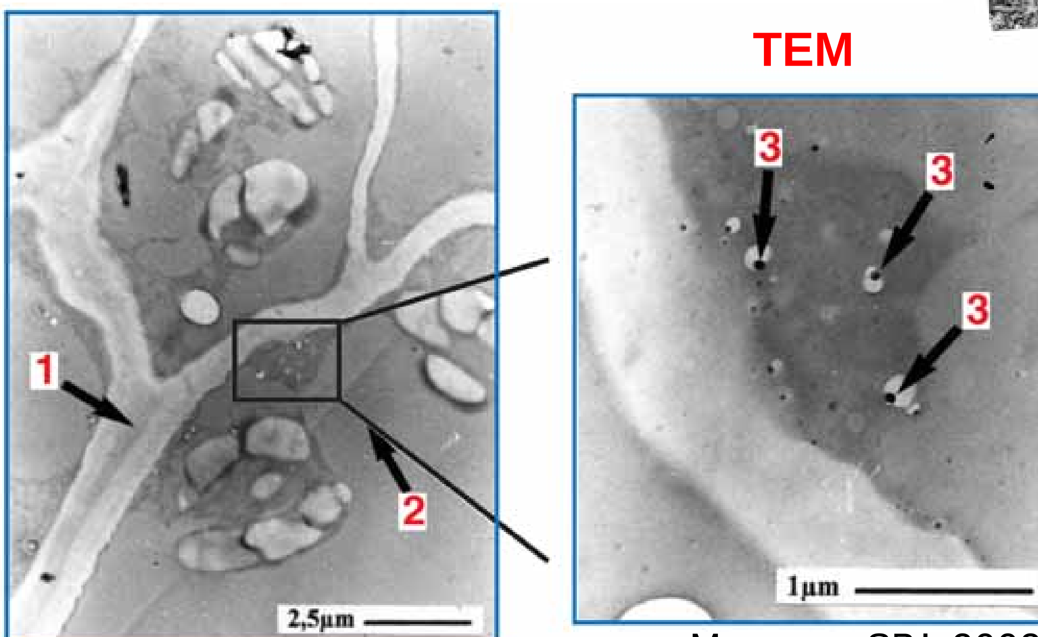
Today with electrons…..

Structural form of elements @ nanometer-scale of resolution



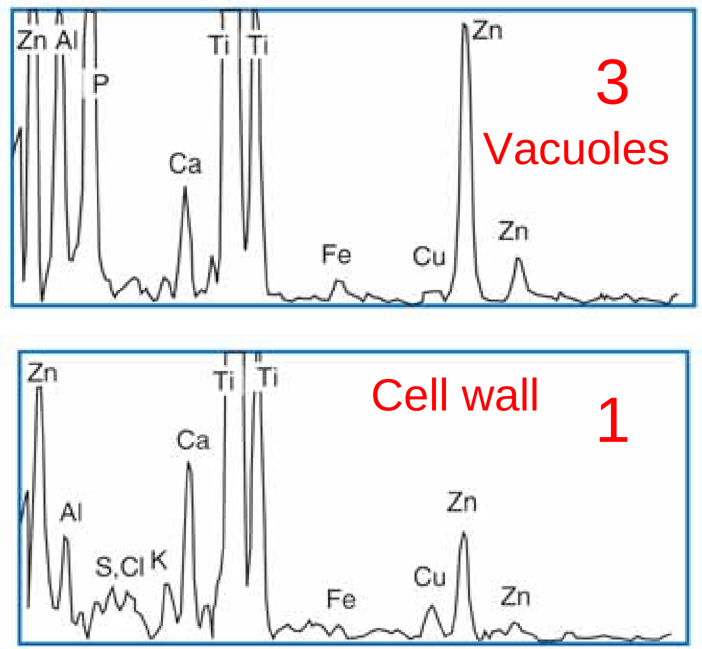
Cells from the mesophyll of *Arabidopsis halleri* leaf

