SILS School, Muggia, september 2017

Synchrotron Radiation & Environmental Science

Pierfranco Lattanzi

Retired scientist

What is environmental science?
(or, better, environmental sciences)

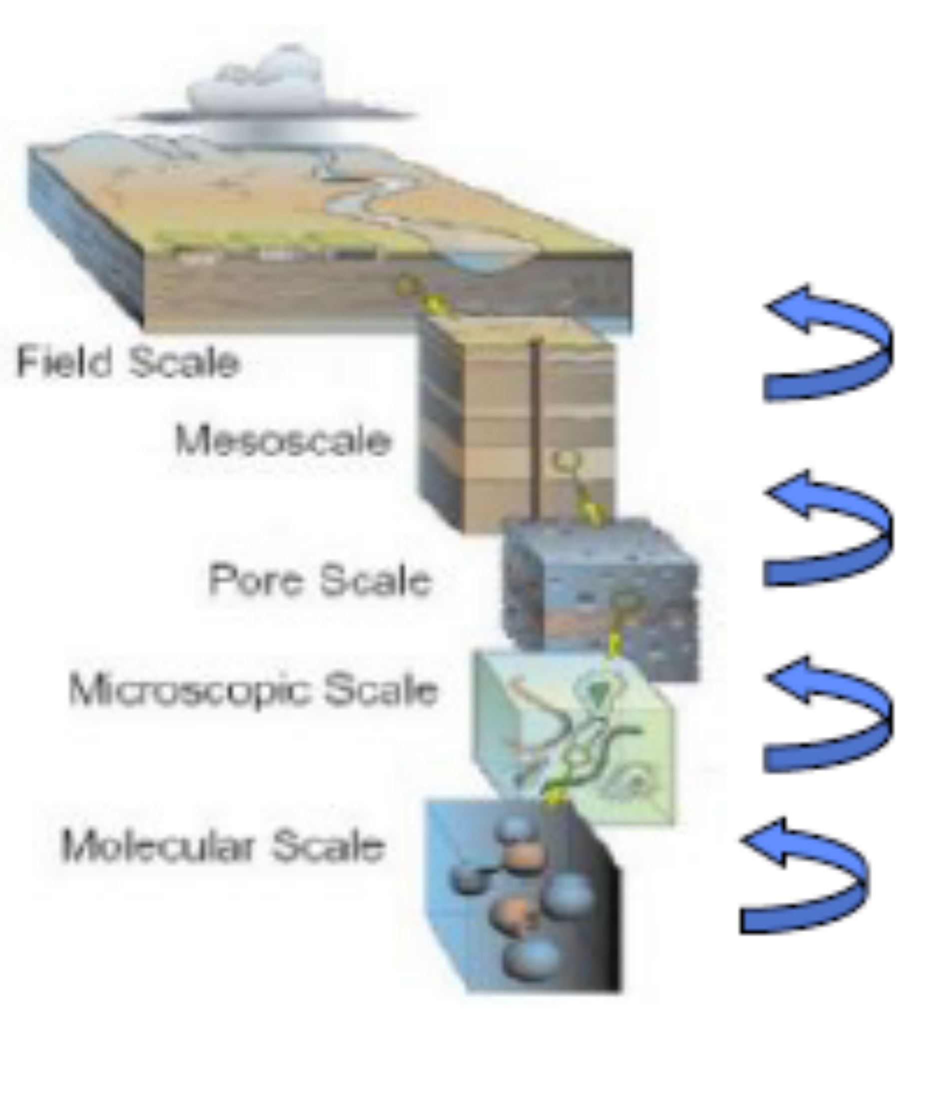
- very broad umbrella covering any phenomenon that may have an impact on life
- Includes practically ***all*** other sciences – obviously life sciences – and physical sciences (chemistry, earth sciences, physics….)
- Truly ***interdisciplinary*** approach

The science of the complexity

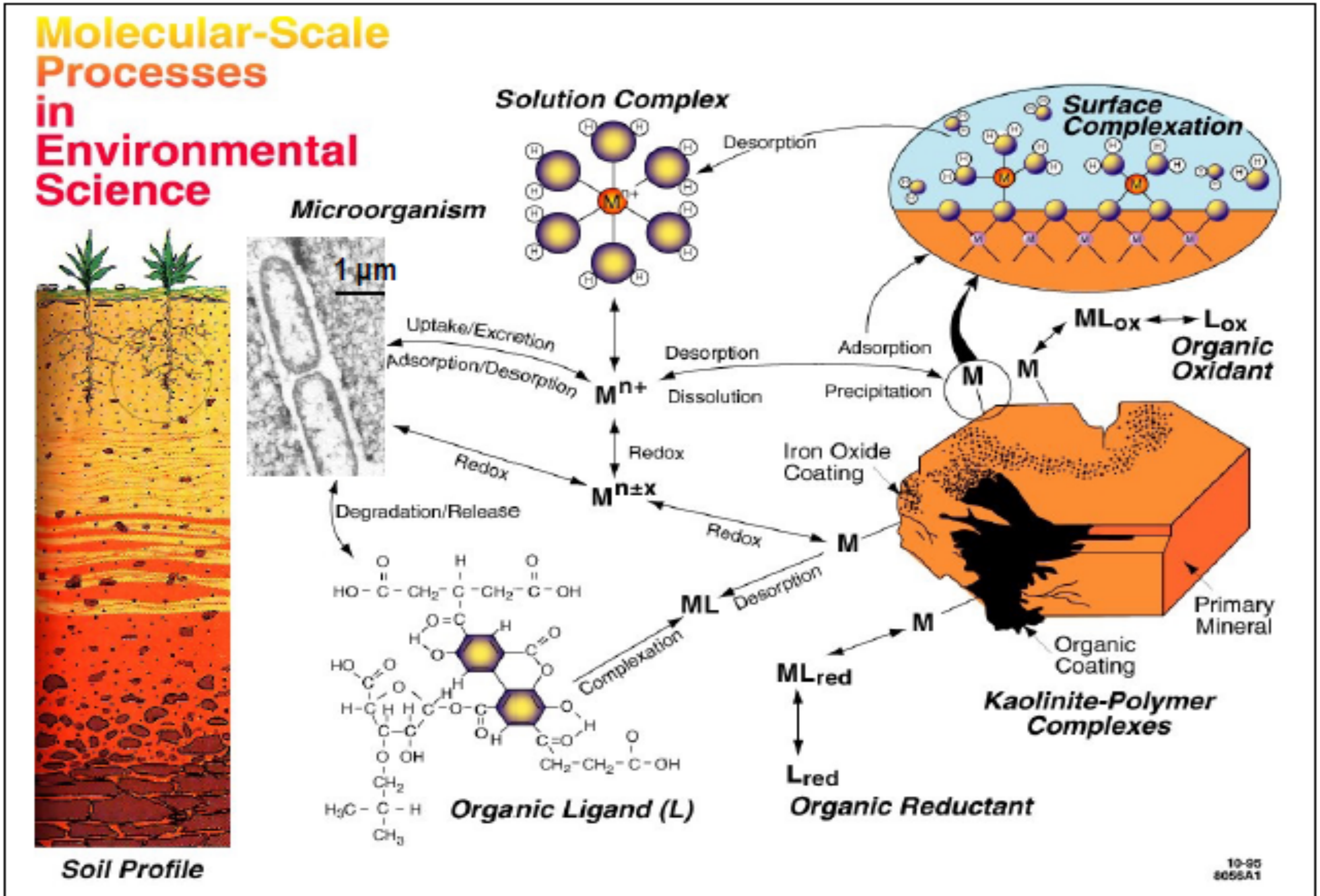
- Typically complex systems, with many parameters of very different nature
- Typical non linear and/or chaotic effects!
- *Butterfly effect (does the flap of a butterfly wings in Brazil set off a tornado in Texas?)*
- **Most studies, especially in the early stages, were descriptive/empirical**

Molecular environmental science (MES)

speciation, distribution, reactivity, transformations, mobility, biogeochemical cycling, and bioavailability of environmental contaminants ultimately depend on molecular-scale structure and properties



MES

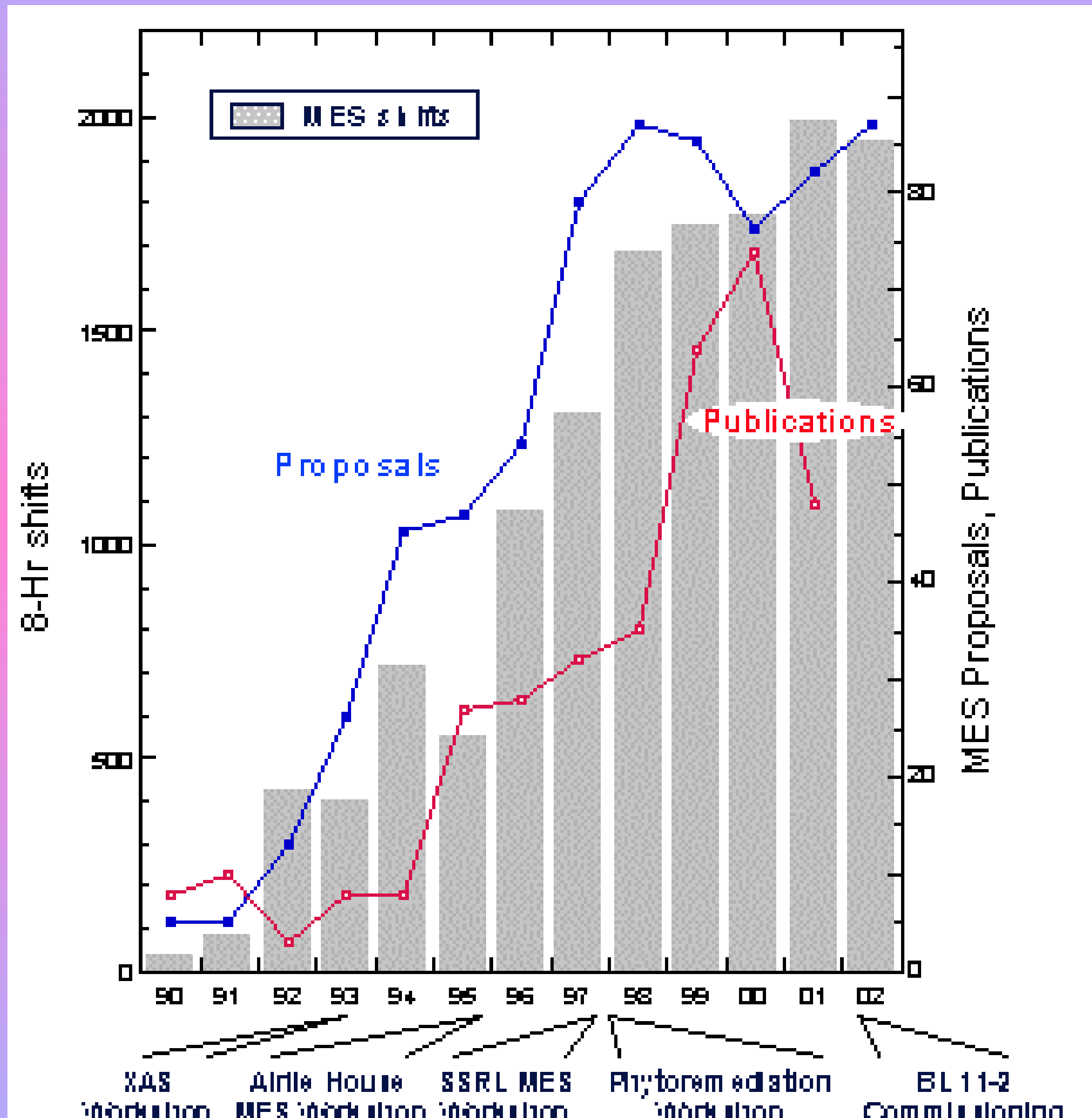


Molecular-Scale Processes in Environmental Science
Solution Complex
Surface Complexation
Desorption
Microorganism
1 µm
Uptake/Excretion
Adsorption/Desorption
Desorption
Adsorption
Dissolution
Precipitation
M
M
ML_{ox}
L_{ox}
Organic Oxidant
M^{n+}
Redox
Redox
$M^{n\pm x}$
Iron Oxide Coating
Degradation/Release
Redox
M
ML
Desorption
Complexation
M
ML_{red}
L_{red}
Organic Reductant
Primary Mineral
Organic Coating
Kaolinite-Polymer Complexes
Organic Ligand (L)
Soil Profile
10-95
8056A1

