Cementitious Materials for Waste Treatment, Disposal, Remediation and Decommissioning Workshop

SCORI
ATILH

Re-use of waste and behaviour of heavy metals : a molecular approach of the transfer mechanisms

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Collaborations

Synchrotons
ESRF, SLS, SOLEIL

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School of MINE - PARIS
Centre de Géosciences

L. De-Windt

CEA

L.Trotignon

Mechanistic approach

- Speciation of metals and metalloïds : role of cement phases (low concentration below hydroxides,… solubility limits)

- Metal behavior in cement at the lab scale (Cr and Pb)
- Metal behavior in slag at the lab scale v.s field scale (same materials)

Case of solid and liquid waste containing heavy metals.

- Speciation of metals and metalloïds within the source term : atomic environment and redox state: affects mobility and toxicity

A lot of examples: Cr^{III}/Cr^{VI}, $V^{III}/V^{IV}/V^{V}$, As^{III}/As^{V},

Inorganic v.s organic form: **Toxicity**

AsH_3>As(-III)>As(III)>As(V)>As-organic

Speciation in the solid phase

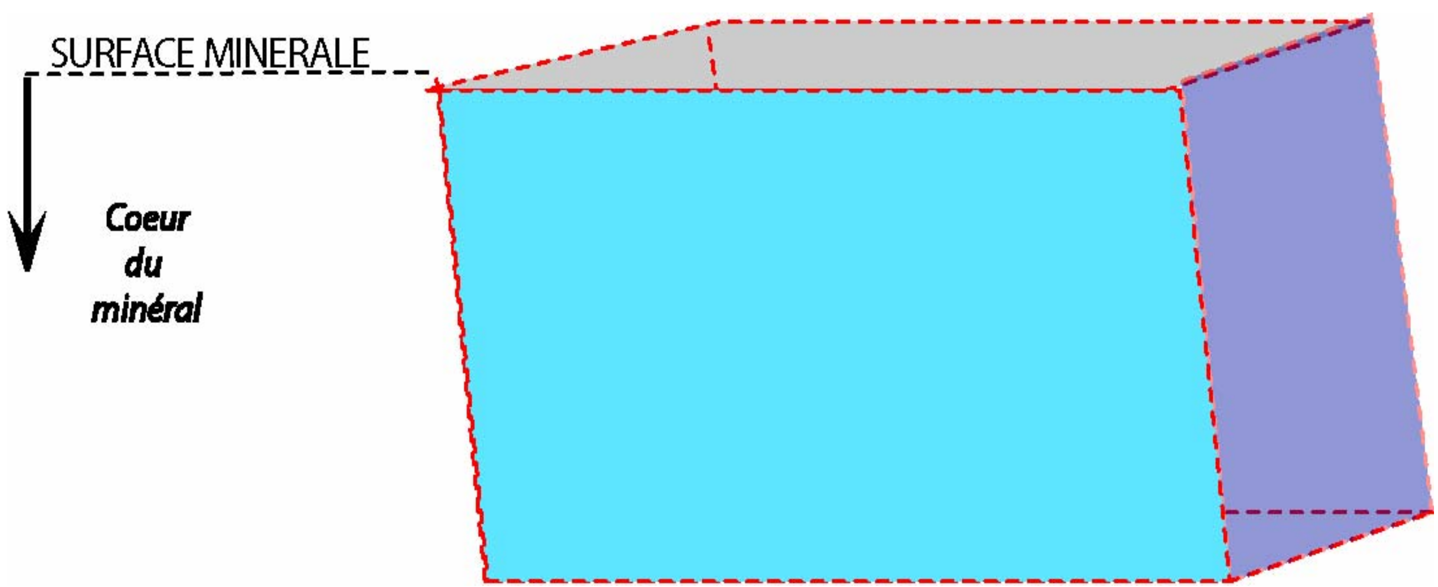
- Presence of a metallic phase (oxide, hydroxide, carbonate, sulfate…)

Table 1. Relation between metal concentration, solubility, and toxicity.