TEM



Manceau –SRI-2003

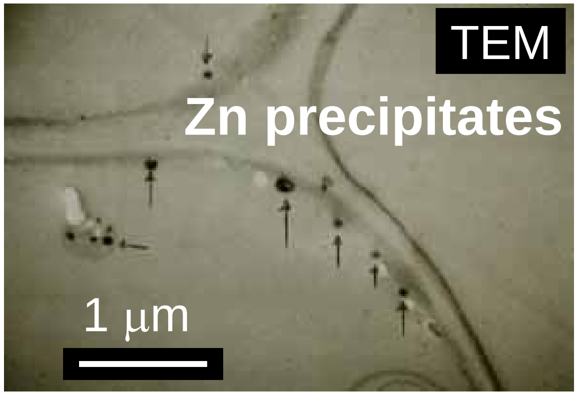
EDS

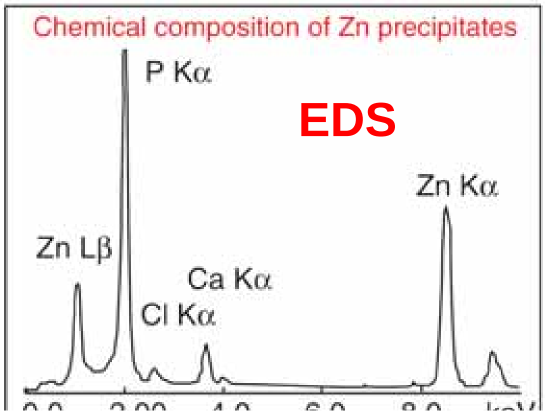


Today with electrons…..

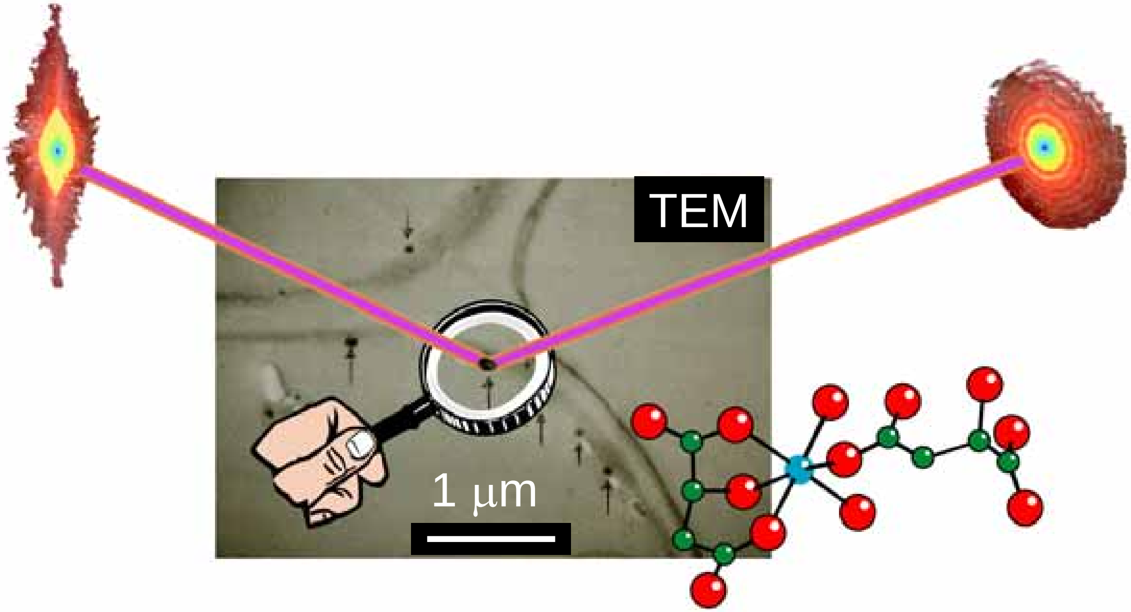
Structural form of elements @ nanometer-scale of resolution

Cells from the mesophyll of *Phaseolus vulgaris* leaf





Tomorrow with x-rays…..