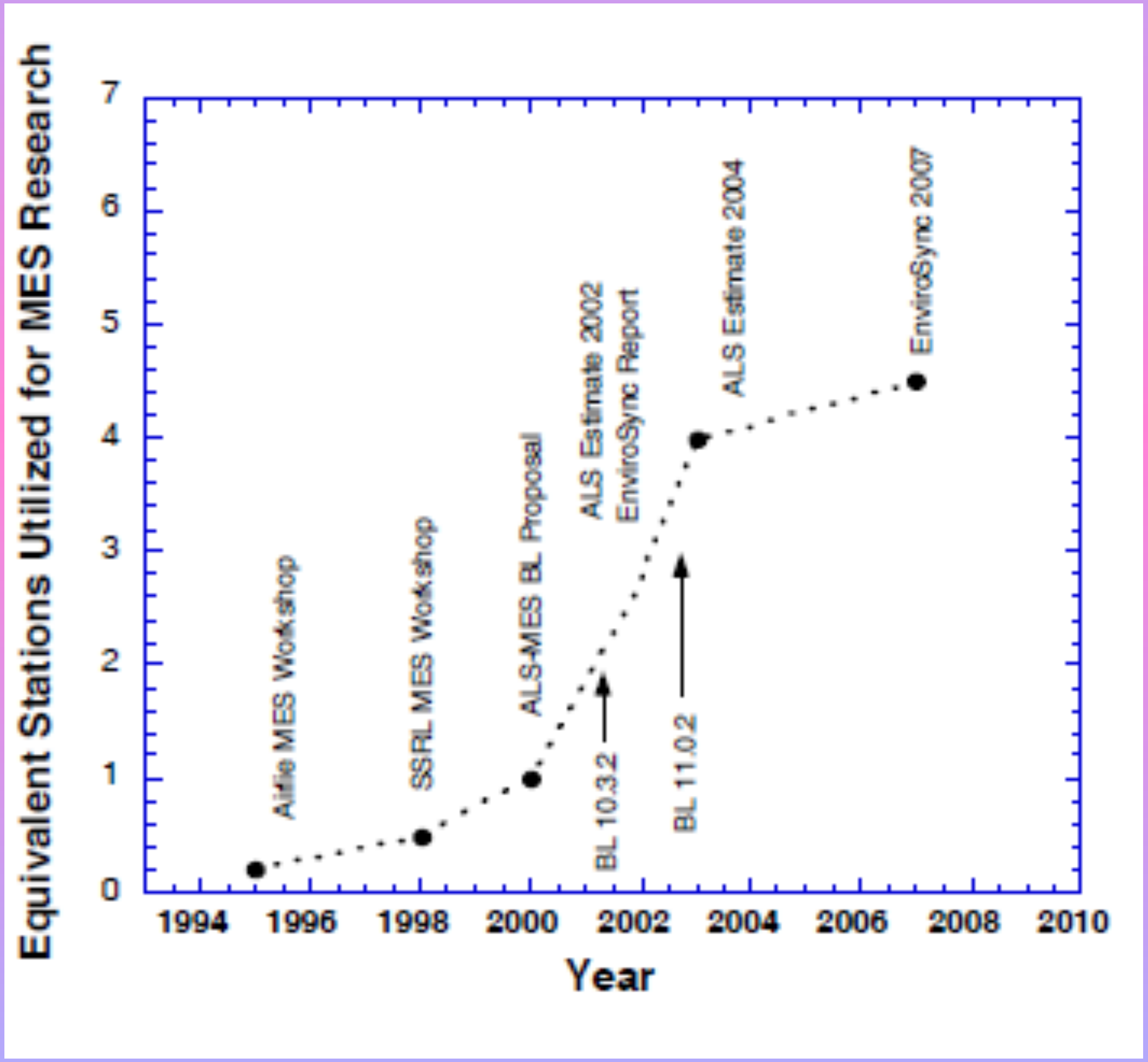
Synchrotron-based MES

- ~ 40 yrs (mostly post 1990)
- Thousands of publications
- 2(3) dedicated beamlines - SSRL, ALS (APS)
- Envirosync group (USA ~ 400 persons)
- Regular meetings (SES – last in Argonne, 2014 – 110 attending, >70 presentations; next this October at Brookhaven)
- Envirosynch project in UK - EnviroSync in Sweden...

MES research at SSRL

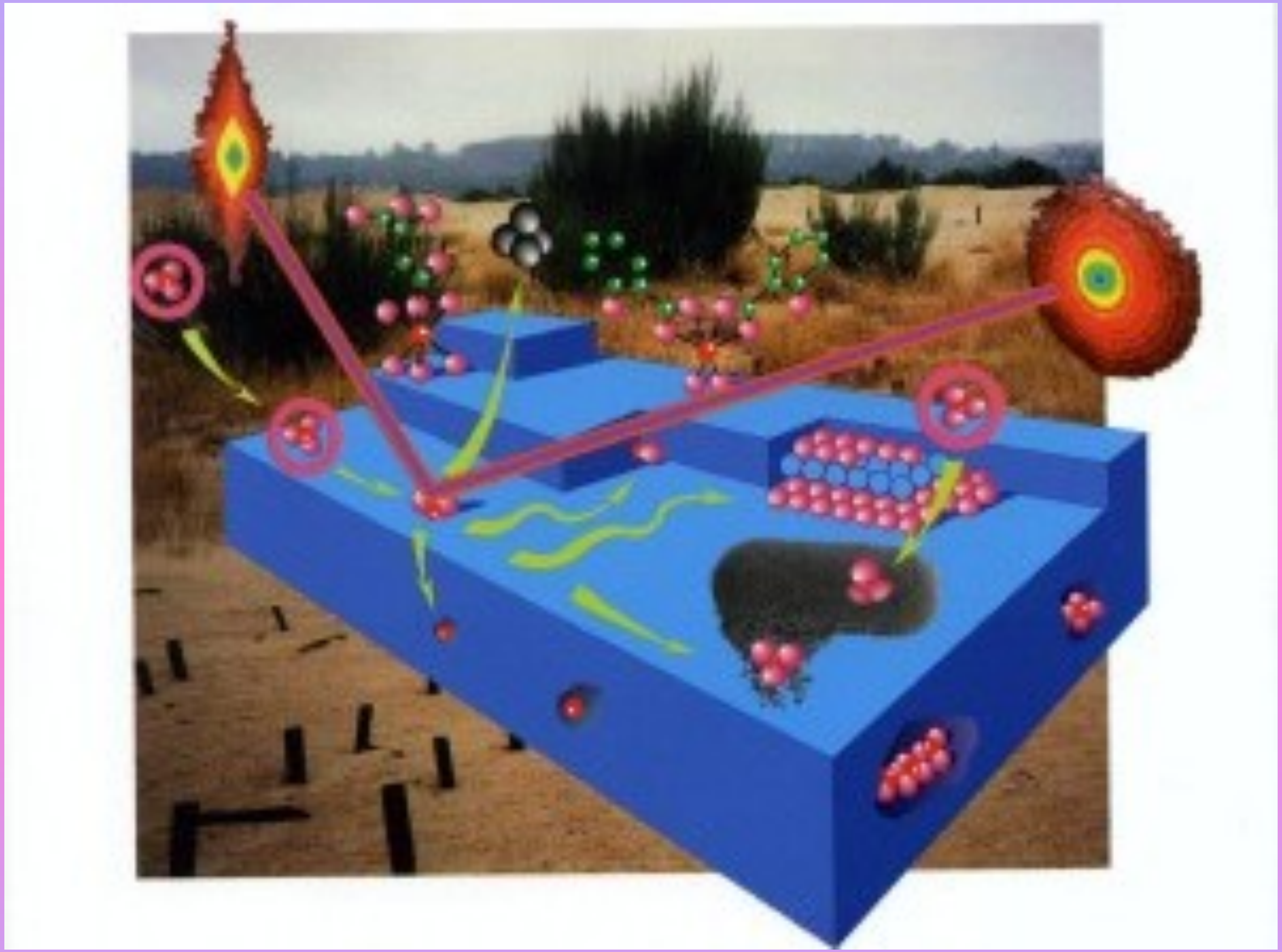


MES at ALS



Equivalent Stations Utilized for MES Research
0
1
2
3
4
5
6
7
1994
1996
1998
2000
2002
2004
2006
2008
2010
Year
Airlie MES Workshop
SSRL MES Workshop
ALS-MES BL Proposal
ALS Estimate 2002
EnviroSync Report
ALS Estimate 2004
EnviroSync 2007
BL 10.3.2
BL 11.0.2

Reviews in mineralogy and geochemistry, vol. 49 (2002)



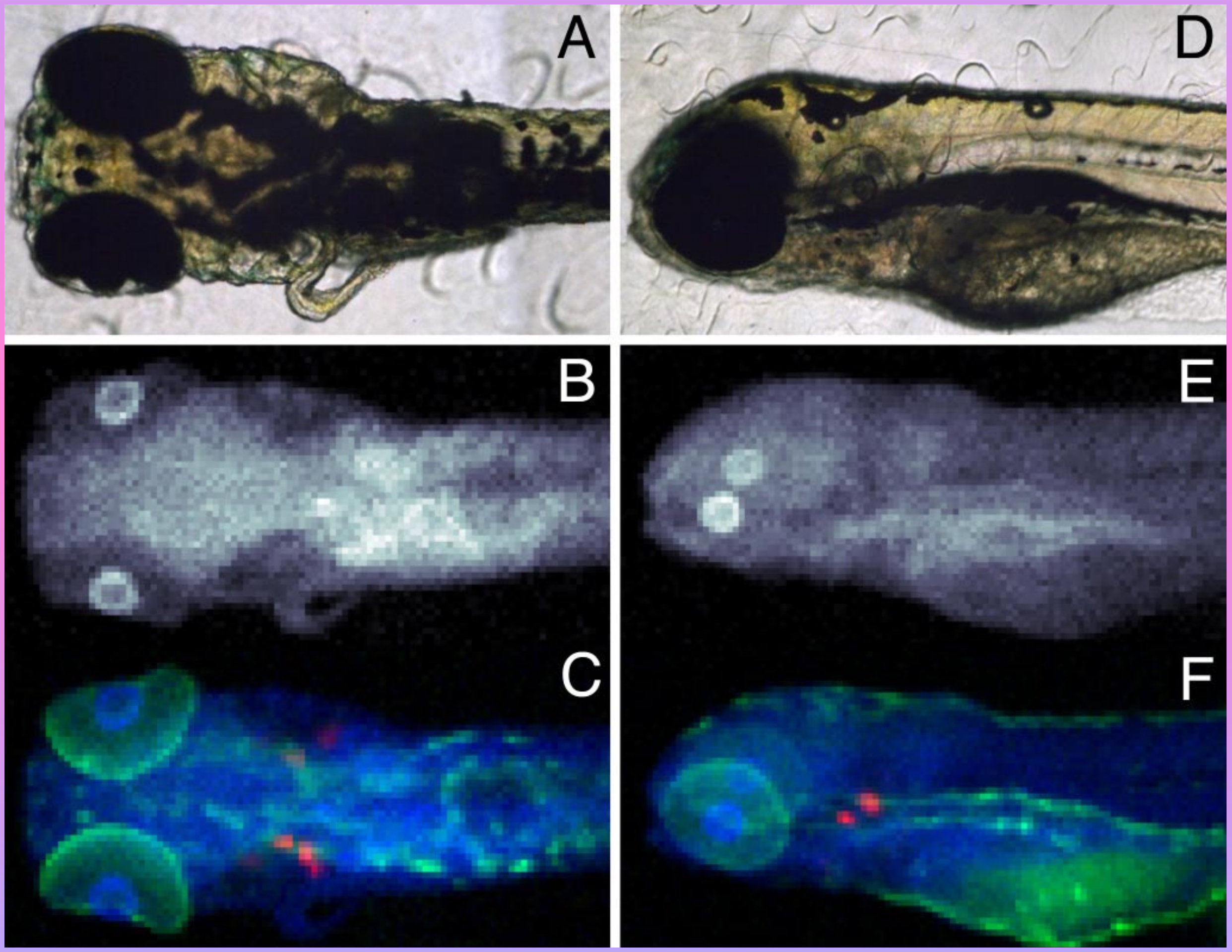
Mineralogical Magazine, February 2008, Vol. 72(1)

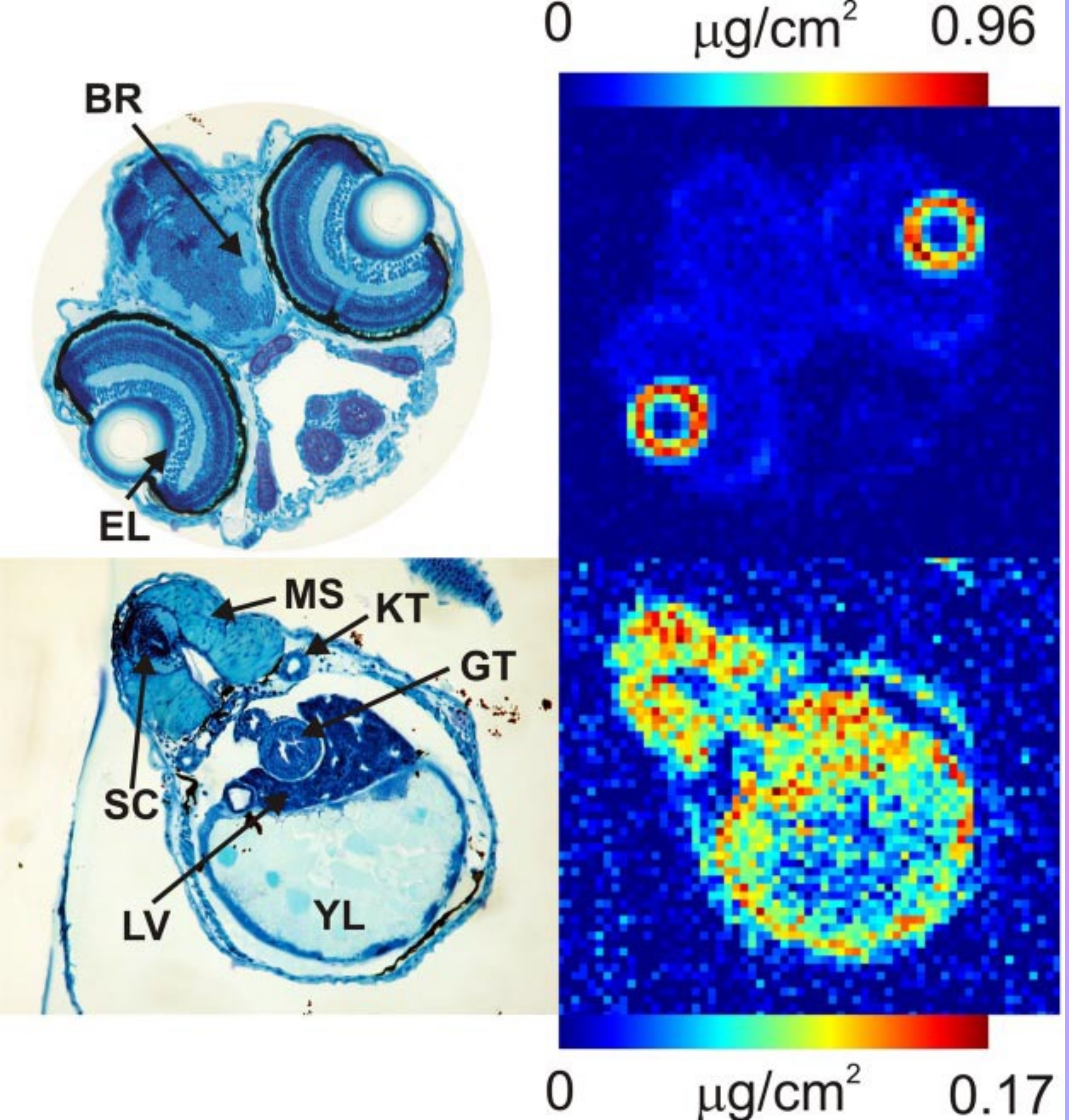
More literature in the School notes

How do environmental scientists use synchrotron radiation?