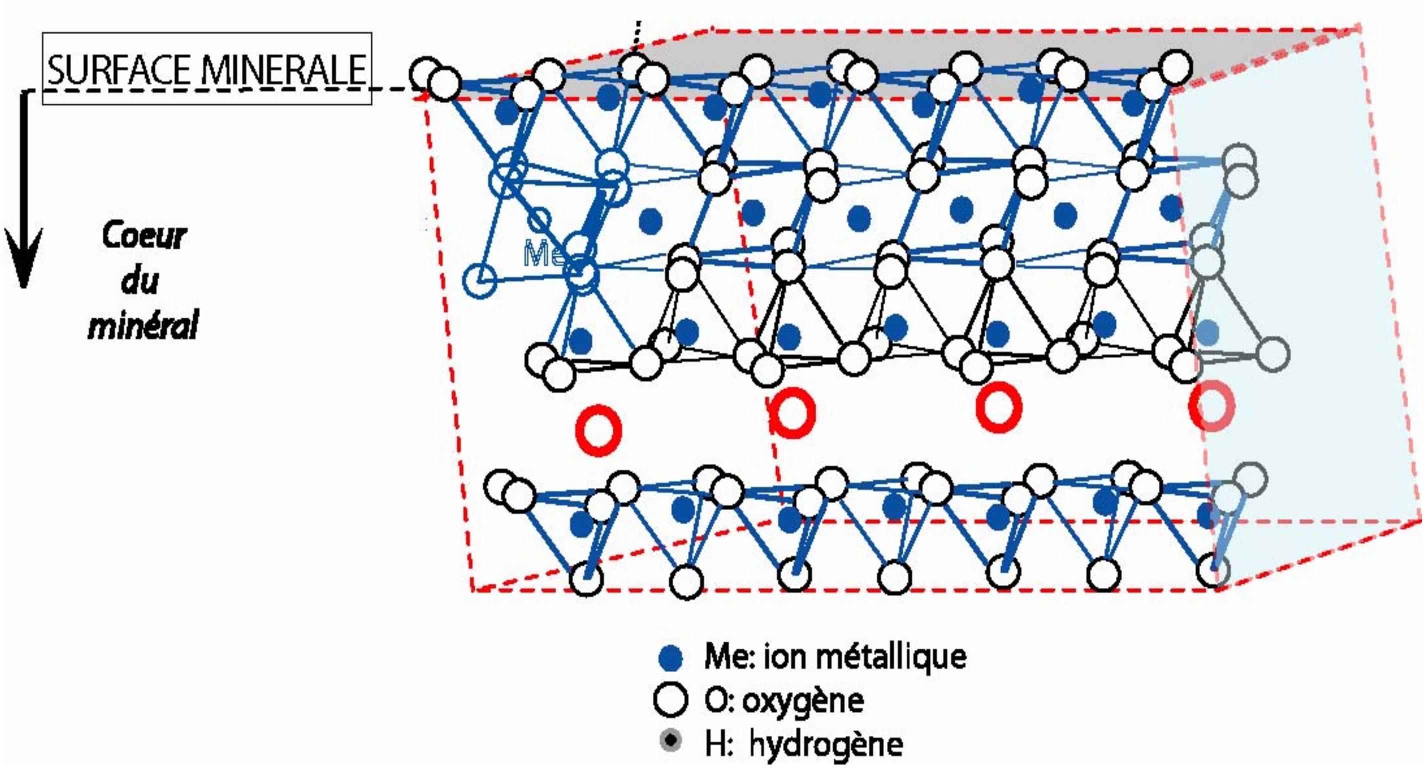
Compound	*Toxicity upon ingestion (mg / kg)*	*Solubility*	*[Co]*
Cobalt	> 7000	2 mg/l	100%
Co oxide	> 5000	8 µg/l	71%
Co sulfate	768	60 g/l	22%
Co chloride	766	76 g/l	24%
Co nitrate	691	240 g/l	20%
Co acetate	503	237 g/l	23%