To perform XRF, XRD and EXAFS @ nanometer-scale of resolution

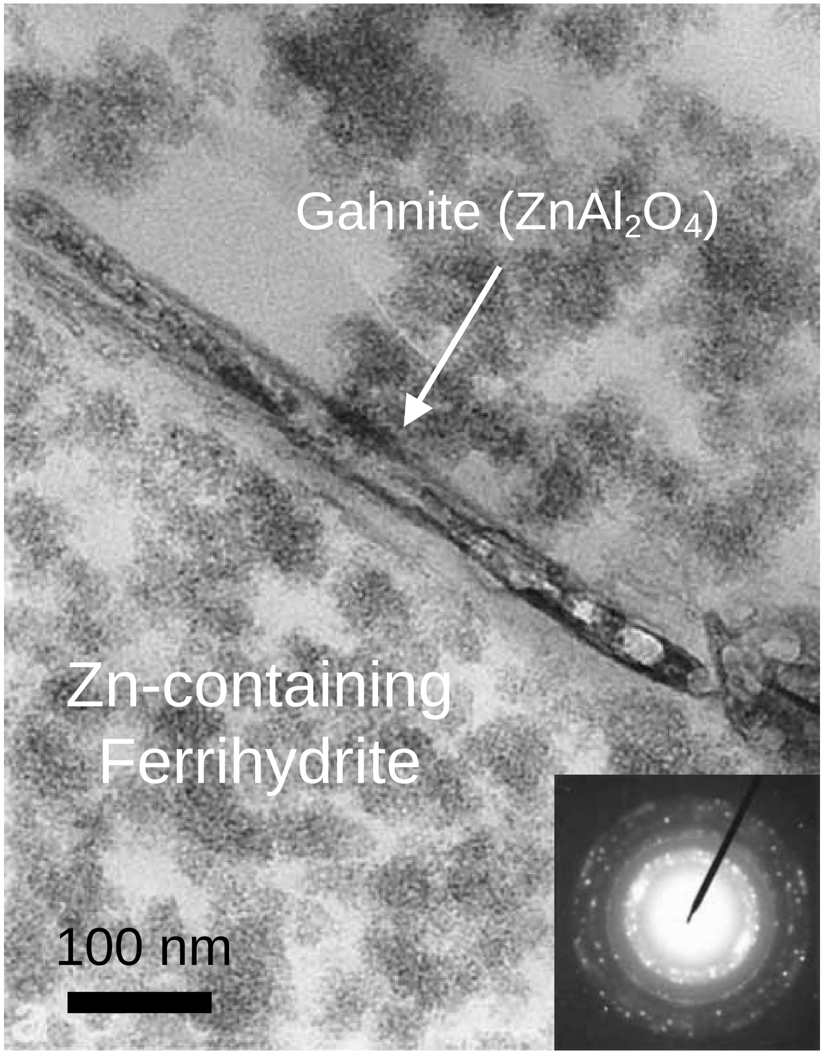
Advantage of X-rays over Electrons

- Since environmental materials are heterogeneous down to the nanometer scale, and the information sought is <u>structural</u> in essence, electrons rather than X-rays are, *a priori*, a better probe.