- Localization of (often very dilute) contaminant species in (often very complex) environmental samples (X-ray imaging)
- “speciation” (chemical and structural state) of contaminant(s) (XAS, XRD)
- Surface and interface studies (SR-XPS, XSW, X-ray reflectivity, GIXAS….)
- Dynamic (time-resolved) in situ studies

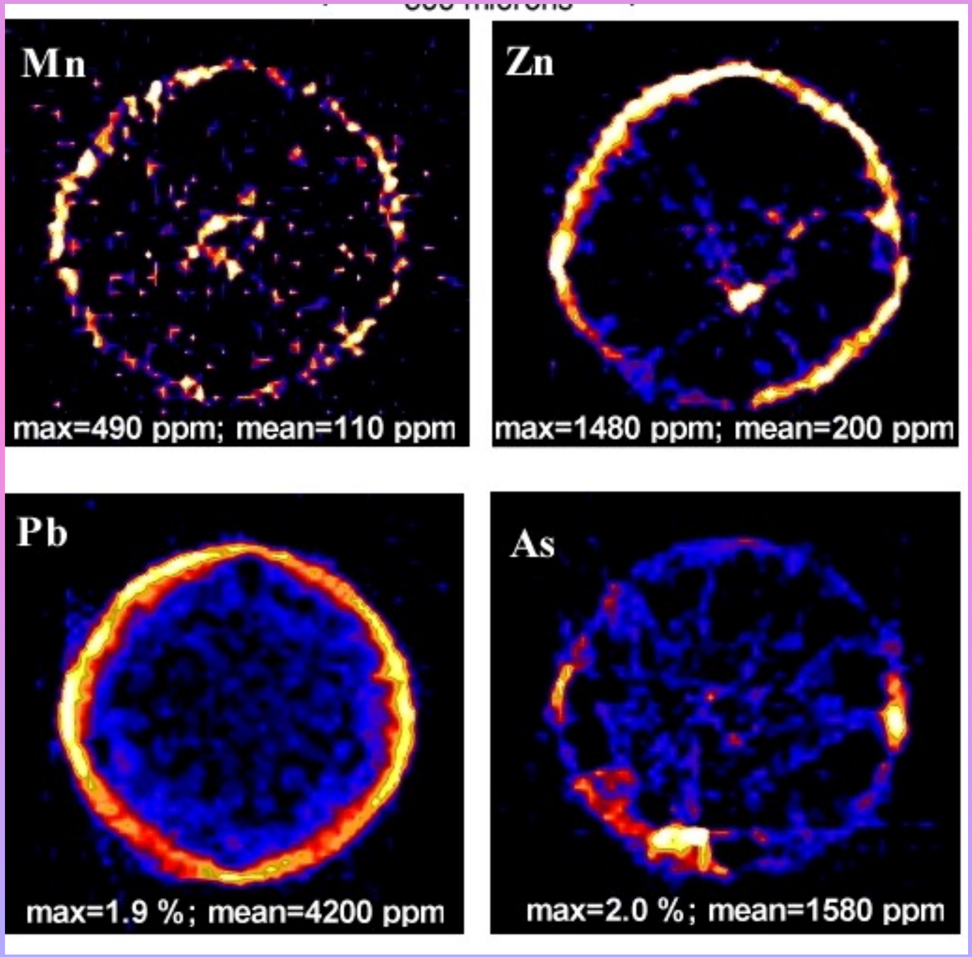
mercury distribution in fish organs




0
μg/cm²
0.96
BR
EL
MS
KT
GT
SC
LV
YL
0
μg/cm²
0.17

Heavy metals in grass roots

X-ray microtomography study



Microdistribution of metals in environmental samples

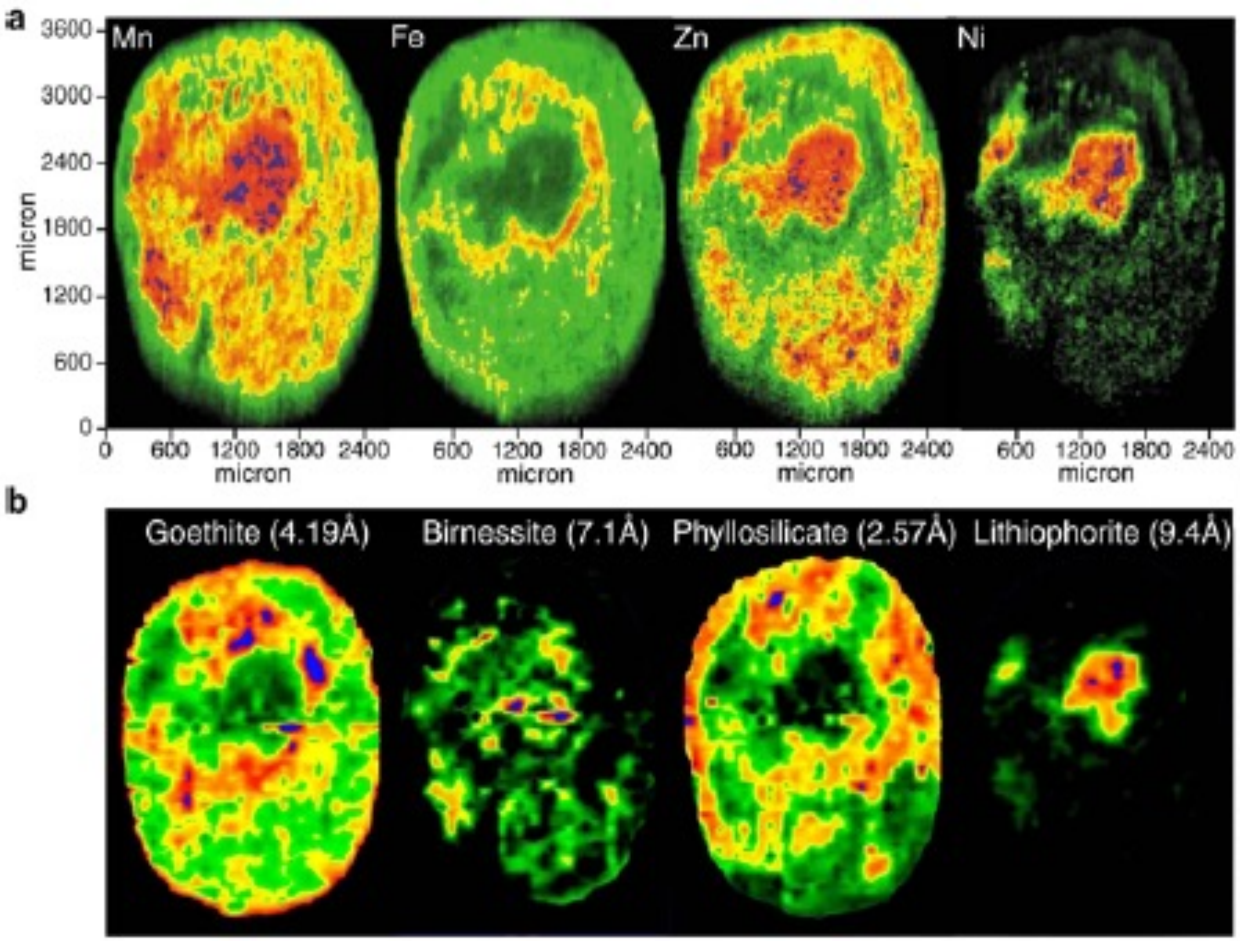
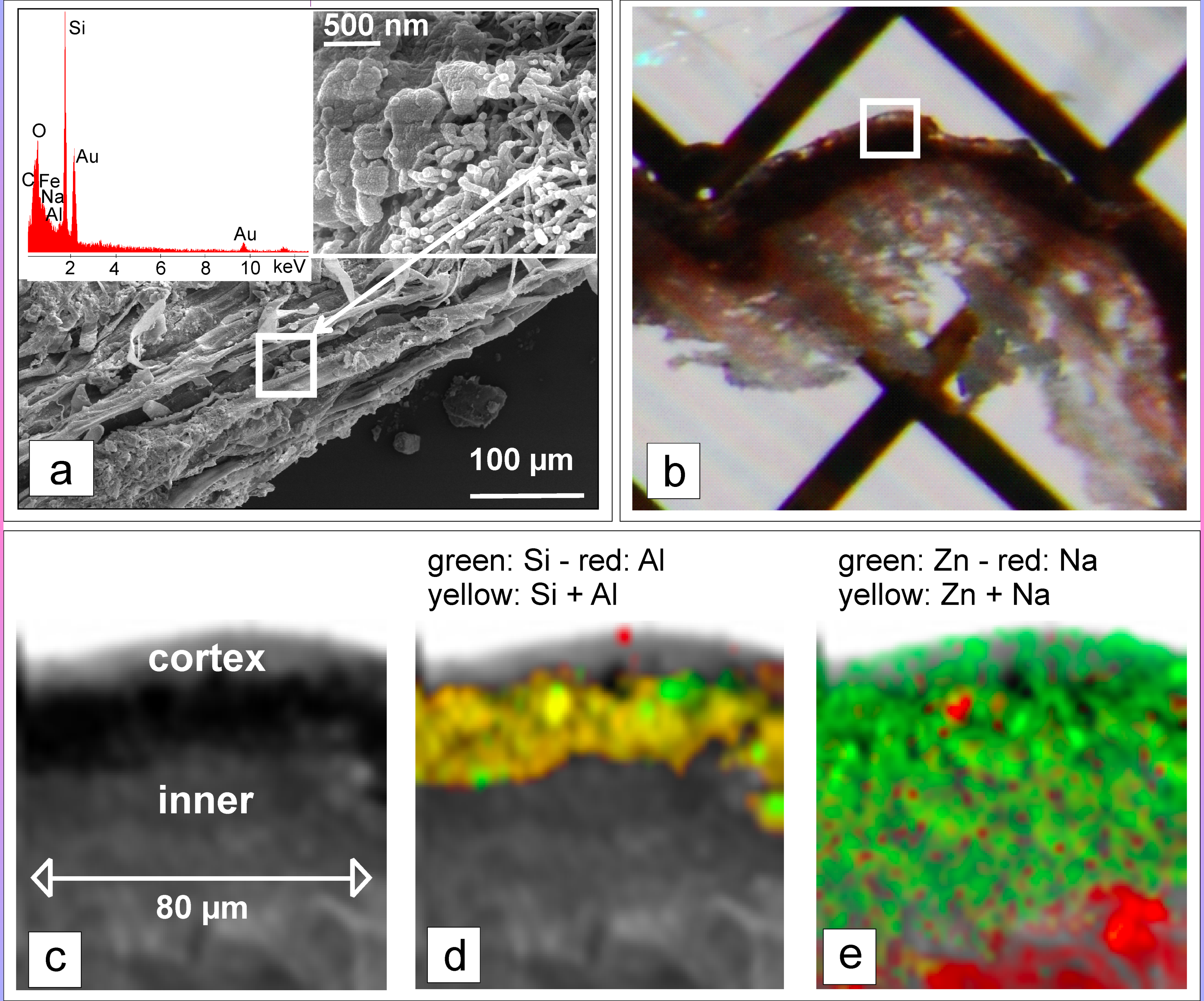


Figure 34. Combined fluorescence (a) and diffraction (b) measurements recorded on a soil ferromanganese nodule. The four top images are elemental maps obtained by μSXRF, and the four images on the bottom are mineral species maps obtained by rastering the sample in an XY pattern, collecting point XRD patterns, and integrating the diffracted intensity of the relevant (hkl) reflections (d-spacings in parenthesis). (from [42])


500 nm
Si
O
Au
C
Fe
Na
Al
Au
2
4
6
8
10
keV
100 µm
a
b
green: Si - red: Al
yellow: Si + Al
green: Zn - red: Na
yellow: Zn + Na
cortex
inner
80 µm
c
d
e