Speciation in the solid phase

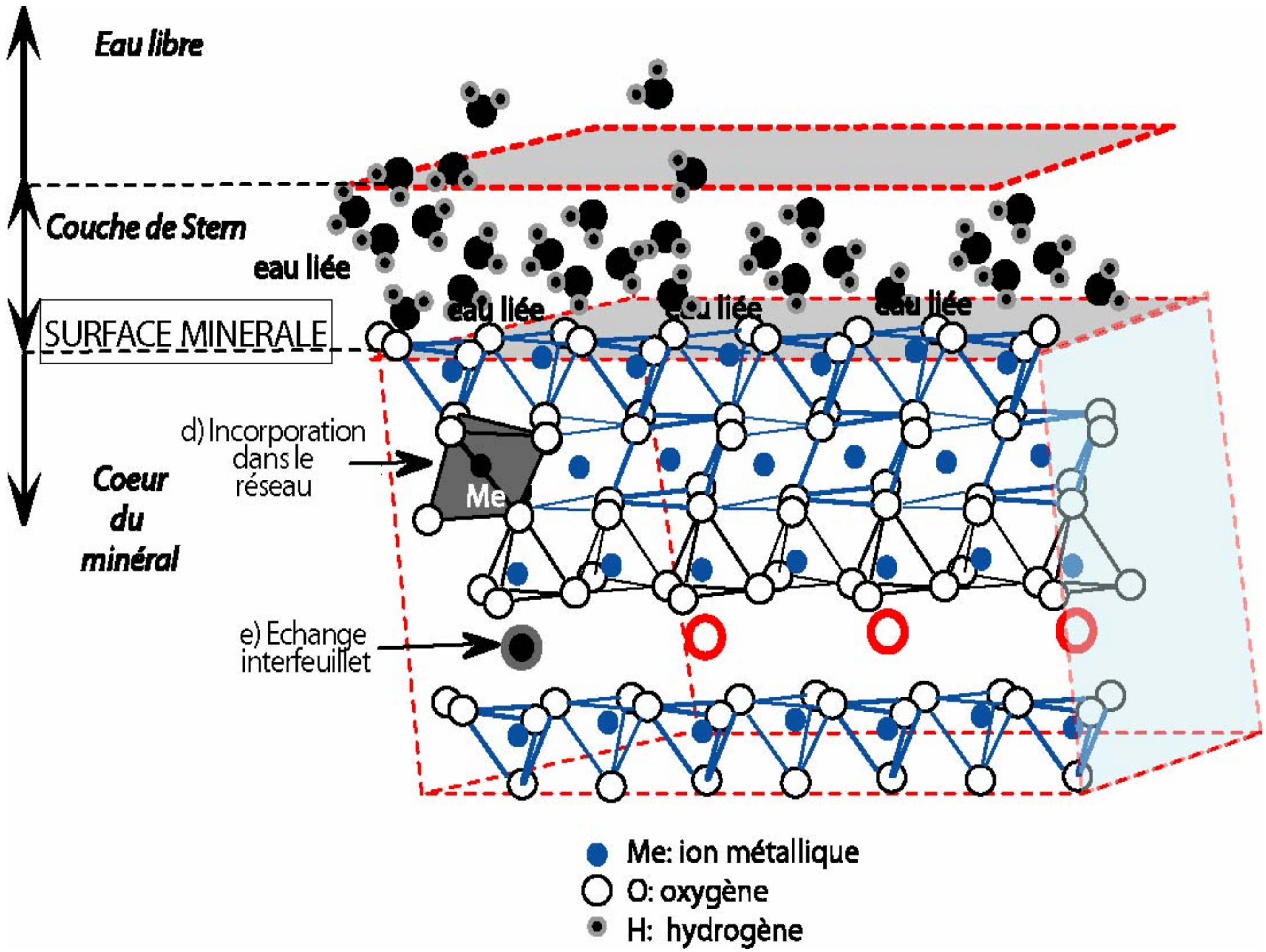
- No metallic phase : more complex: interaction between minerals and dissolved elements



