Introduction to SR for Environmental Sciences

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Take home message:

XRF + XAS + E-CT + XRD + …

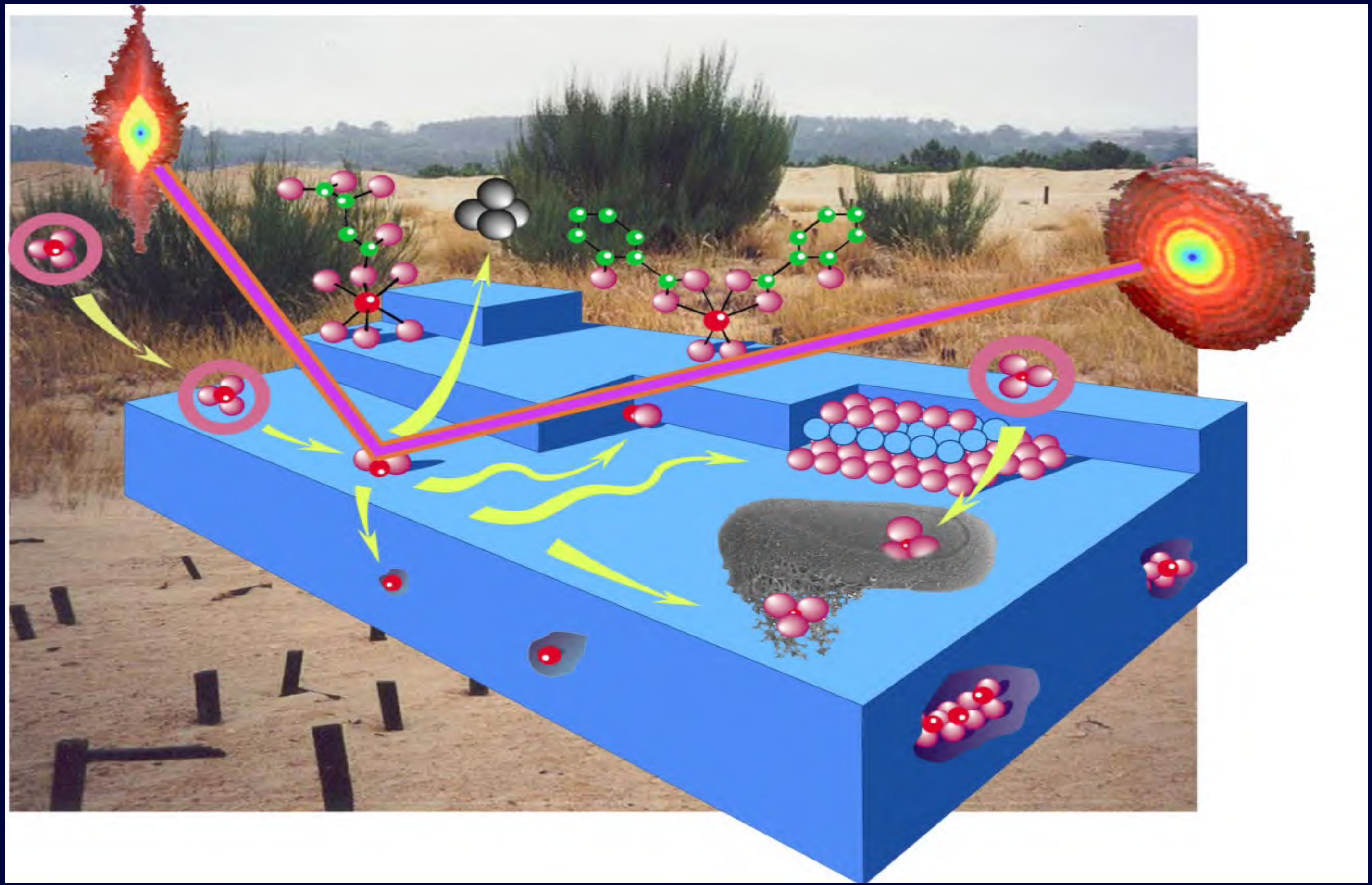
+

IMAGING

✺ Paradigm:

Speciation ↔ Solubility ↔ Bio-availability ↔ TOXICITY

Toxicity of TE is linked to their bio-availability, itself linked to the chemical form at atomic scales ➔ speciation



Bio-geochemistry goals:

- Disentangle concentration & speciation in the evaluation of eco-toxicity of trace elements
- Identify mobile/imobile forms and detoxification forms for the biosphere

WHY ?

… to evaluate/attenuate the chemical risk, to « heal » the environment

Difficulties :

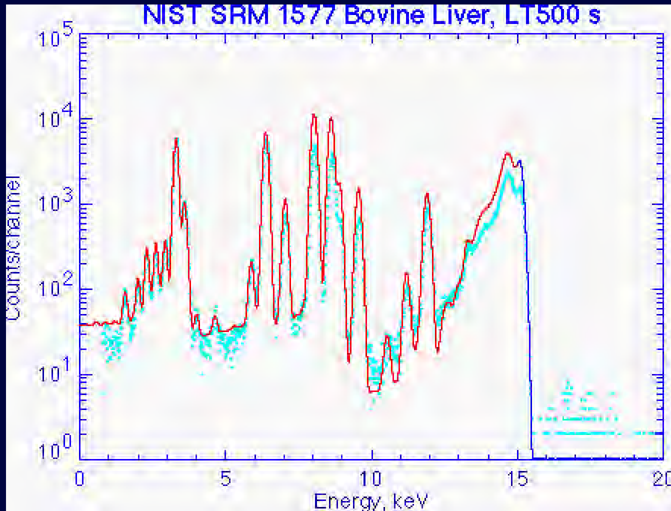
- scientific challenge because of the low abundance of most toxic elements (e.g. As, Hg, Cd), of the problems of the *in-situ* characterization of their chemistry and of the high heterogeneity of natural systems