Chemical speciation of contaminants

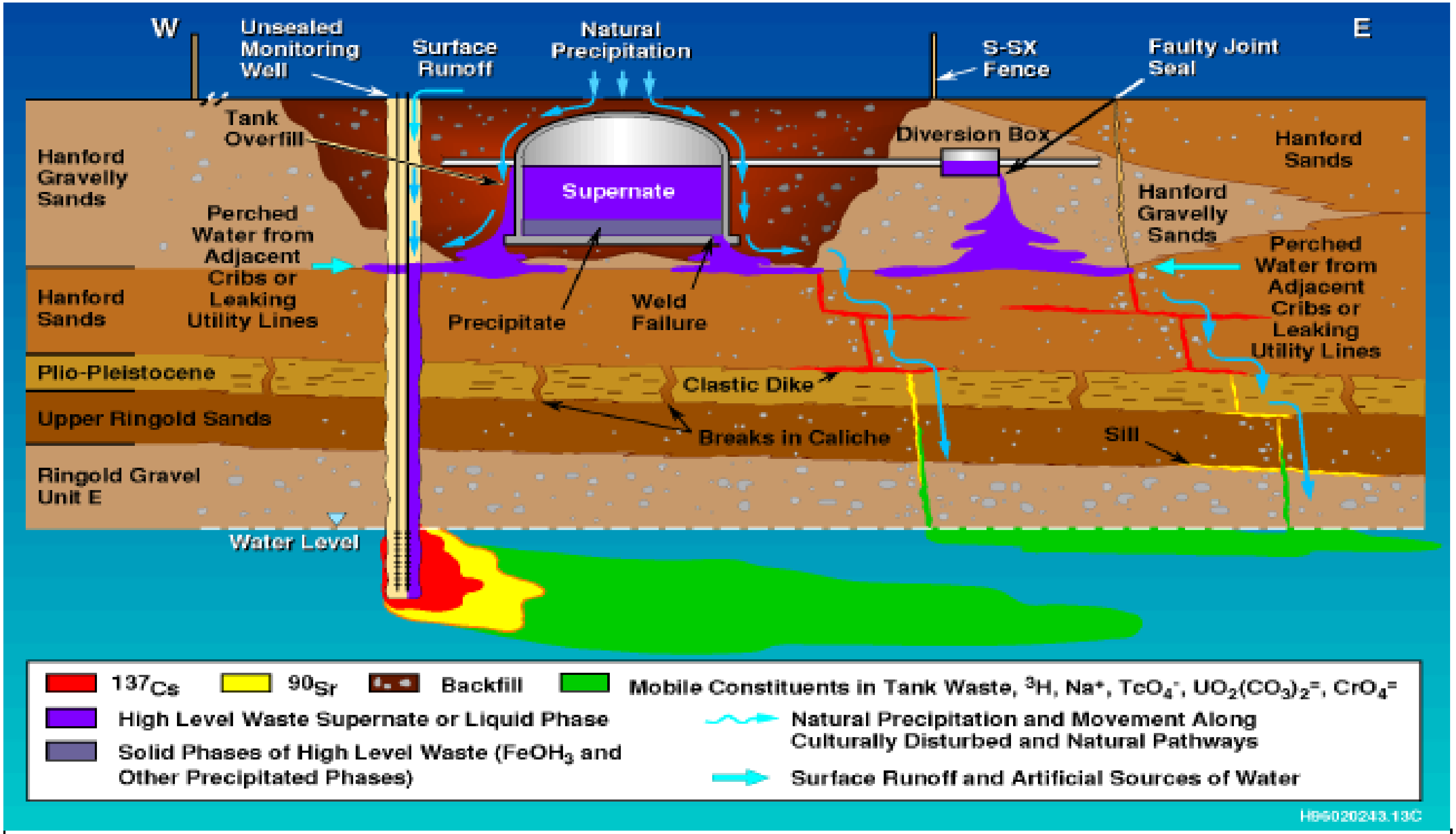
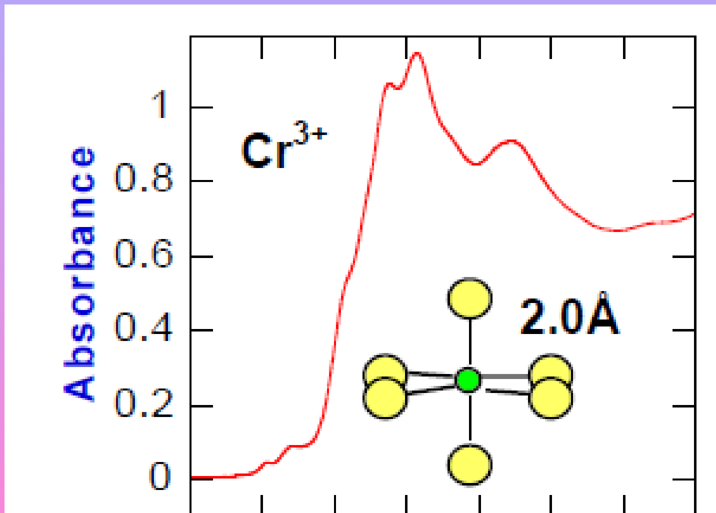
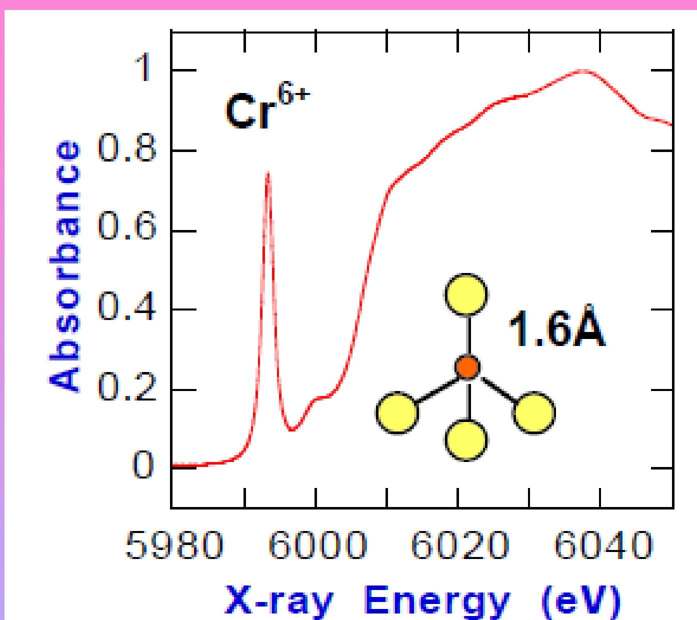
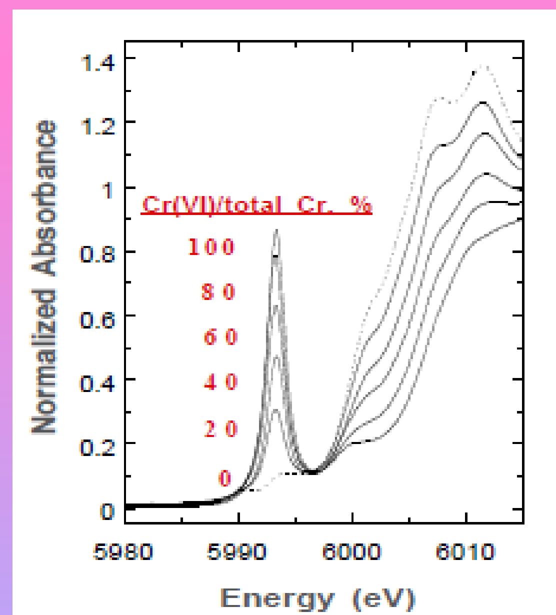


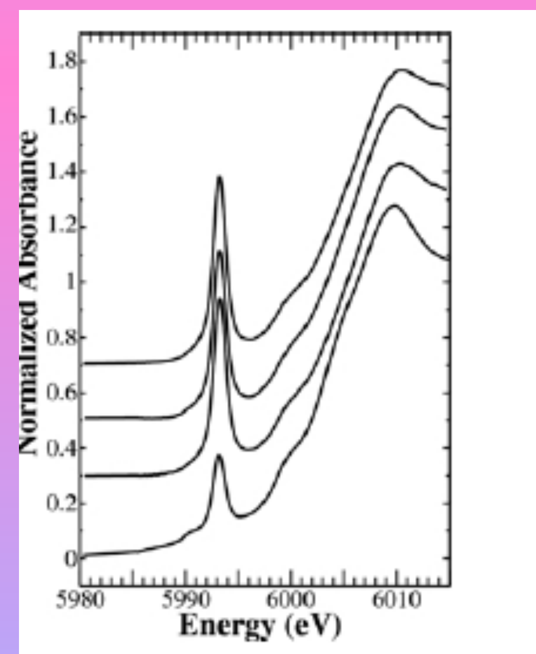
Figure 23. Hypothetical pathways for movement of S-SX Tank Farm leachates in the Hanford vadose zone.

XAS discrimination of chromium valence states



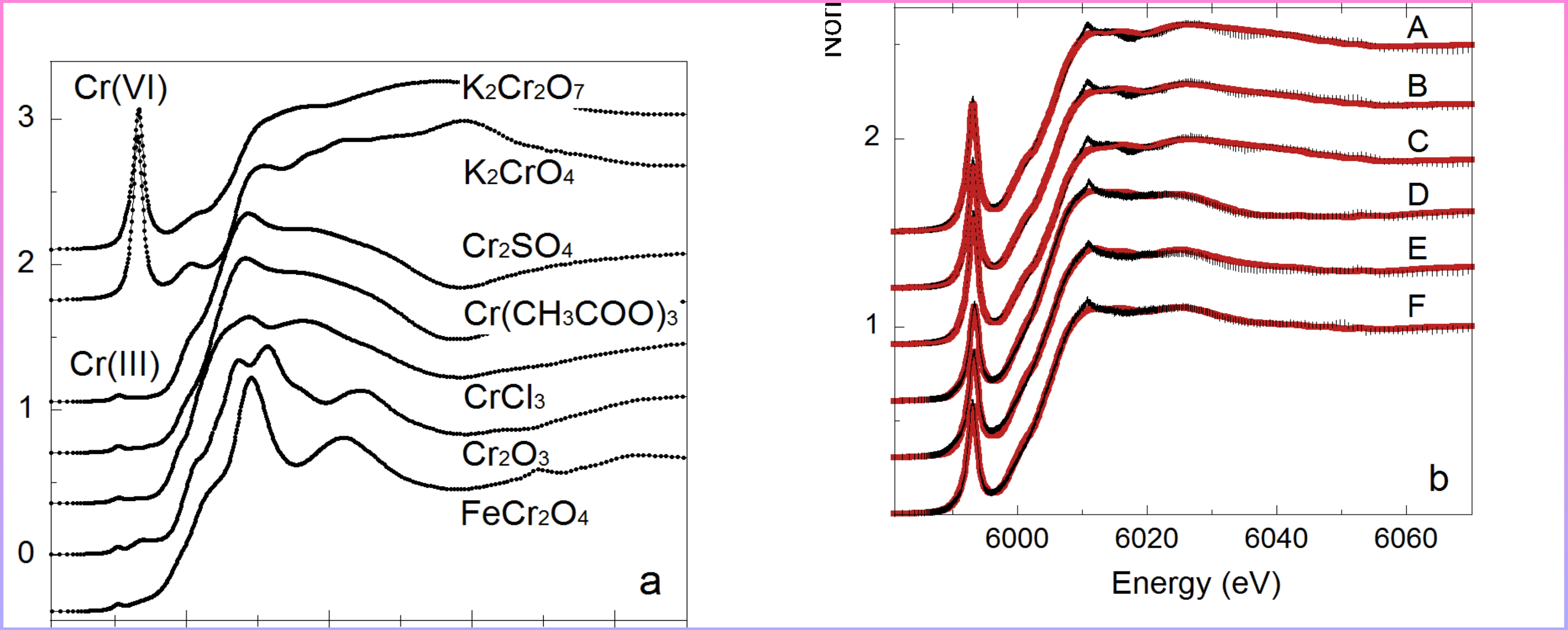






Cr(VI) highly toxic – Cr(IIII) moderately toxic

- Attempts at reduction Cr(VI) to Cr(III) in a contaminated soil by whey addition



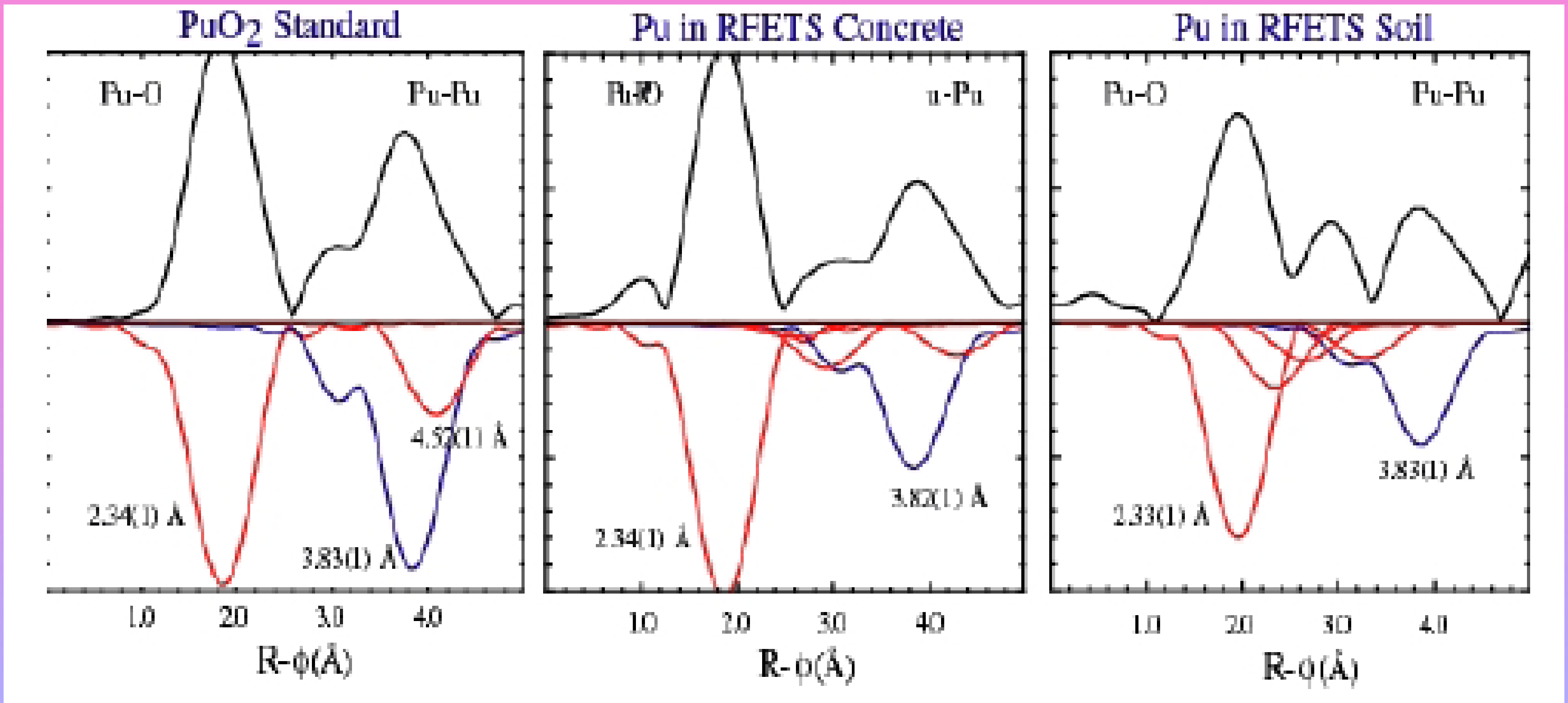
Chemical speciation of plutonium by XAS

- Decommissioning of Rocky Flats nuclear facility

The mobility of plutonium is higly dependent on speciation

Pu(IV): highly insoluble – can be mobilized only as particulate (e.g. by wind)

Pu(VI): mobile in solution as PuO_2^{2+} species



Soluble transport models are not applicable to Pu migration in RFETS soils; particulate (i.e., erosion) transport is the dominant transport mechanism for Pu migration at the site.

This conclusion translates directly into **very substantial cost savings**, because focused efforts toward erosion modeling, and land configuration studies to control particulate transport. It also helped to define cleanup levels.

Thus Pu XAFS measurements developed into a decision-making tool that saved the company millions of dollars by focusing site-directed efforts in the correct areas, and aided the DOE in its efforts to clean up and close the RFETS.