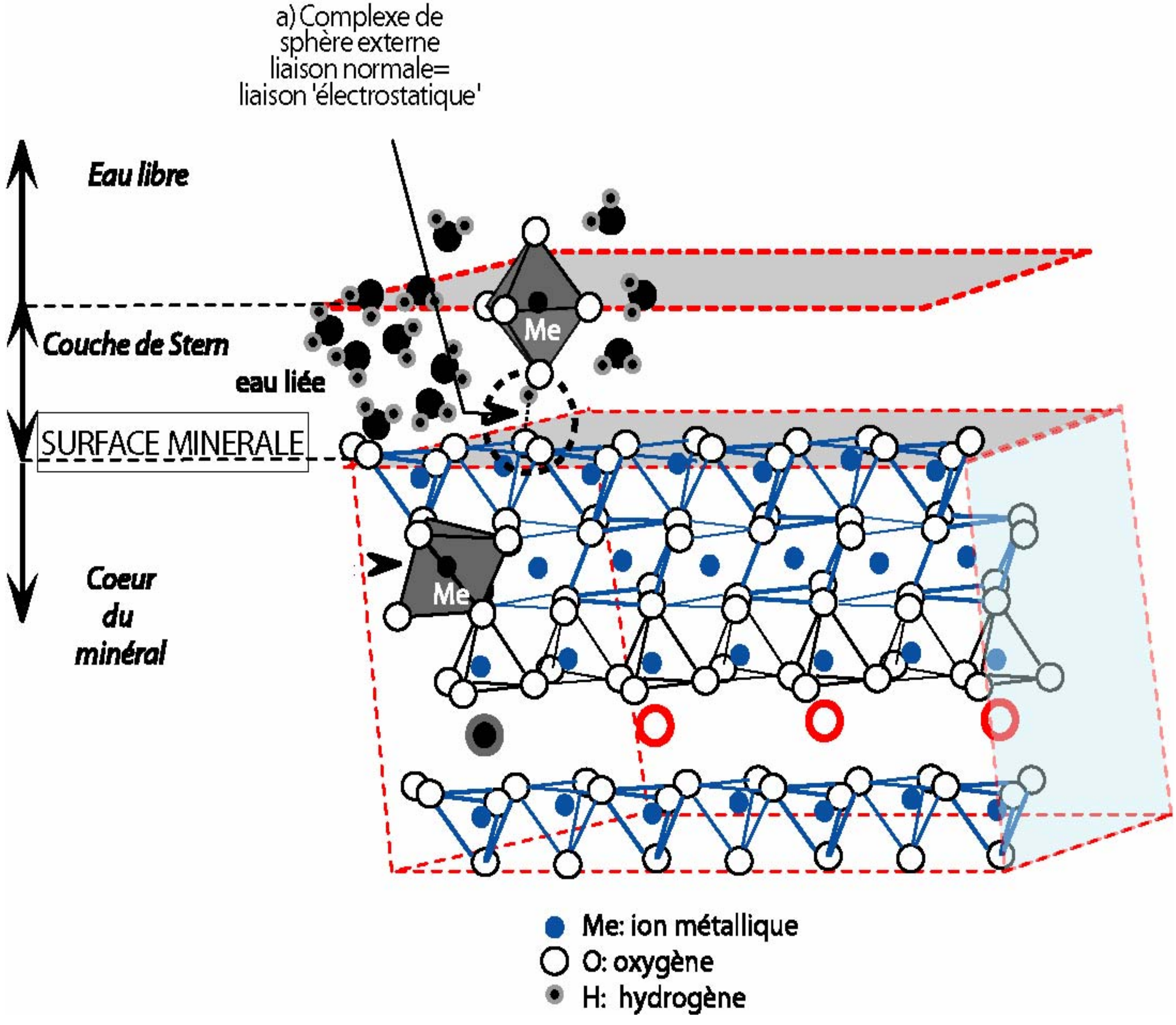
Speciation in the solid phase