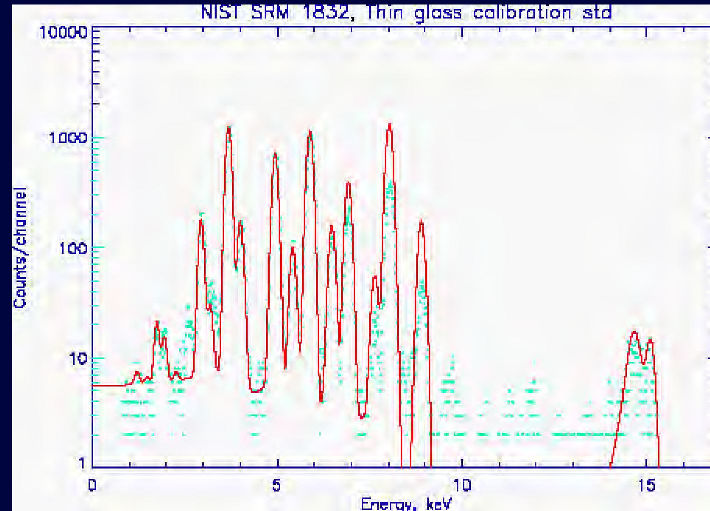
Techniques :

- X-Ray fluorescence (XRF) => chemical correlations
- X-Ray diffraction (XRD) => identification of host phases
- X-Ray absorption (XAS) => chemical forms at atomic scales
- X-ray tomography (XCT) => morphology & anatomy

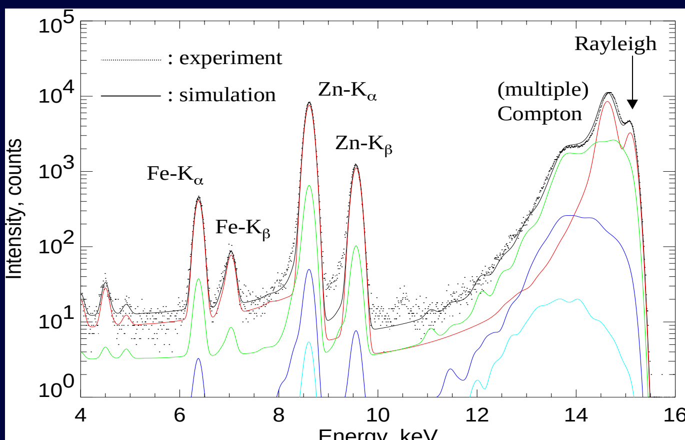
µ Fluorescence : M-C Simulation / Experiment

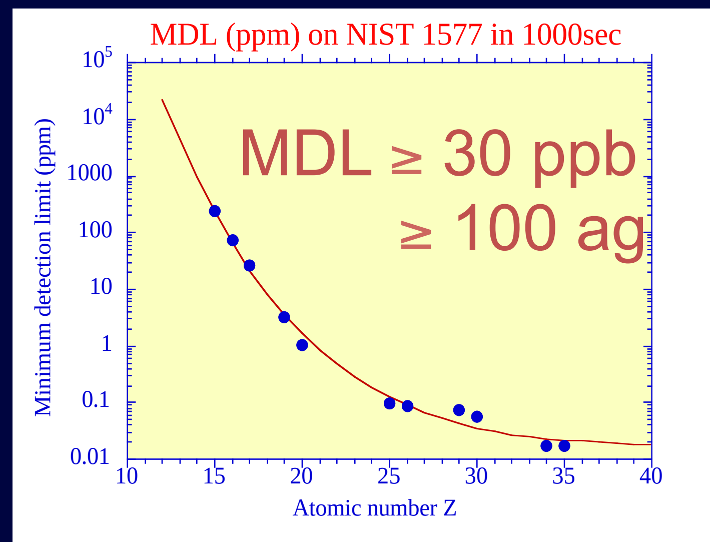
collab. : L. Vincze, T. Schoonjans, Mitac, Univ. of Antwerp





Currently:
1E13 ph/s
47 nm,
MDL=**30 zg**





Polypropylene 2 µm

MDL, E=15 keV, 1 x 2 µm^2

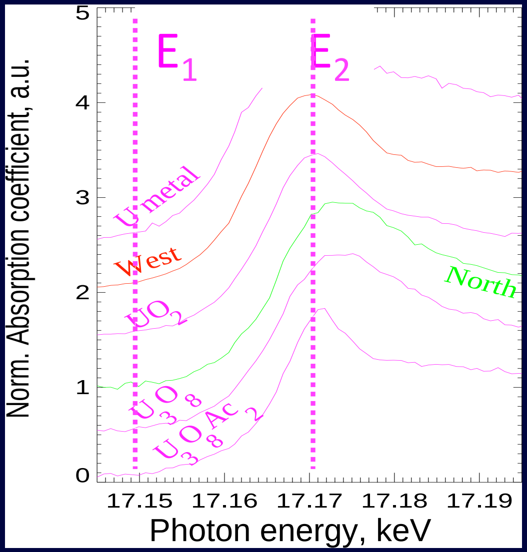
µ - speciation: post-Chernobyl aerosols XANES on Uranium L_{III}

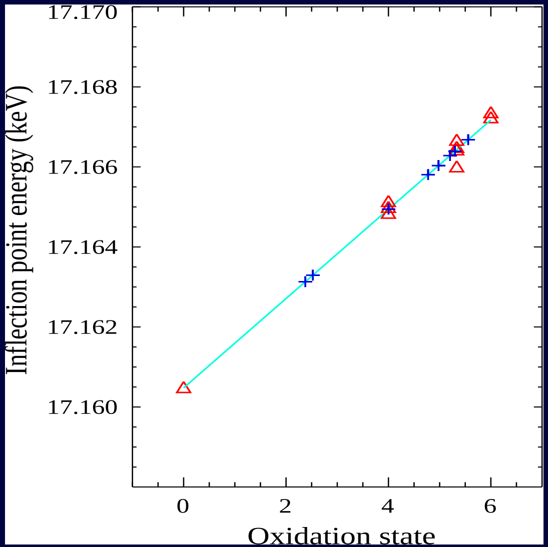
Univ. of Ås, Norway: B. Salbu, T. Krekling, O.C. Lind