UNIVERSITÀ DEGLI STUDI FIRENZE
DST DIPARTIMENTO DI SCIENZE DELLA TERRA

Mercury speciation in *Pinus nigra* barks from Monte Amiata (Italy): An X-ray absorption spectroscopy study

presentation by Valentina Rimondi at SIMP-SGI-SOGEI-AIV meeting, september 2017

Tree barks: a new tool for atmospheric Hg biomonitoring?

✓Easy species recognition
✓Low systemic uptake from soil
✓Year-round ubiquity
✓Low cost sampling



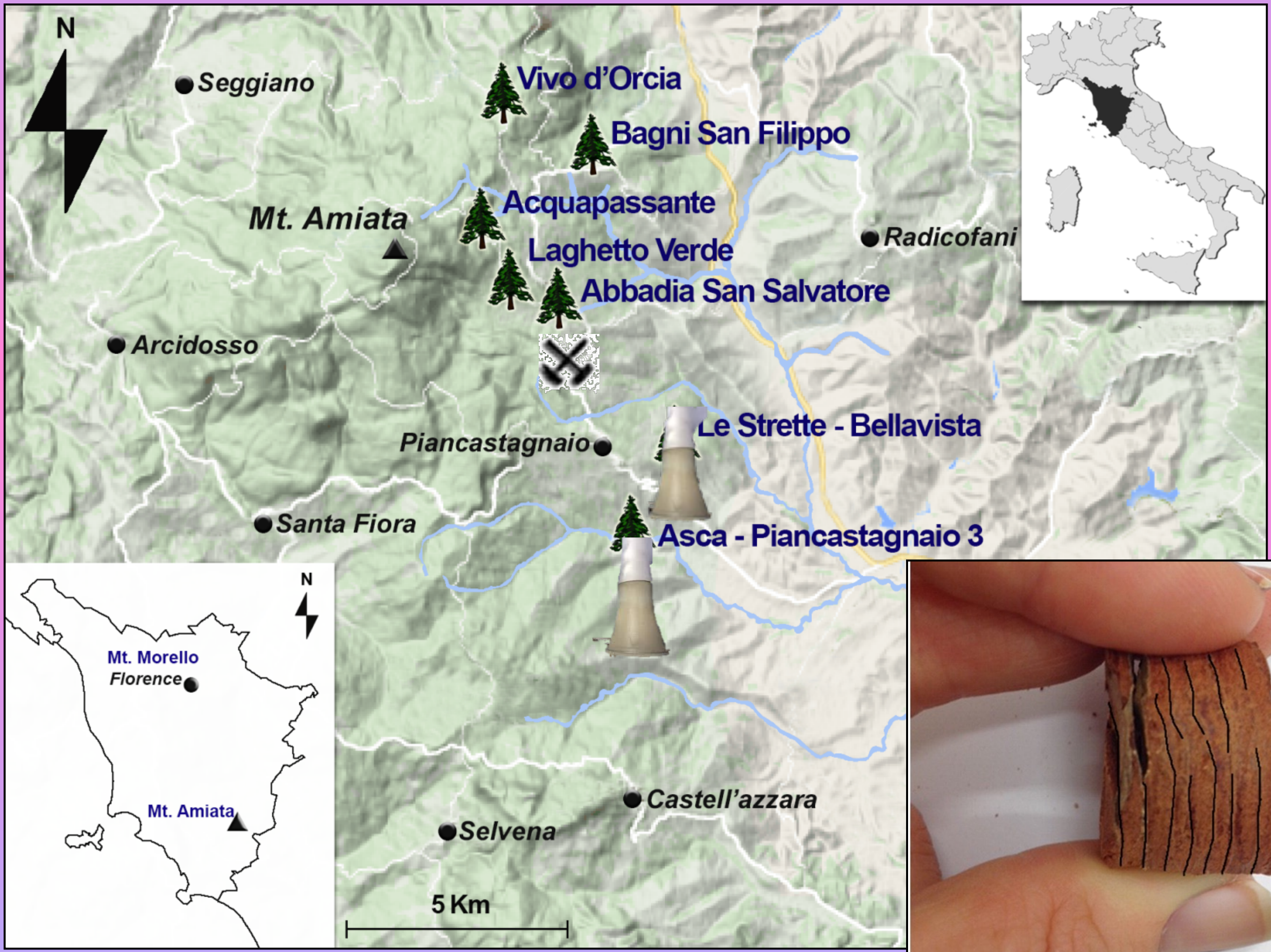


Tree barks: a new tool for atmospheric Hg biomonitoring?

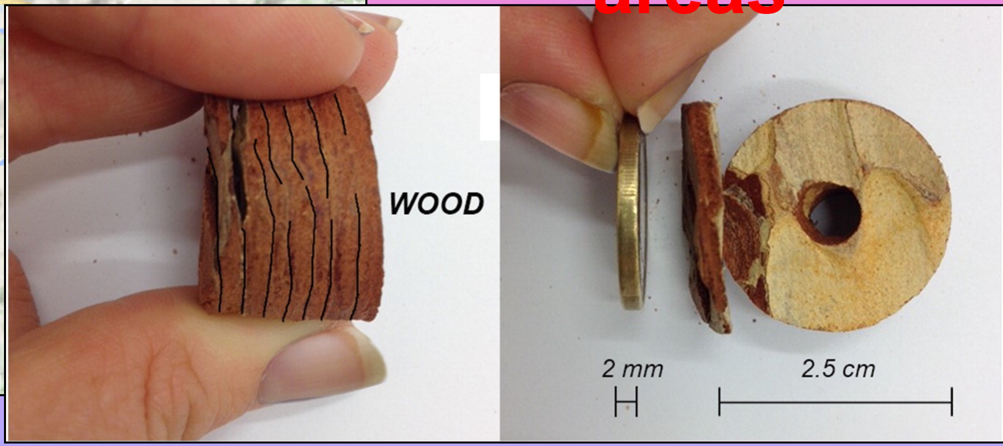
- Very little literature
- Low levels of pollutant accumulation
- Poor knowledge on the mechanism(s) of Hg accumulation on barks

Monte Amiata Hg district

Chiarantini et al. 2016- Sci. Total Environ. 569-570; 105-113

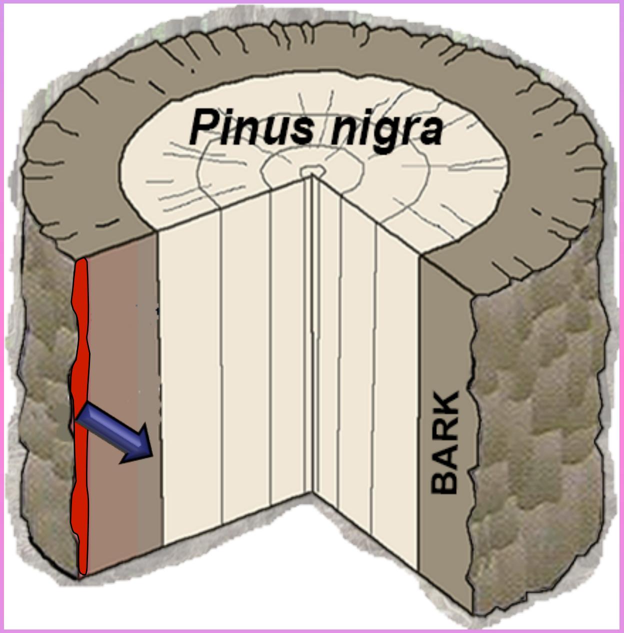


***Pinus nigra* barks: mining and geothermal areas**



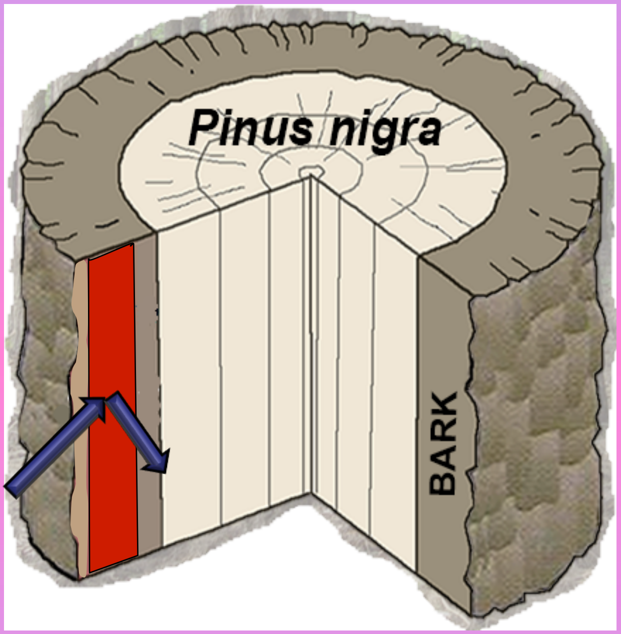
High Hg concentration: **up to 8 mg/kg**

Reference sites



Decreasing Hg from ouside to inside layers

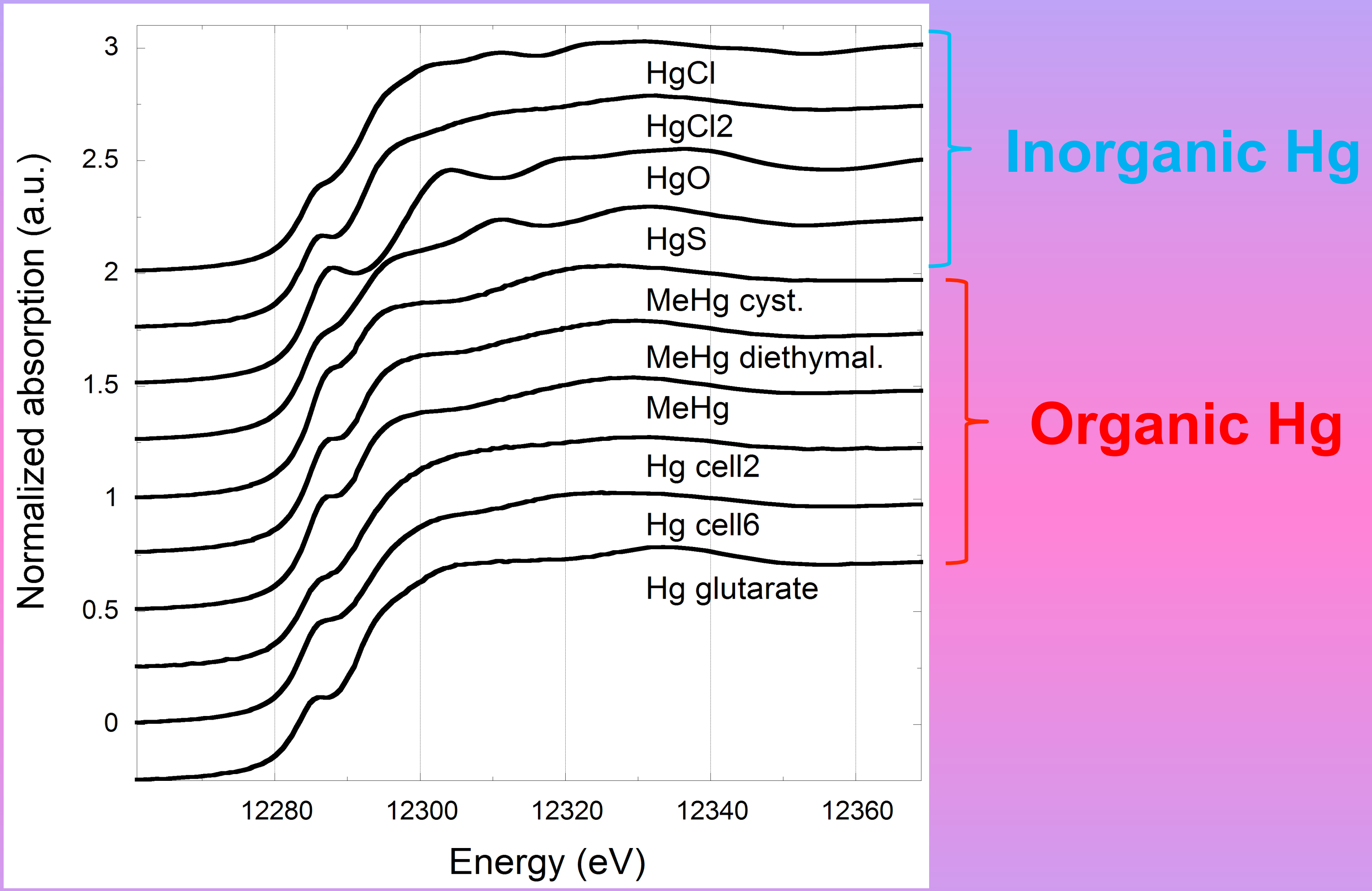
Highly polluted sites



Increasing Hg in **intermediate** layers

Change in Hg speciation?