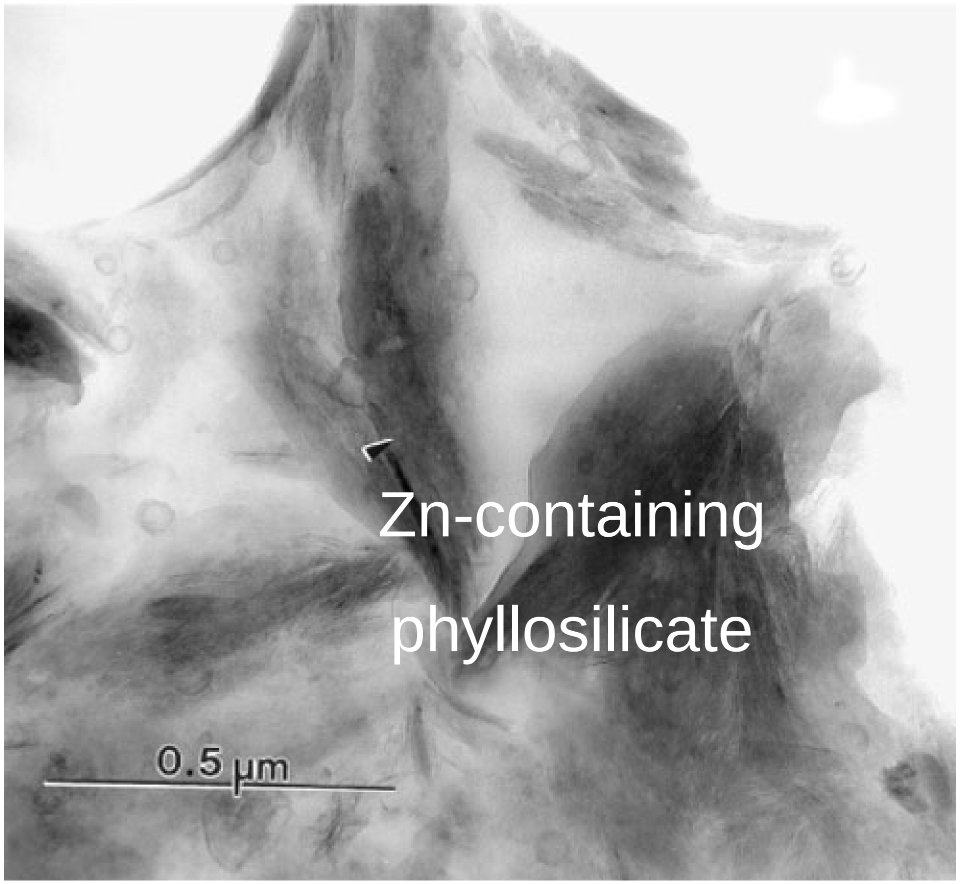
However, x-rays have several advantages over electrons:

- X-rays techniques (XRF, spectroscopy) have higher elemental detection limits;
- Many experiments do not require a UHV environment;
- Possibility of varying the lateral size of the beam from about $10\ mm^2$ to less than $0.1\ \mu m^2$;
- X-rays have a much higher penetration depth than electrons;
- X-ray spectroscopy (mostly EXAFS) allows one to determine the local structure of sorbed and incorporated metal species with unrivalled precision.