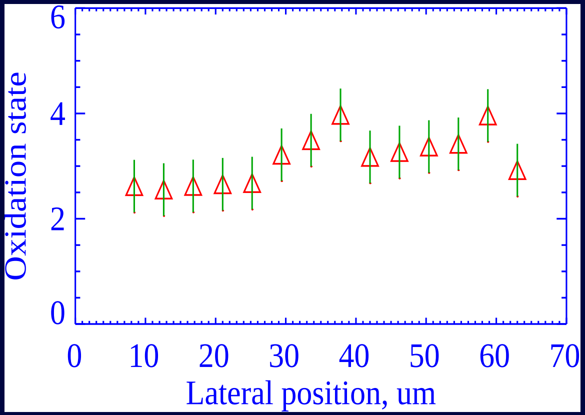
Univ. of Antwerp, Belgium, K. Janssens

- calibration: U metal, UO_2 and U_3O_8 ($0^+ - 6^+$)
- FWHM ≥ 0.15 eV, δE ≈ 0.8 eV/q
- **2 x 5 µm**, flux 10^9 ph/s., **2 - 5** sec./point

Salbu *et al*,
Nucl. Instr.& Meth. A **467-468**, 1249-1252, 2001





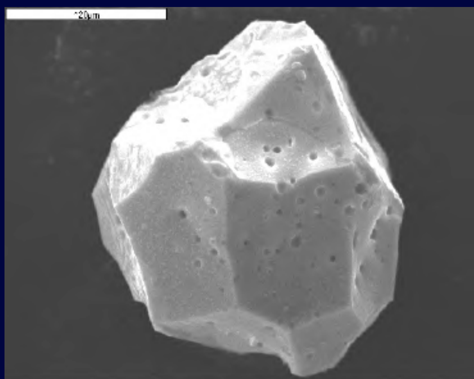


Xanes line scan across a particle

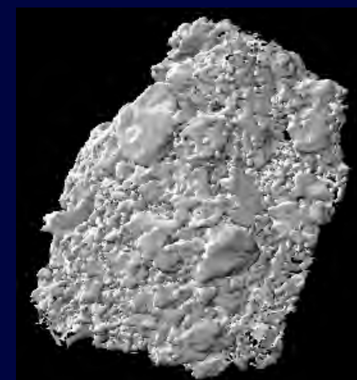
Spectroscopy = starting point of combined analyses:

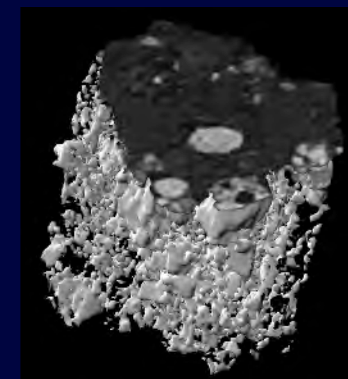
- Xanes calibration spectra
- multi-elemental analysis

SEM Image

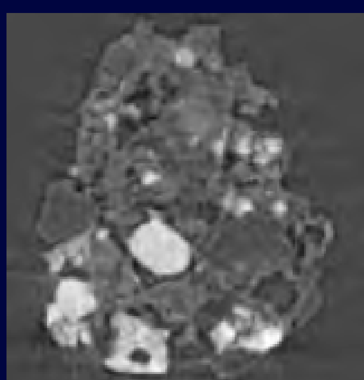


μ-tomo, 1 μm res., E = 20 keV

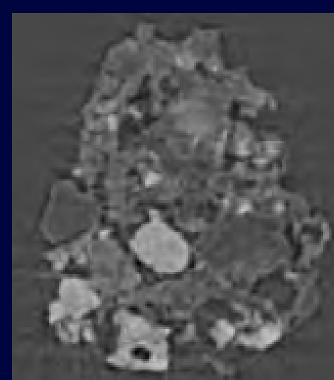




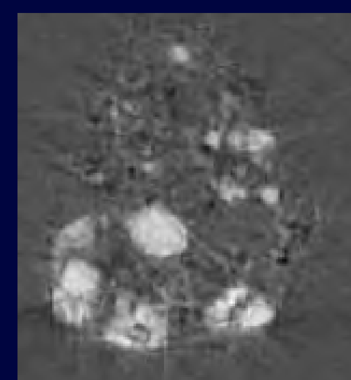
Xanes-Tomography = XANET / Spectro-tomography



E ≈ 17.2 keV



E ≈ 17.1 keV

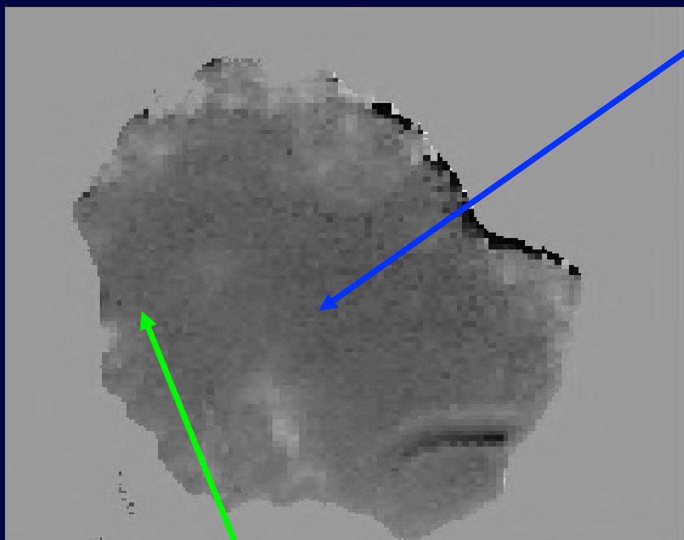


Difference

Dual energy tomography: (U. Bonse, 1986)

Particle weathering rate vs. U oxidation state

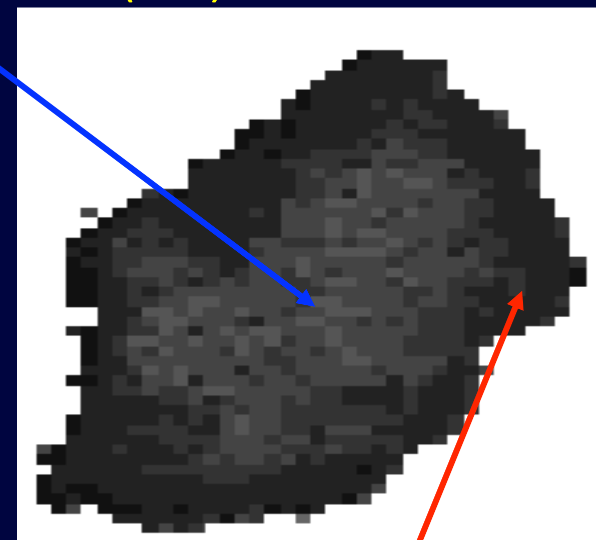
West: initial release (explosion)