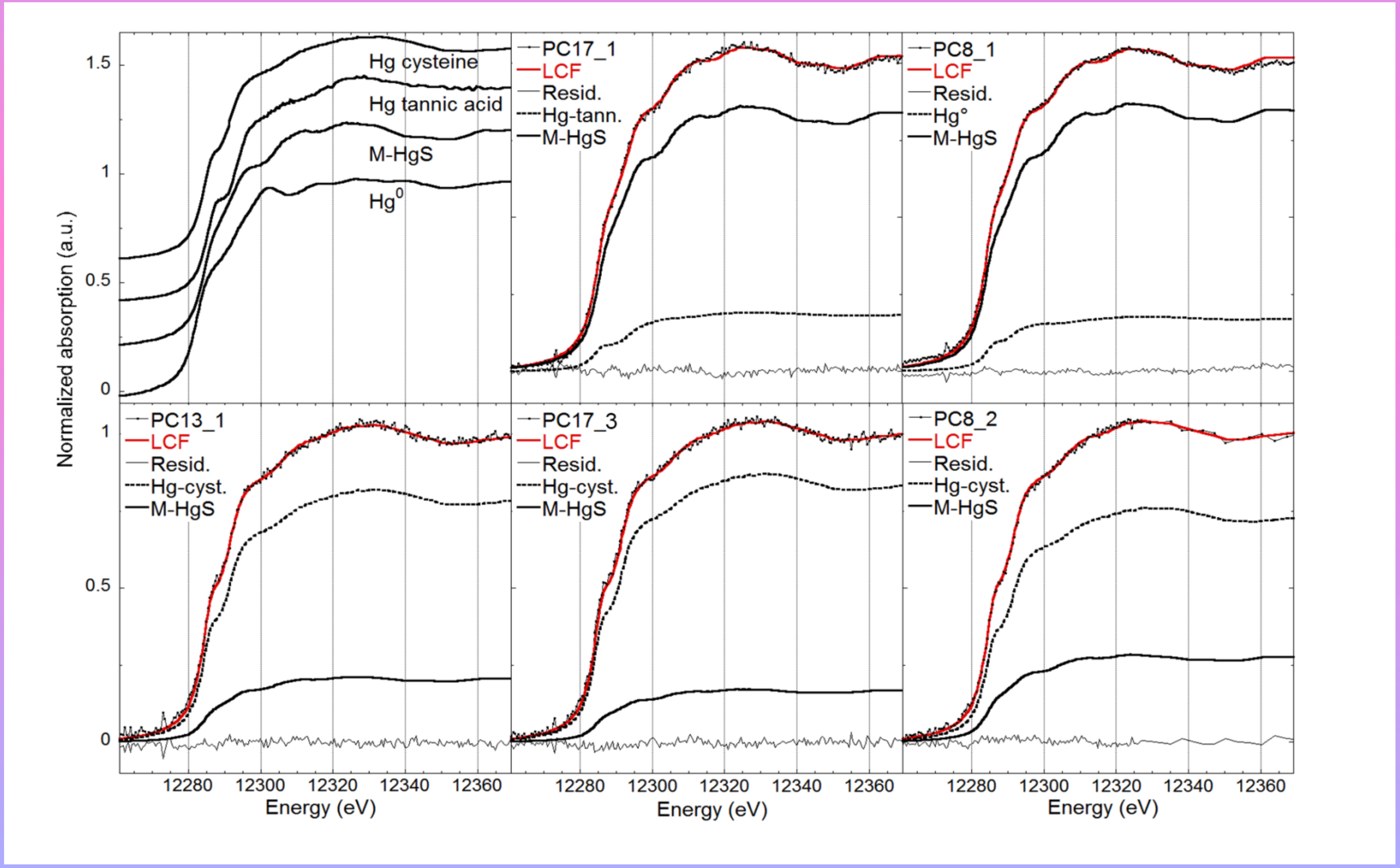
Reference standards



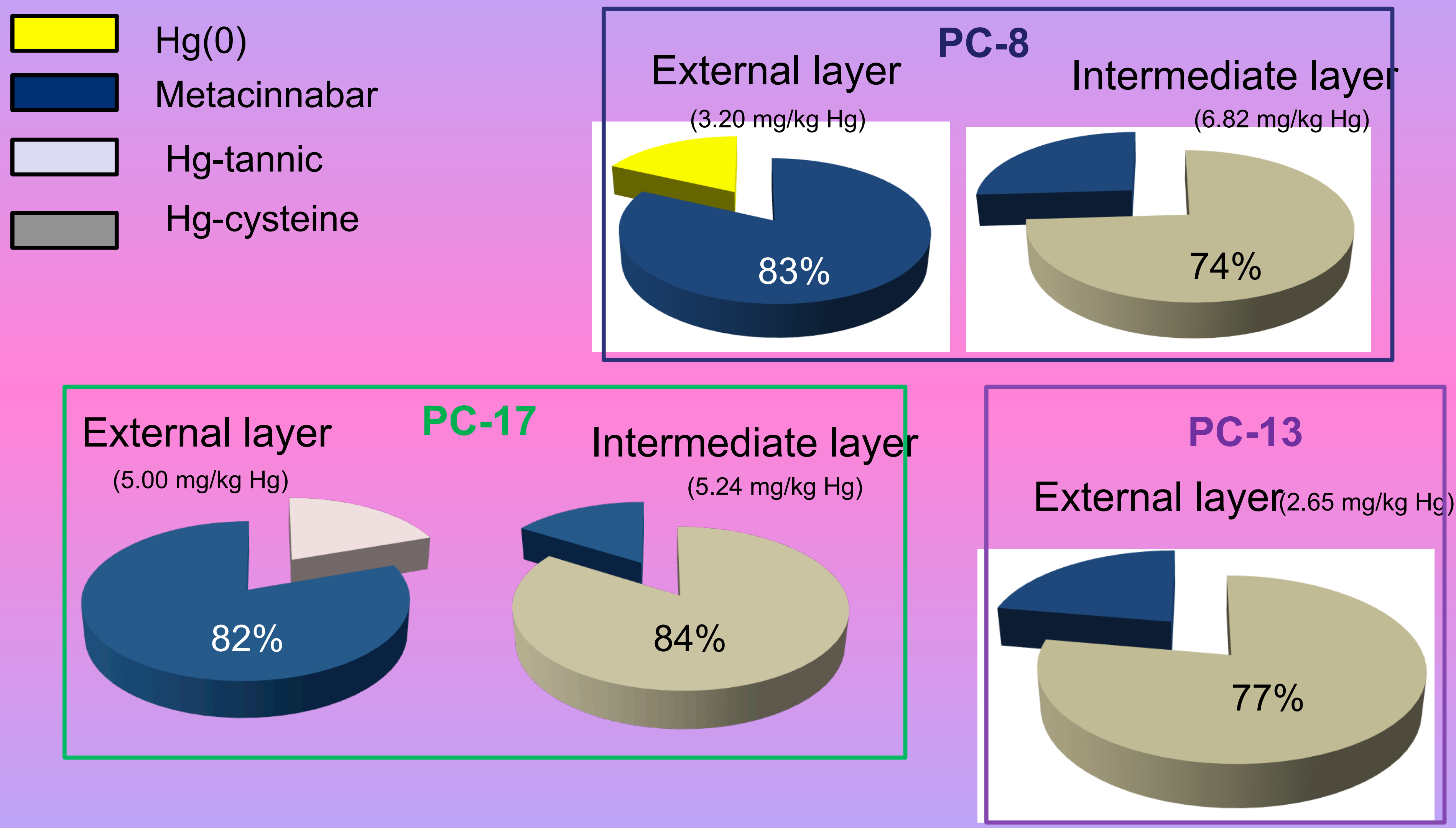
References: Hg sulfides, oxides, chlorides, hydroxyls and carboxyls (tannic acid and cellulose), sulfur (thiols, sulfides, sulfates), methylate, and glutarate bondings

Results

Meaningful fit with only four reference compounds: **metacinnabar**, **Hg bound to tannic acid**, or **Hg cysteine**, and **Hg^0**



Results


Hg(0)
Metacinnabar
Hg-tannic
Hg-cysteine
PC-8
External layer
(3.20 mg/kg Hg)
83%
Intermediate layer
(6.82 mg/kg Hg)
74%
PC-17
External layer
(5.00 mg/kg Hg)
82%
Intermediate layer
(5.24 mg/kg Hg)
84%
PC-13
External layer
(2.65 mg/kg Hg)
77%

Conclusions

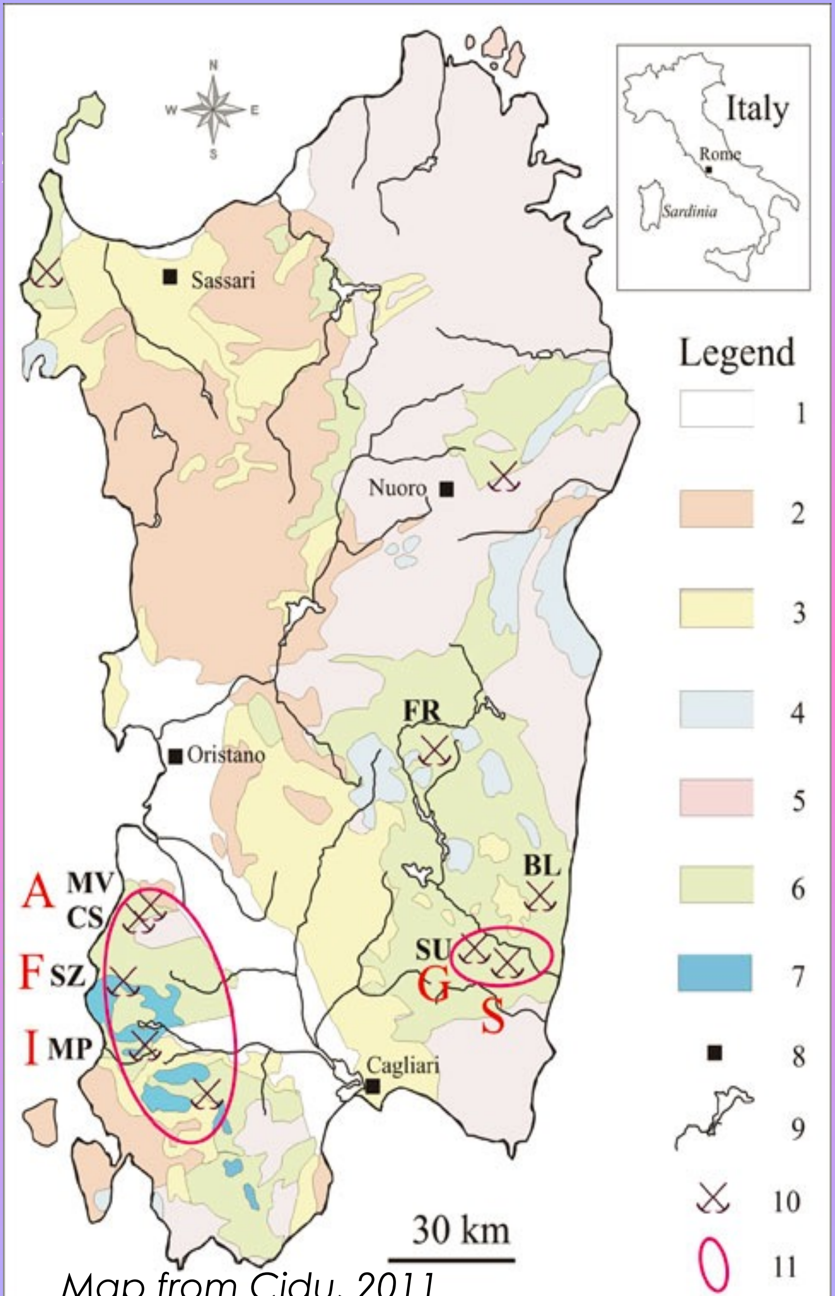
- Metacinnabar and Hg(0): original species deposited from atmosphere
- Hg-cysteine and Hg-tannic: interaction between inorganic species and bark surface
- Mercury bound to «soft» donor as thiols in cysteine-like molecules (proteins)
  - Mercury bound to OH and COOH groups in tannins

Investigation of Zn speciation in biominerals by synchrotron radiation techniques

Daniela Medas

Department of Chemical and Geological Sciences, University of Cagliari

email: dmedas@unica.it - daniela.medas@yahoo.it

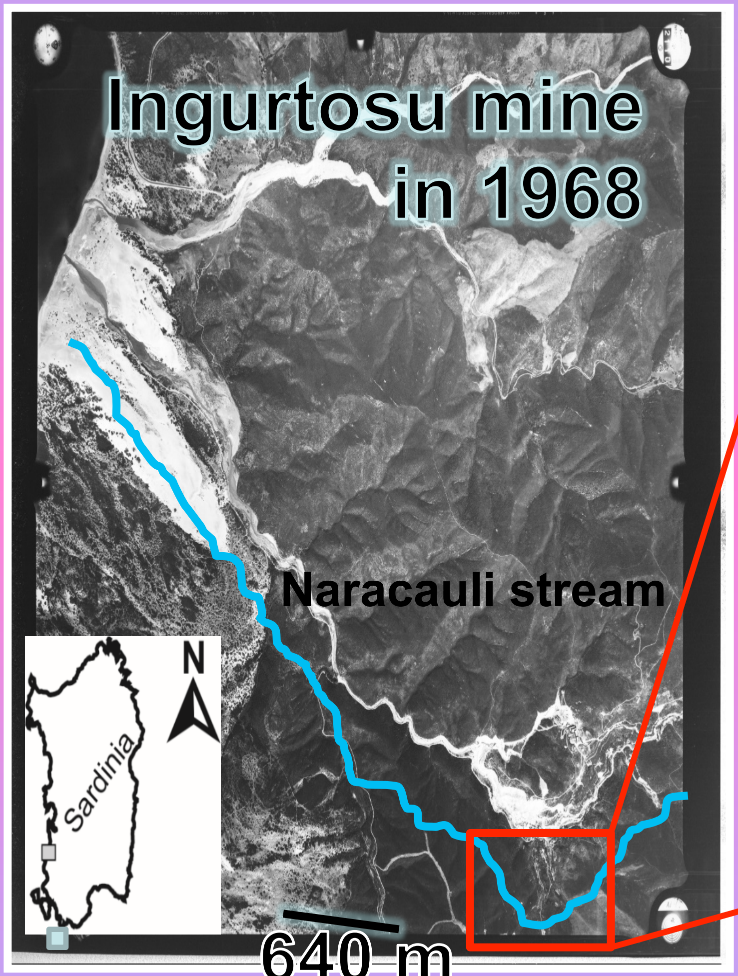


Map from Cidu, 2011

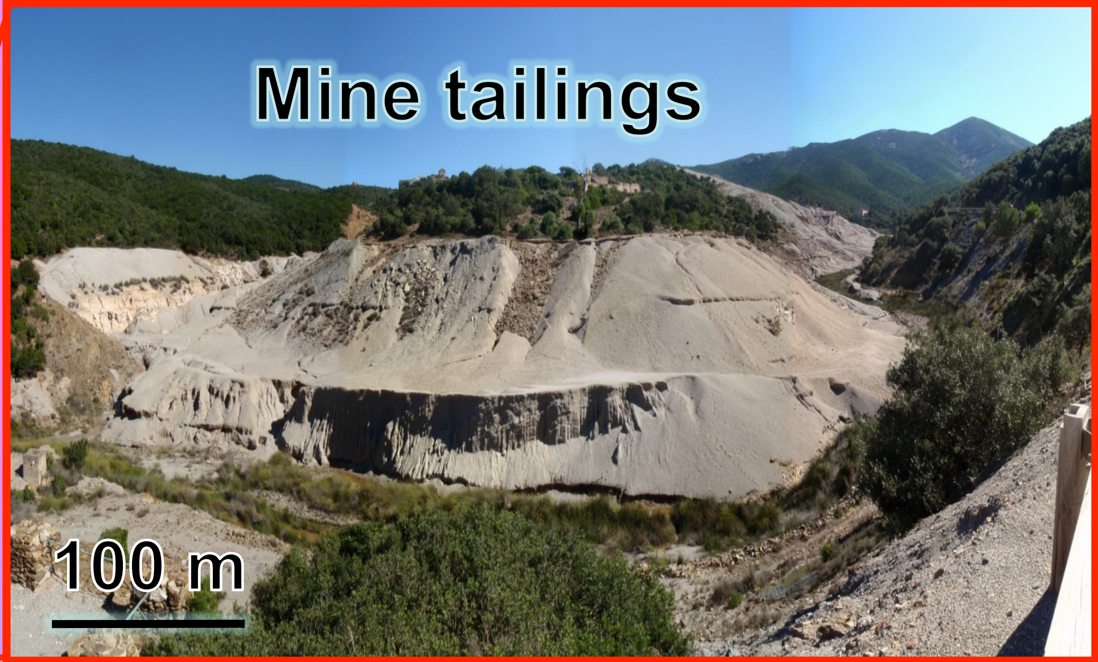
ABANDONED MINING AREAS IN SARDINIA (ITALY)

- ~ 100 abandoned mine sites.
- Huge problems of heavy metals dispersion.