Nanoparticles can be imaged by TEM with unrivalled lateral resolution



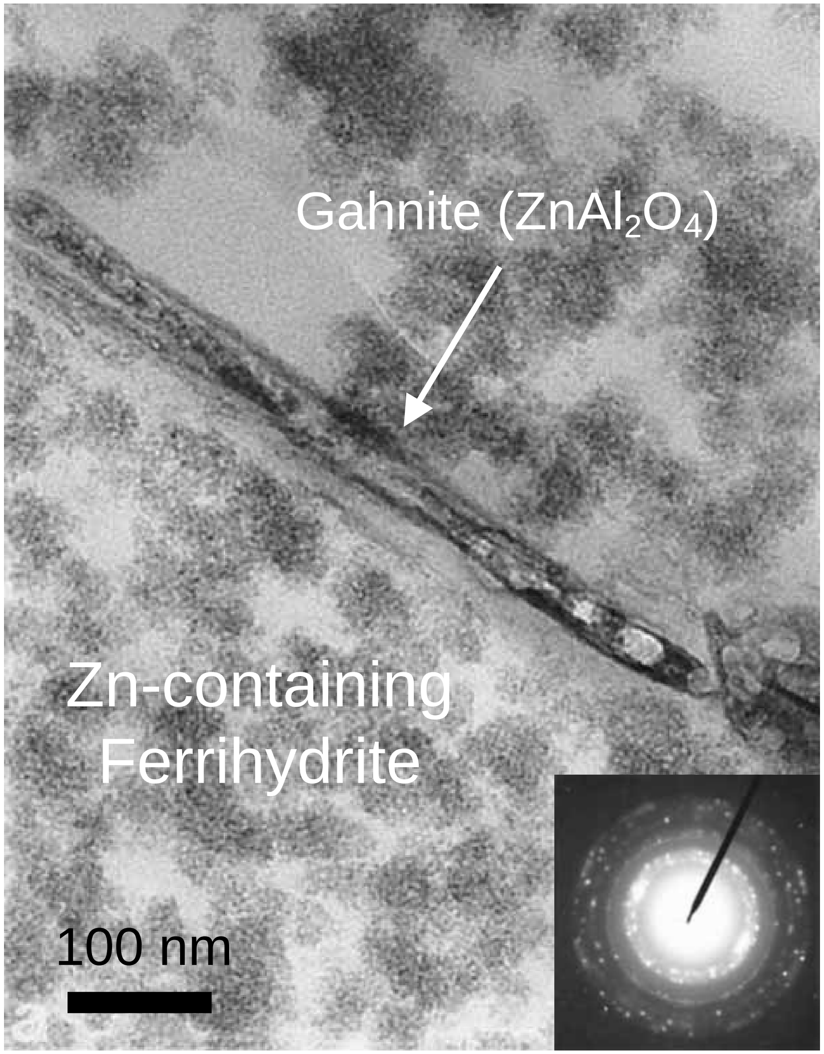
From Hochella et al. (1999)