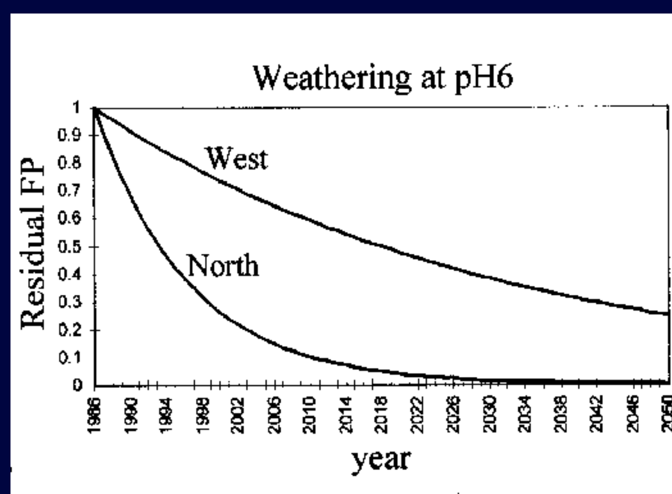
Oxidation state: +2.5 $\pm$ 0.5

Oxidation state: +4 $\pm$ 0.5

North: subsequent release (fire)



Oxidation state: +5 $\pm$ 0.5

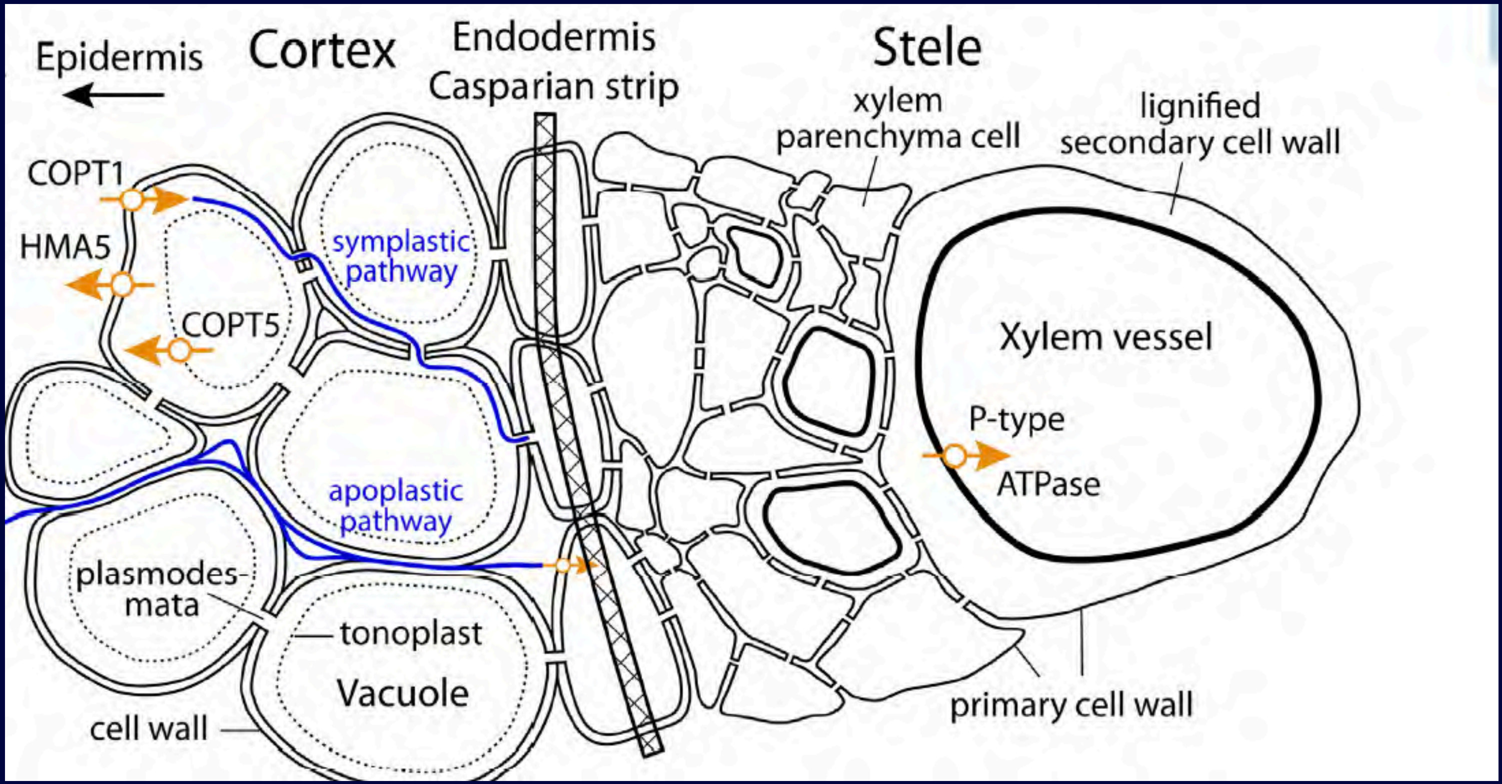


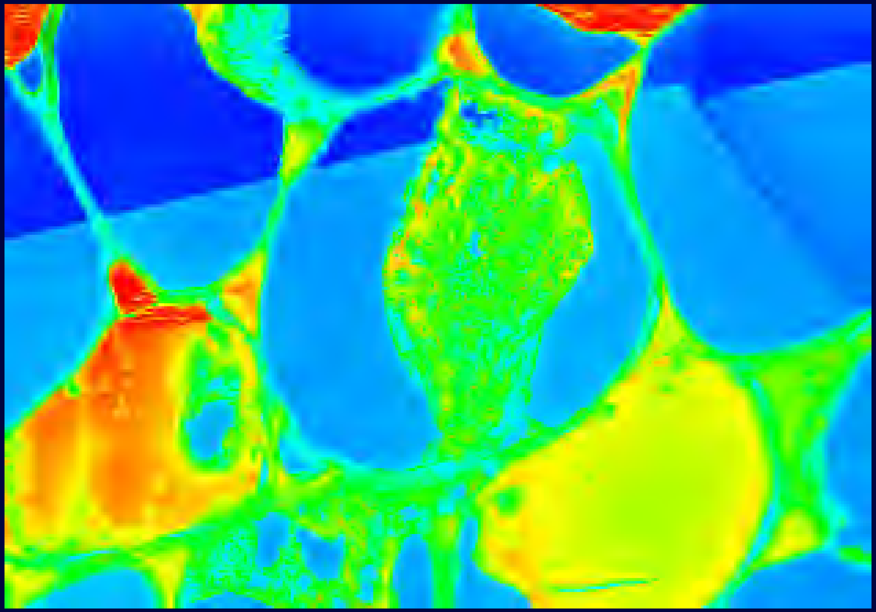
Cu storage in roots and export from roots to shoots

(A. Manceau, ISTerre, CNRS&UJF)

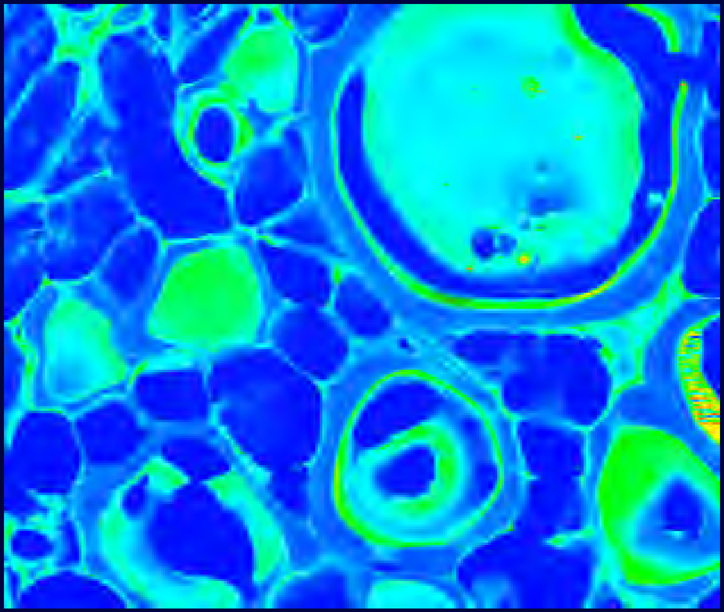
Copper is essential for:

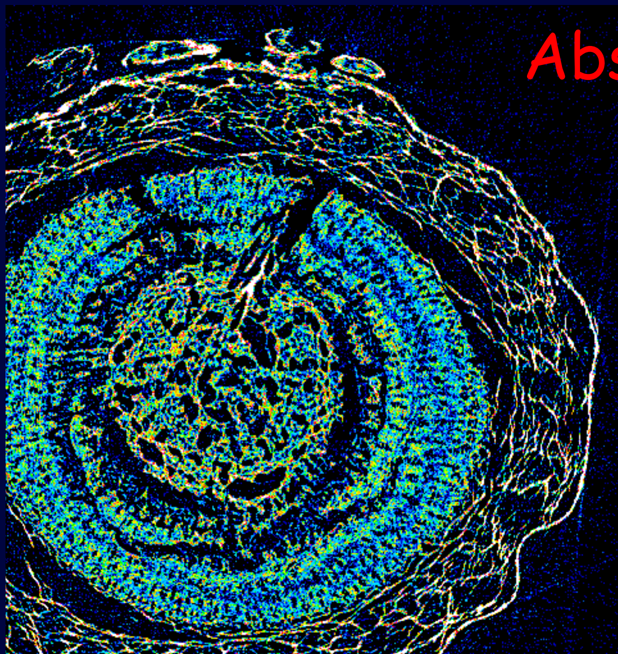
- photosynthesis
- mitochondrial respiration