Zn EXTREME ENVIROMENT



Ingurtosu Pb-Zn mine closed on 1968 after more than 100 years of intense activity.

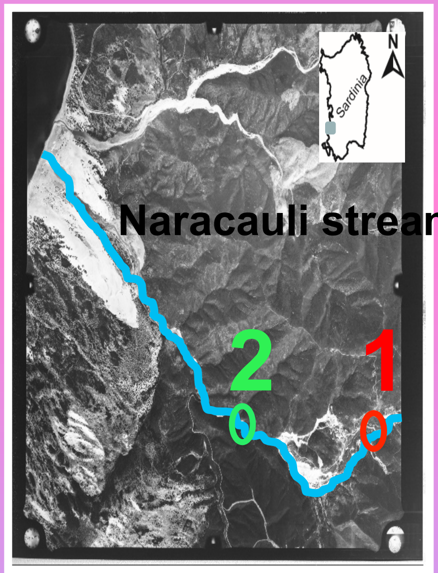


- ✓ No remediation actions.
- ✓ Zn from ppb to several hundreds of ppm in waters.


Piscinas beach
(downstream of the mine dump)
Tailings transported
by the Naracauli river
on this beach

BIOMINERALIZATION AT NARACAULI

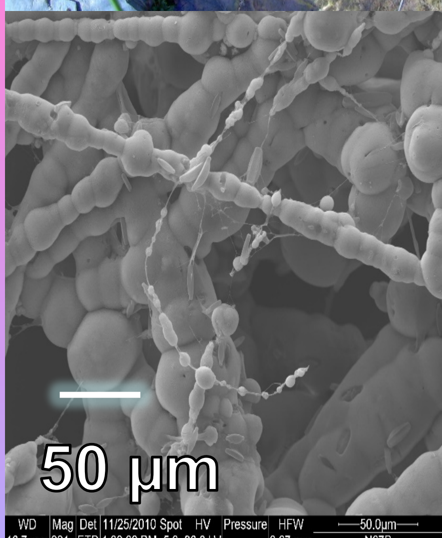
Two different types of biomineralization



Hydrozincite $Zn_5(CO_3)_2(OH)_6$

Amorphous Zn-Si

Hydrozincite
$Zn_5(CO_3)_2(OH)_6$



Late spring – early summer

Scytonema sp.

Tubules: 30-50 µm

Crystalline

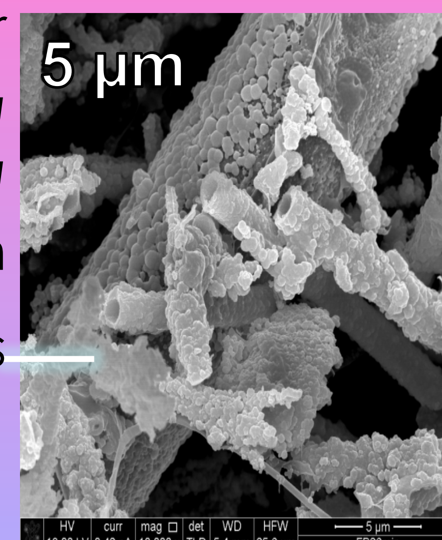
Amorphous Zn-Si

Summer

Leptolyngbya frigida

Tubules: ≈ 2 µm

Amorphous (XRD)



HYDROZINCITE AND RAIN EVENTS

March 18, 2009
No biofilm

March 25, 2009
First state of development (biofilm+biomineral)

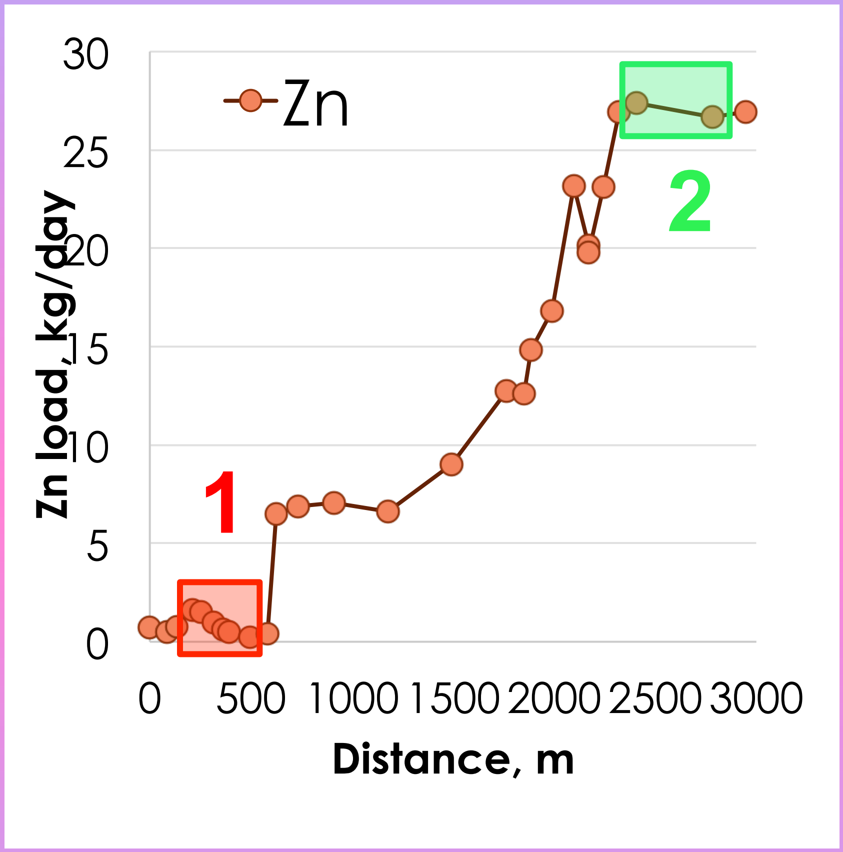
April 17, 2009
After heavy rain (63 mm/d)
No biofilm

May 7, 2009
No biofilm

May 21, 2009
New biofilm - biomineral restarts to precipitate

August 19, 2009
Mineralized biofilm

IMPORTANCE OF BIOPRECIPITATES- FIELD STUDIES

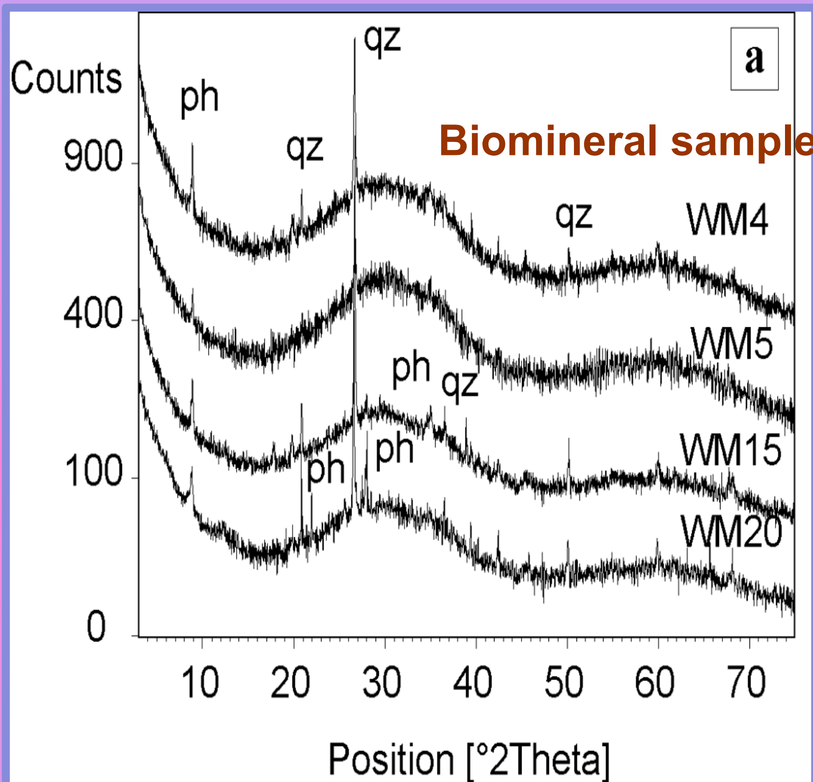


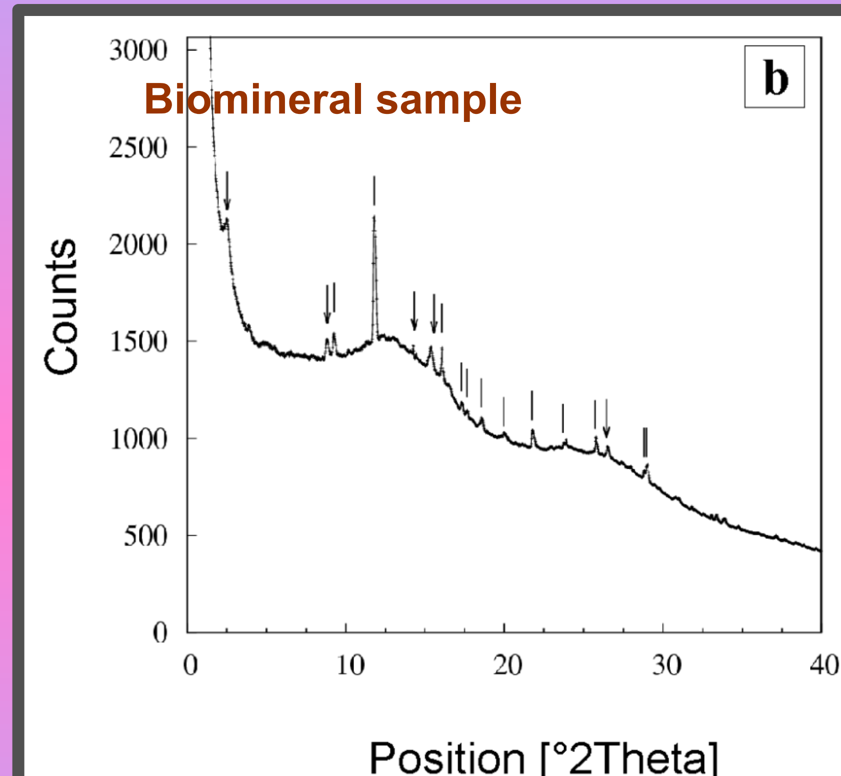
~ 0.7 kg Zn/day **lost** due to **Zn-Si biomineral** precipitation

~ 1.2 kg Zn/day **lost** due to **hydrozincite** precipitation

biominerals:
<u>natural filters of heavy metal contamination</u>

THE ZINC SILICATE BIOMINERALIZATION: conventional XRPD and S- R XRPD

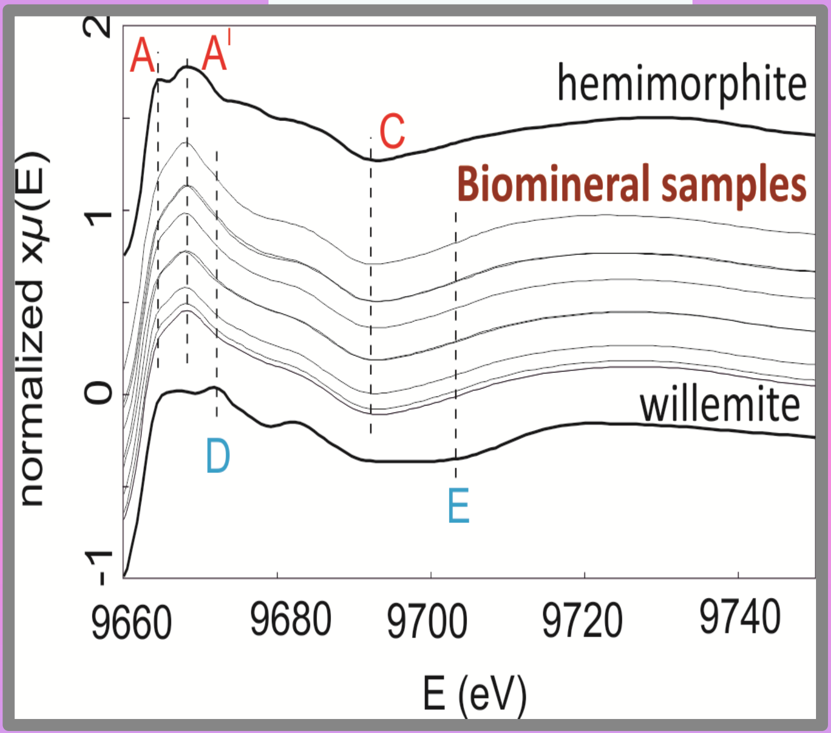




Dominantly amorphous nature of the biomineral
Minor contribution from quartz and other phyllosilicates

ZINC K-EDGE X-RAY ABSORPTION SPECTROSCOPY (1)