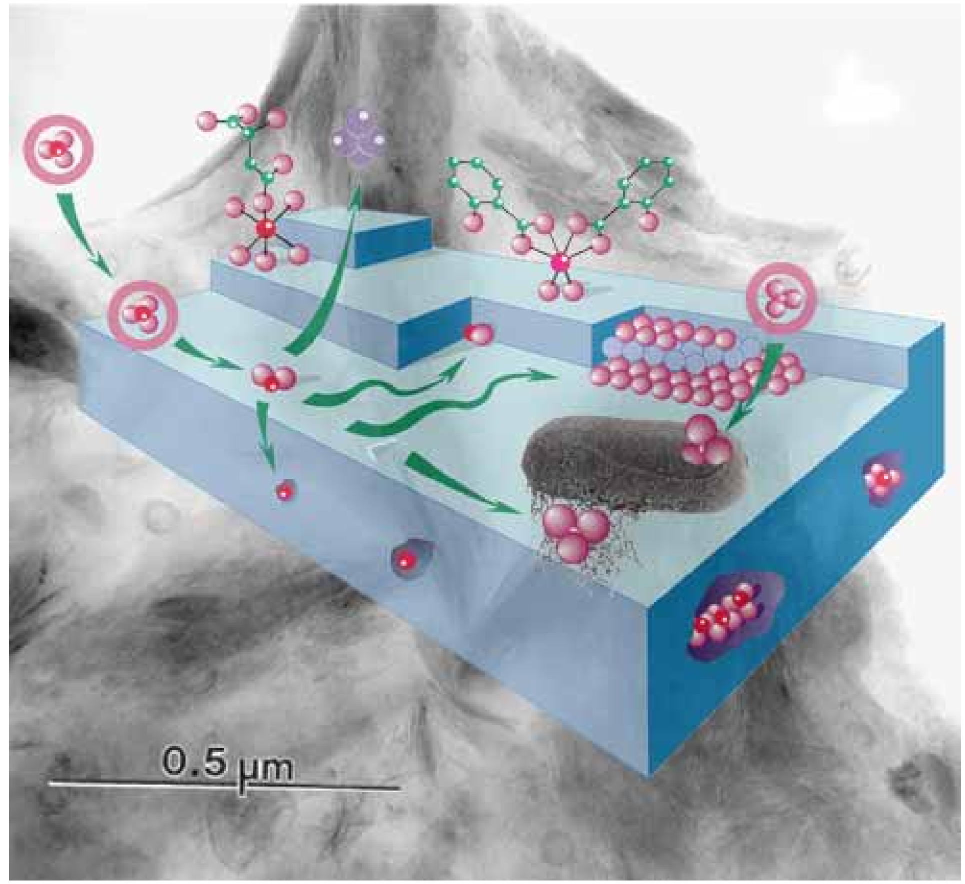


From Buatier et al. (2001)

Electron diffraction is well suited to identify minute crystallites

Nanoparticles can be imaged by TEM with unrivalled lateral resolution





But TEM does not provide structural information on the form of metal contaminants at the molecular scale

Concluding Remarks

- X-ray **fluorescence**, **diffraction**, and **absorption** TOGETHER can be used to identify trace metal species in natural and contaminated earth materials. For numerous questions relater to the speciation of metal(loid)s contaminants in natural matrices, the synergetic use of these three techniques offers unique access to the problem.

> Towards the full determination of heavy metals speciation in environmental systems?

- Though *Nature* is heterogeneous at all scales, the **micrometer scale** is well adapted to study **nanometer-sized** environmental particles because these particles often aggregate.

- **Nanometer resolution** is needed to explore the cell machinery, and highly warranted to study individual environmental nanoparticles.

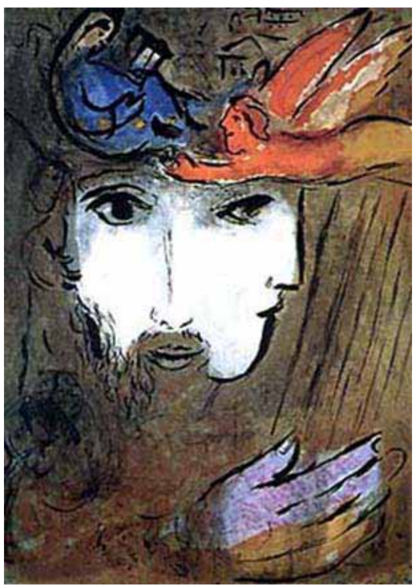
- **Lower resolution** is required to assess and quantify the **representativity** of observations made at high resolution.

- Though ***heterogeneity***, ***multiplicity*** and ***variability*** are an endless source of complexity… they are also the inspirational source of eternal beauty.

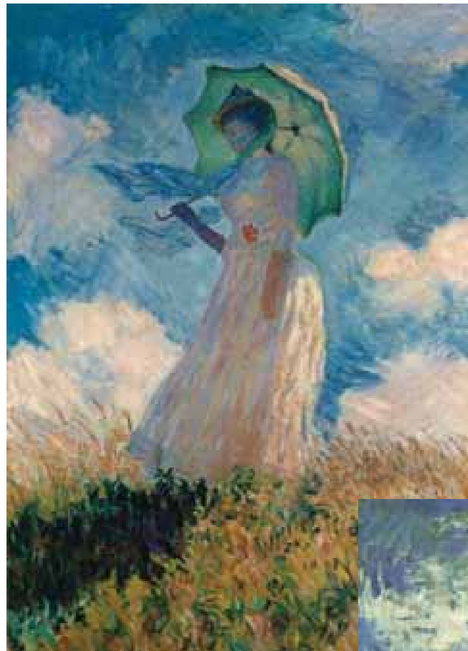
Heterogeneity

Kandinsky

Multiplicity



Chagall



Monet

Variability

Monet

Monet

Acknowledgements

Synchrotron facilities:

X-ray microprobe studies

Bulk EXAFS studies on highly-diluted samples

Collaborators…..

Funding agencies: CNRS, DOE

References

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