- lignin synthesis
- root growth
- ethylene sensing
- reactive oxygen metabolism


Epidermis
Cortex
Endodermis
Casparian strip
Stele
xylem
parenchyma cell
lignified
secondary cell wall
COPT1
HMA5
COPT5
symplastic
pathway
apoplastic
pathway
Xylem vessel
P-type
ATPase
plasmodes-
mata
tonoplast
Vacuole
cell wall
primary cell wall



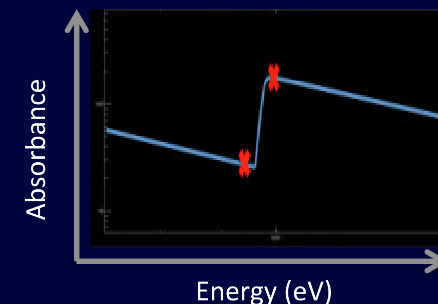
Res. ≈ 70 nm





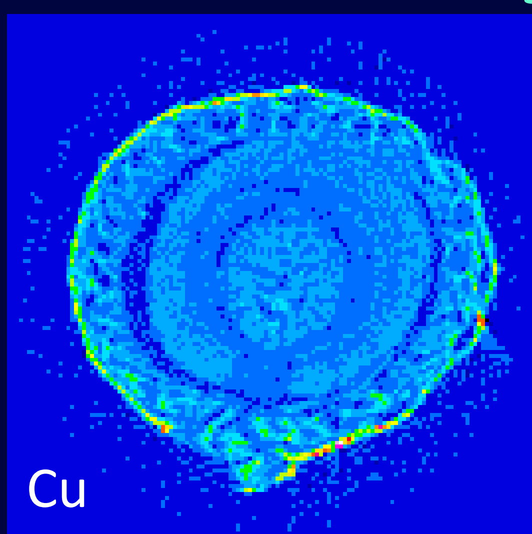
Absorption tomography (from 8.3.2)