XANES



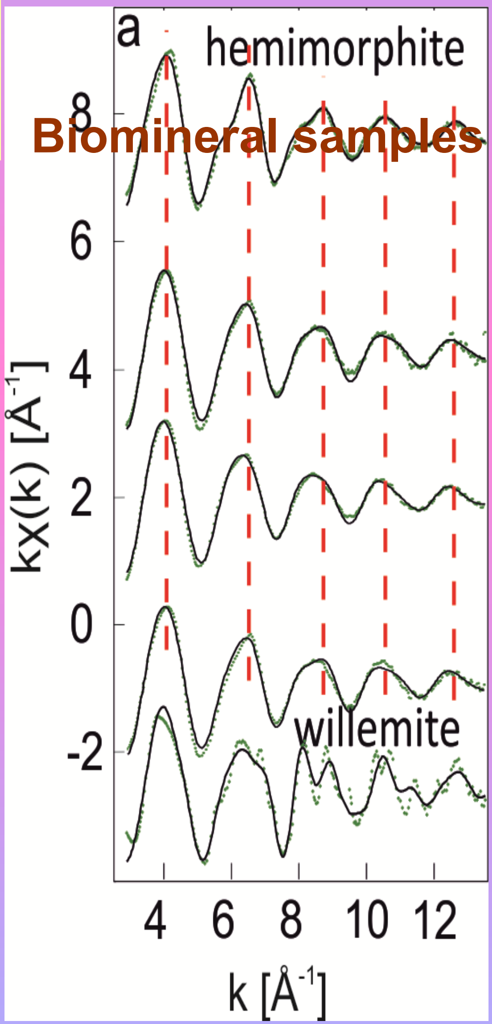
The best matching reference compound: hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$

Natural samples data: weaker structural features

⇩

Amorphous nature of Zn environment in the biomineral

EXAFS spectra



Similar XANES spectra: coordination chemistry is largely the same

ZINC K-EDGE X-RAY ABSORPTION SPECTROSCOPY (2)

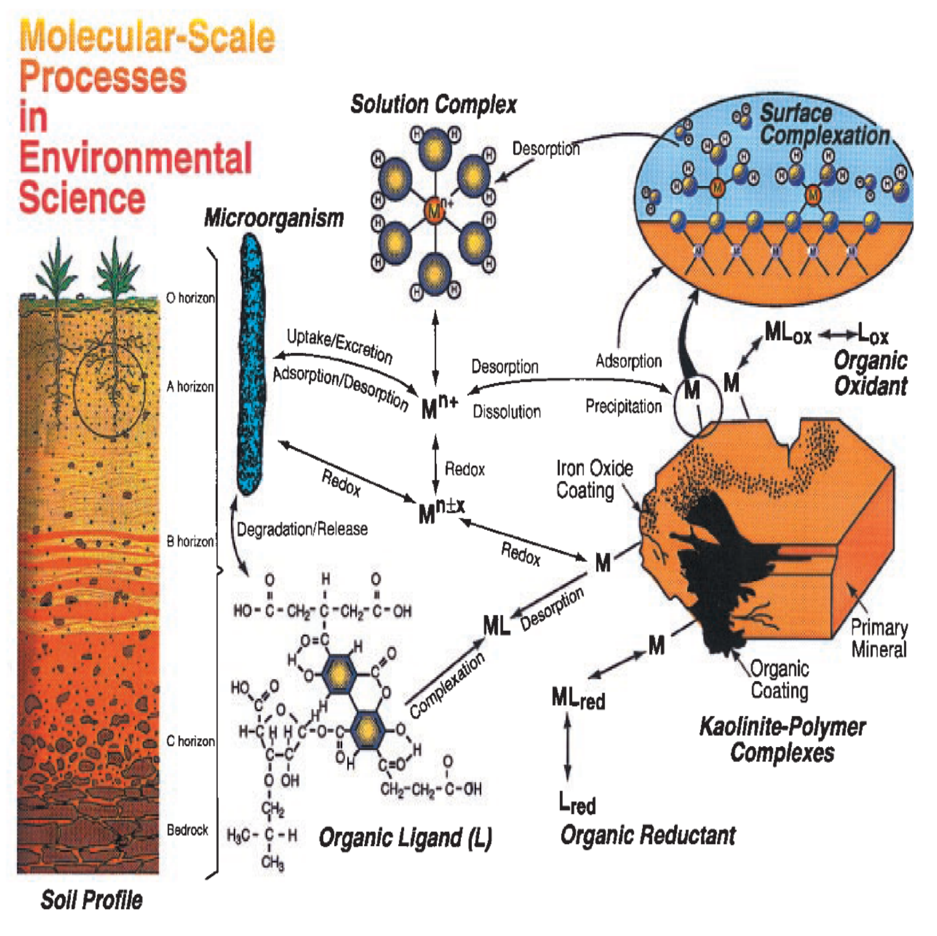
	CN	R (Å)
Hemimorphite – reference compound		
ZnO	4	1.93
ZnSi	3	3.24
ZnZn	4	3.40

(ICSD, Inorganic Crystal Structure Database)

	CN	R (Å)
Biomineral samples (N = 9)		
ZnO	4	1.95±0.01
ZnSi	1	2.99±0.03
ZnZn	1.5±0.5	3.27±0.03

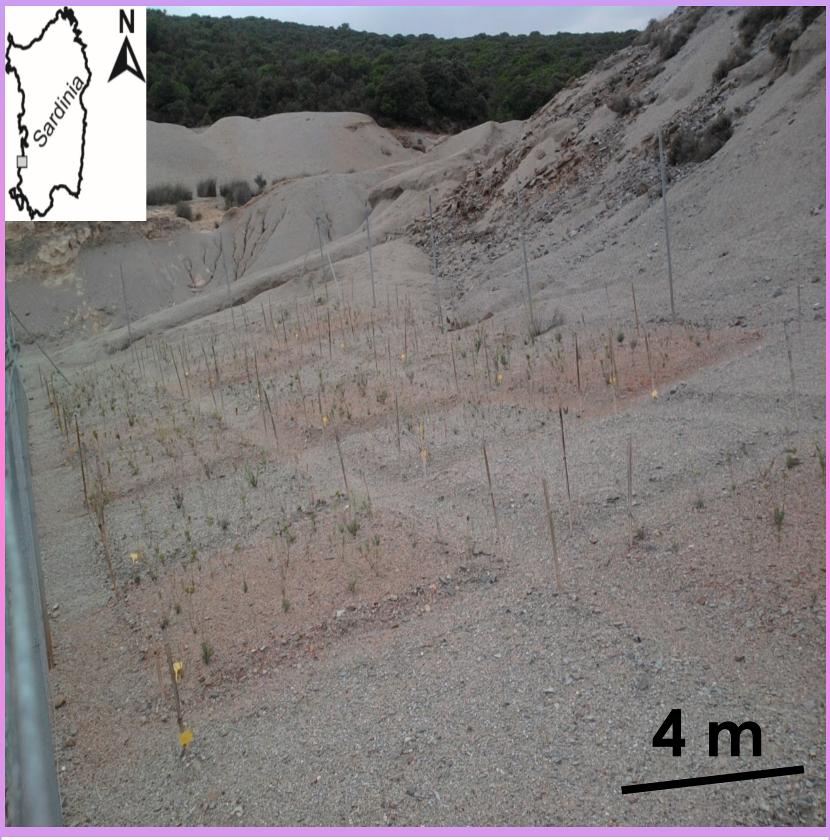
ZnO_4 tetrahedra are not simply dispersed into the structure, but form a Zn-rich mineral phase analogous to hemimorphite

BIO-GEO INTERACTIONS AT THE MINERAL ROOT INTERFACE



- Attenuation can occur also via processes at the rhizosphere.
- Synchrotron techniques allow us to achieve molecular scale knowledge on **dispersion** and **attenuation** of **metals** into the **environment.**

INGURTOSU FIELD TRIAL – phytostabilization by using pioneer species and selected soil microbes



An area of about 7.50 m x 22.50 m on the field site was divided into 27 subplots.

Soil vitalizing microbes:
- ✓ Bacteria (N-fixation).
- ✓ Mycorrhiza (P plant uptake).

Inorganic amendments
- ✓ red ViroMine^{TM}.

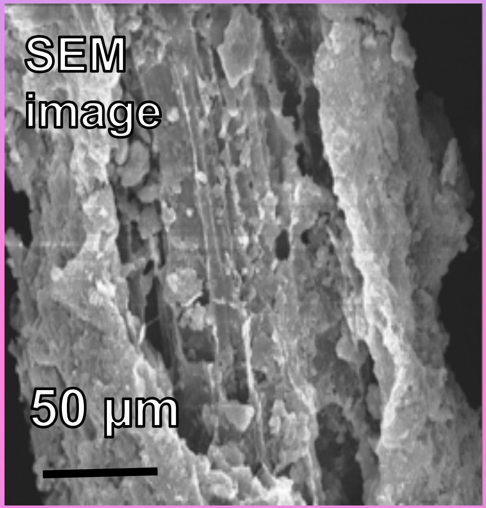
What **effect** on **rhizosphere processes**?
- ✓decreasing or preventing metal mobility (stabilization)
- ✓biomineralization.
- ✓Others…..

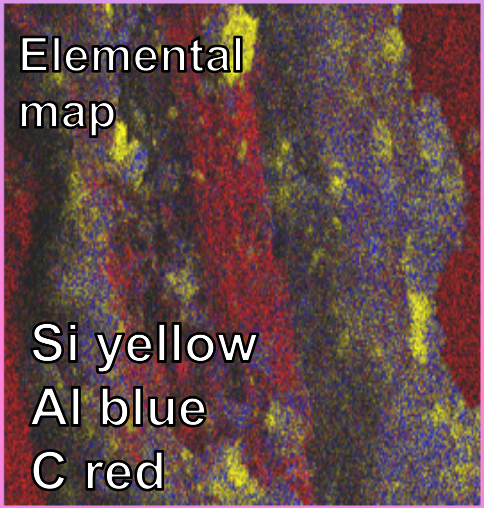
Euphorbia pithyusa L.

DISTRIBUTION OF ELEMENTS IN ROOTS

Euphorbia pithyusa L.

Scanning Electron Microscopy

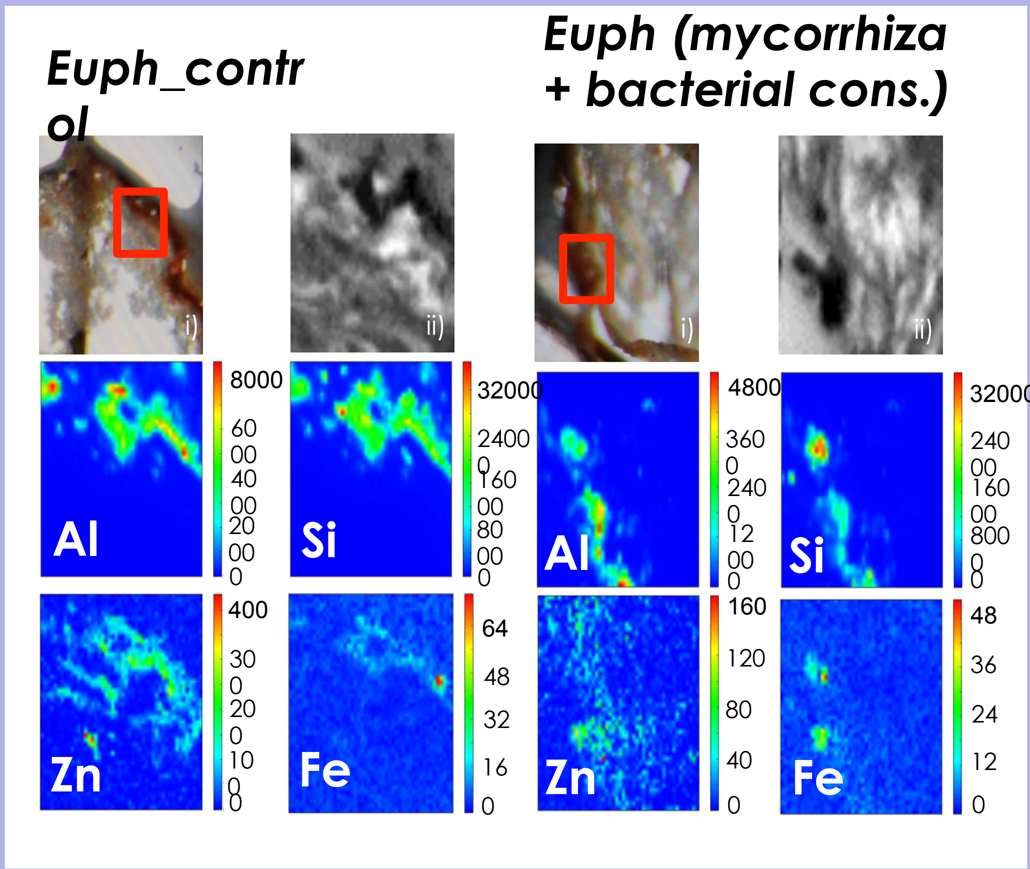




Root epidermis: mainly Si and Al.
Inner part (vascular tissue with the remaining degraded cortical cells): high concentration in C.

DISTRIBUTION AND SPECIATION OF ZINC IN ROOTS

Soft X-ray Microscopy combined with Low Energy XRF mapping:



EXAFS ANALYSIS

	CN	R (Å)
entire root (N = 5)		
ZnO	4.9±0.6	2.01
ZnSi	1.6±0.8	2.97
ZnZn	2.7±0	3.85
Euph_CP1a		
ZnO	4.5(5)	2.01(1)
ZnZn	1*	3.24(1)
ZnZn	2*	3.41(1)
Euph_CP1b		
ZnO	4.6(5)	2.03(1)
ZnSi	0.9(1)	3.02(1)

No variation in Zn speciation for the different soil treatments

SUMMARY

BIOMINERAL

- ✓ **Adaptation** of **bacterial life** along the stream and **variation** in **bioprecipitates**: natural filters.
- ✓ **Conventional XRPD** and **SR-XRPD** (synchrotron radiation XRPD) and **EXAFS** (extended X-ray absorption fine structure) investigation:
    - **Amorphous** nature of the biomineral.
    - **Zn** coordination **environment** similar to **hemimorphite.**

PLANT-ROOT INTERFACE

- ✓ Some **selected plants** grow on **mine waste** substrates.
- ✓ Al and Si play a significant role in the interaction between soil and plant roots: **biomineral processes**.
- ✓ **Zn** is concentrated in an **external rim** made of Si, Al and O forming a **Zn-silicate**.