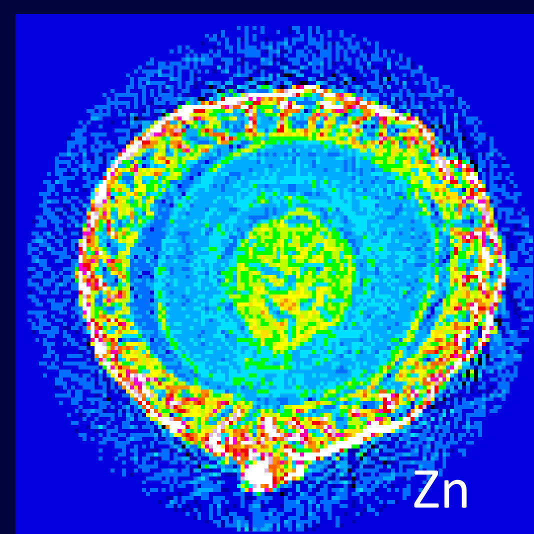
Cu, Zn K edges

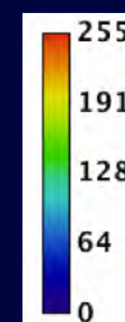


Absorption contrast (Zn)
(from ALS-8.3.2)

Fluorescence tomography (from ALS-10.3.2)

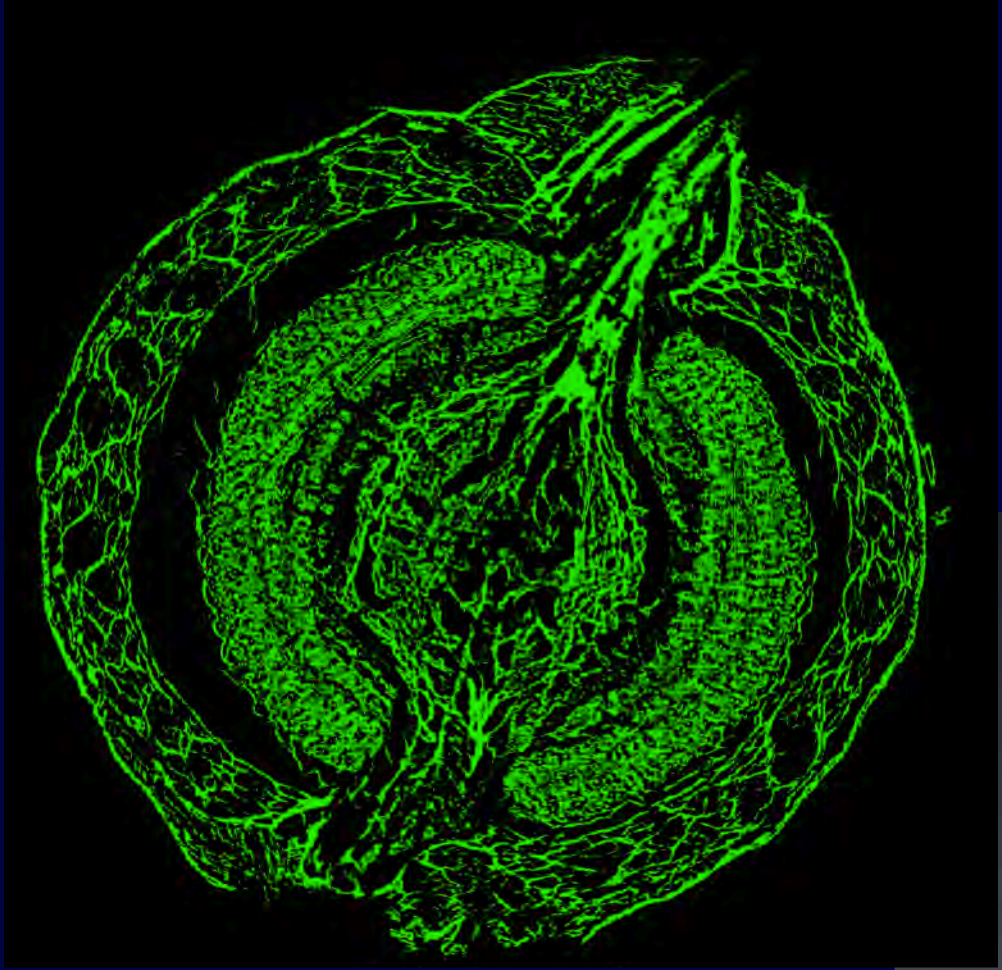
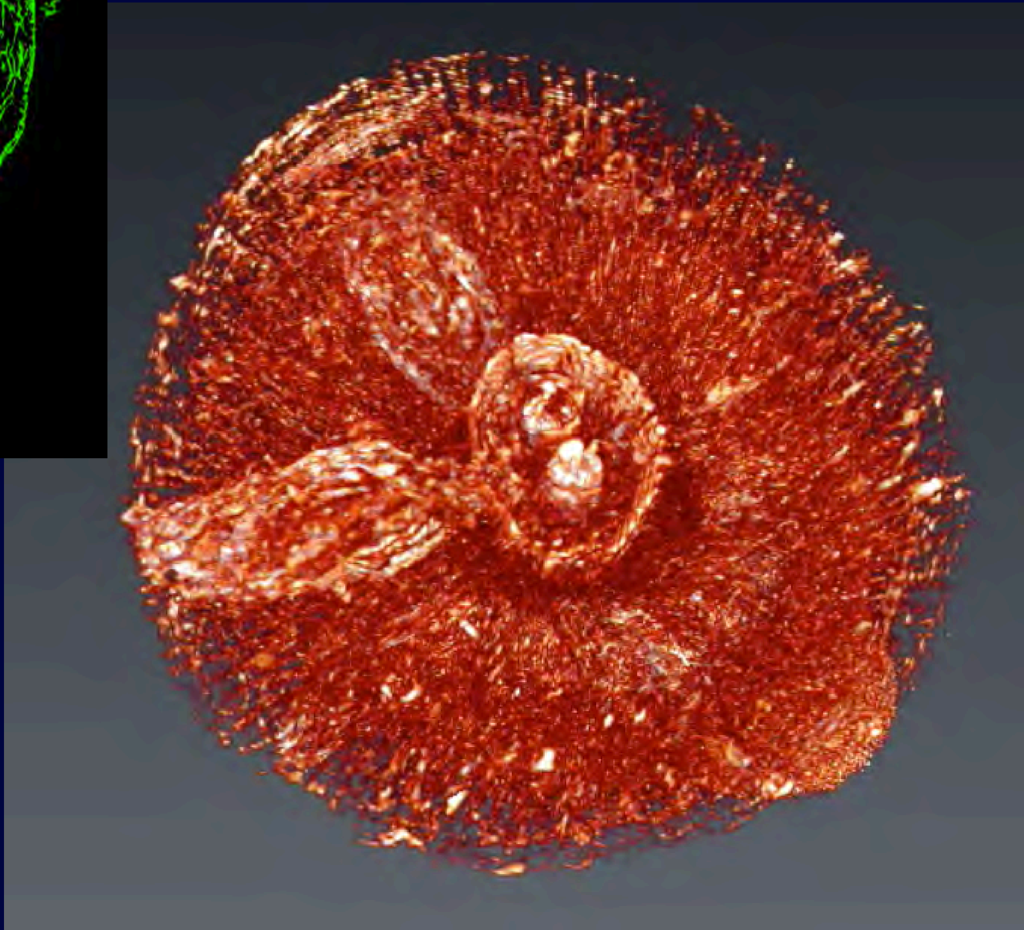






Res. 5 µm

Distribution of Cu and Zn by AT/FT

3D XANES tomography

XANES
absorption spectroscopy
oxidation state

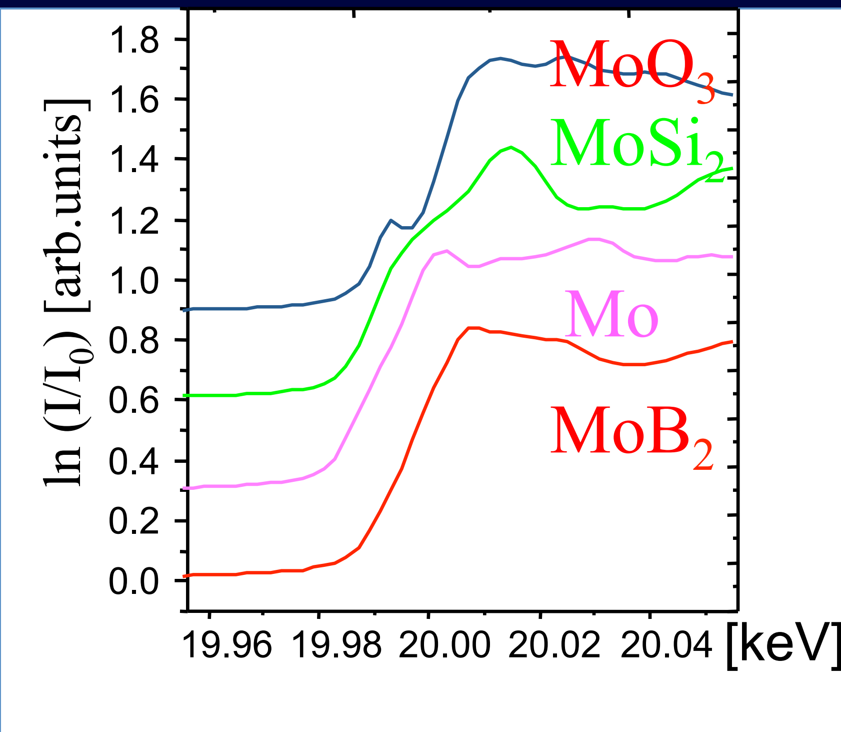
X-ray tomography
absorption radiography
morphology

Tomography with chemical speciation

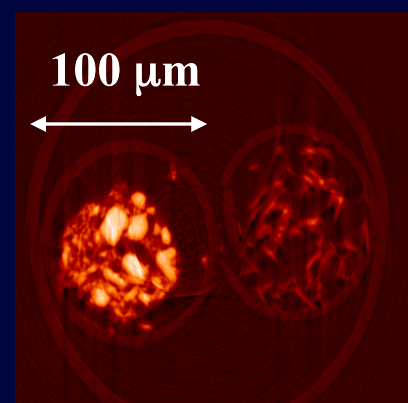
Sample: Mo compounds in cap. (Ø100 µm)

$t_{exp.}$/image: 0.2 s

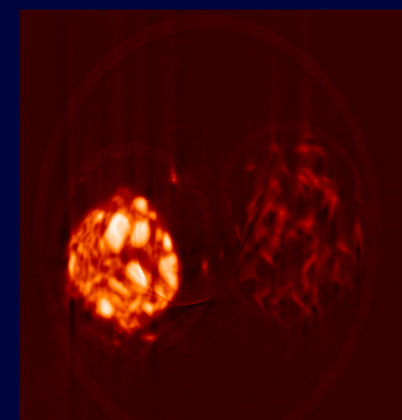
resolution: ~ 1 µm



E_{inc}=19.956 keV



E_{fin}=20.056 keV



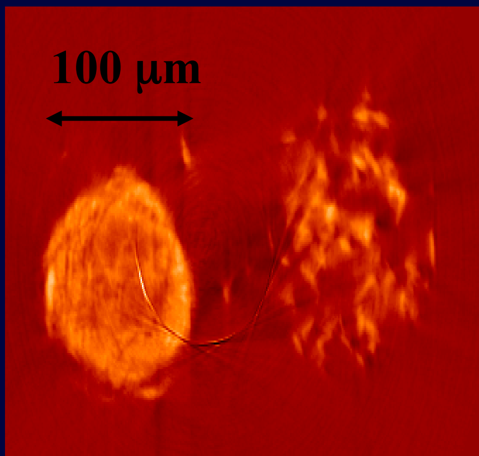
Rau ***et al***, Nucl. Instr.& Meth. A , 200C, 445-450, 2003

Voxel resolved **XANES** spectra (2eV)

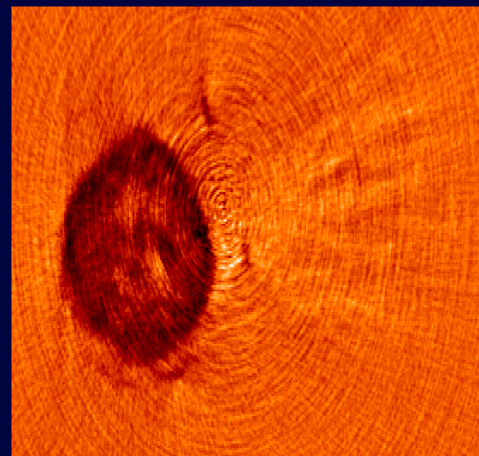
-Scientific case: phase separations in metals

3D imaging: Difference of same reconstructed slice at characteristic energies

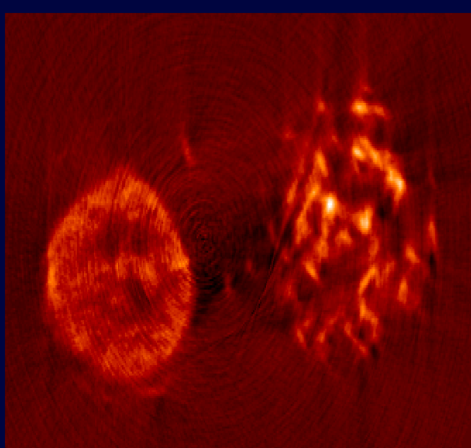
energy 4-energy 2



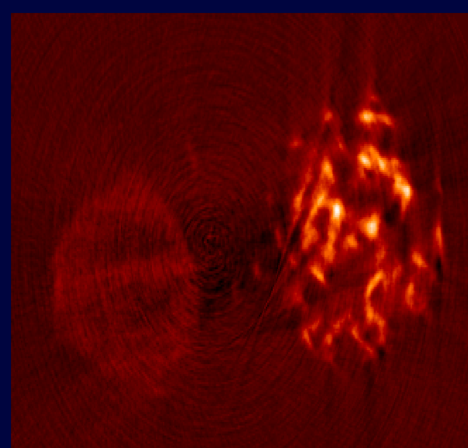
energy 5-energy 6



energy 5-energy 3



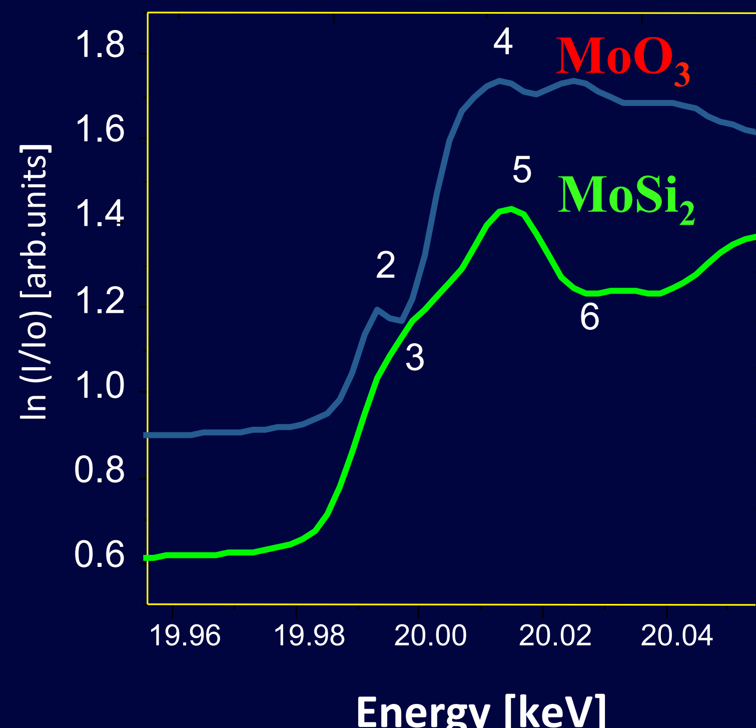
energy 6-energy 3



$MoSi_2$ MoO_3

3D XANES full field imaging with a CCD HR camera (0.7 μm resolution)

PIXEL resolved XANES spectra



EnviroSynch

Environment – Synchrotron

Erasmus for All Master
in **EcoX** Equipex (**A. Manceau**)

- 5^{th} year students; program of 18 months
- 2 semesters of Courses + practicals/lab = 2 x 30 ECTS
- 1 semester of internship in **member**/**partner** labs
- 30% redundancy: backbone + options on 3 campuses

New member

Members

FRANCE – Université J. Fourier, Grenoble
ASimionovici, BLanson, PDonnadieu, LSpadini, MMunoz

Royaume Uni – Manchester University
MDenecke +

Allemagne – Karlsruhe Institute of Technology
JGöttlicher +

Synchrotron partners

ESRF, Grenoble
PGlatzel, PCloetens, ASolé,
JSusini, MCotte

Diamond, Oxford
FMosselmans

ANKA, Karlsruhe
JGöttlicher

CLS, Saskatoon
IPickering, GGeorge

Invited lecturers

PFenter, KNagy - Univ. of Illinois, RDähn- PSI Villigen, AManceau - ISTerre,
TReich - Univ. of Mainz, LMichot - LEM + + +

Courses in Grenoble

Backbone

X-ray Absorption/Emission Spectroscopy – PGlatzel
24 h – 3 ECTS

Crystal structure & organization of finely divided solids – BLanson
56h – 6 ECTS

Methods and tools of modern mineralogy - ASimionovici + MMunoz
24 h – 3 ECTS

Imaging with electrons: SEM and TEM – PDonnadieu
24 h – 3 ECTS

Mineralogy and Environment – MMunoz + ASimionovici
24 h – 3 ECTS

Environmental Chemistry – LSpadini
24 h – 3 ECTS

Soil chemistry and pollution – ASimionovici
24 h – 3 ECTS

XCT, XAS imag., Hyperspectral imag. – PCloetens, ASolé, ASimionovici
24 h – 3 ECTS

Lecturers – PFenter, KNagy, RDähn, AManceau, TReich, FMosselmans, LMichot **24 h – 3 ECTS**

TOTAL **248h** - 30 ECTS

Starting ≥ Fall 2014