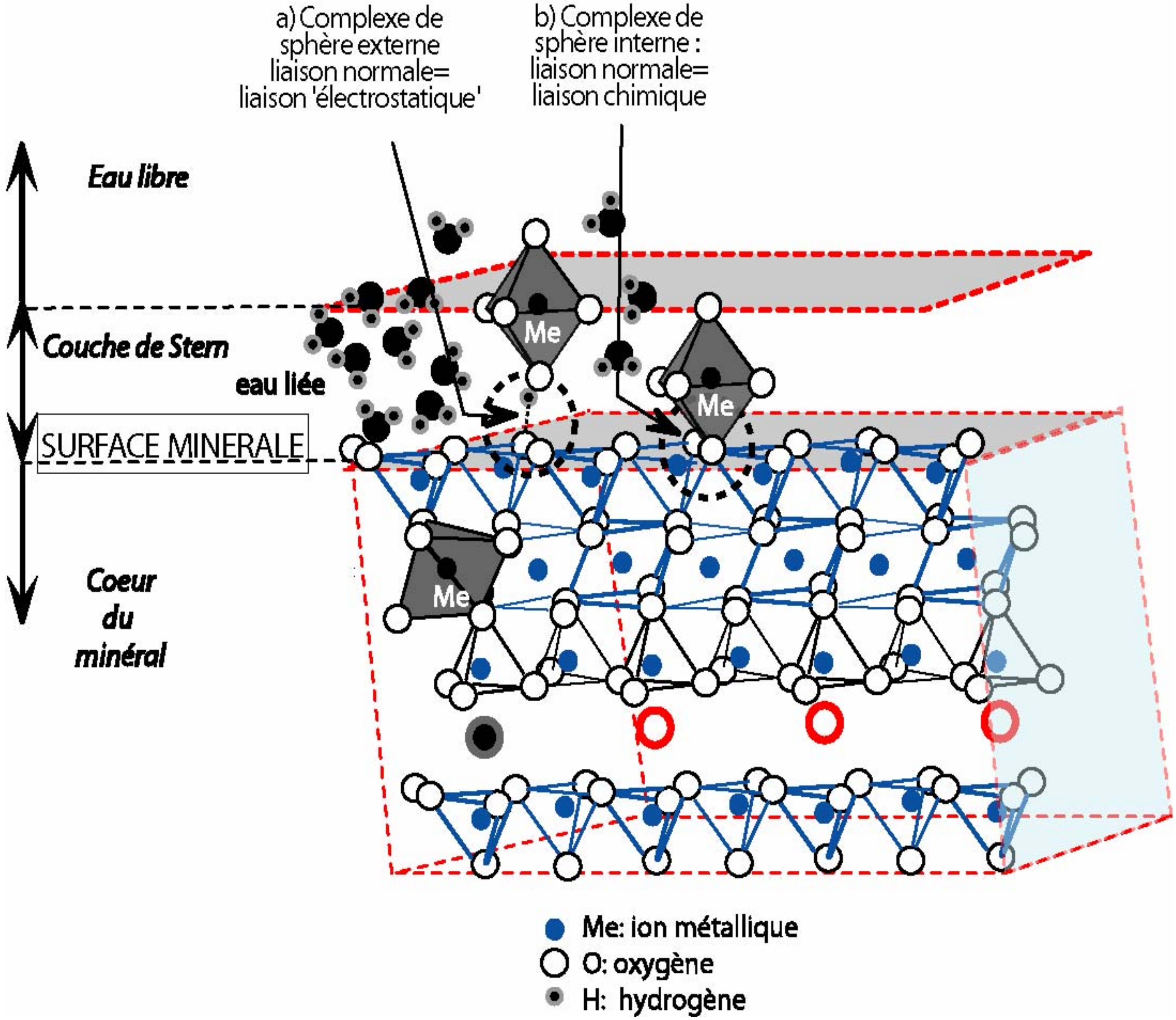
Speciation in the solid phase



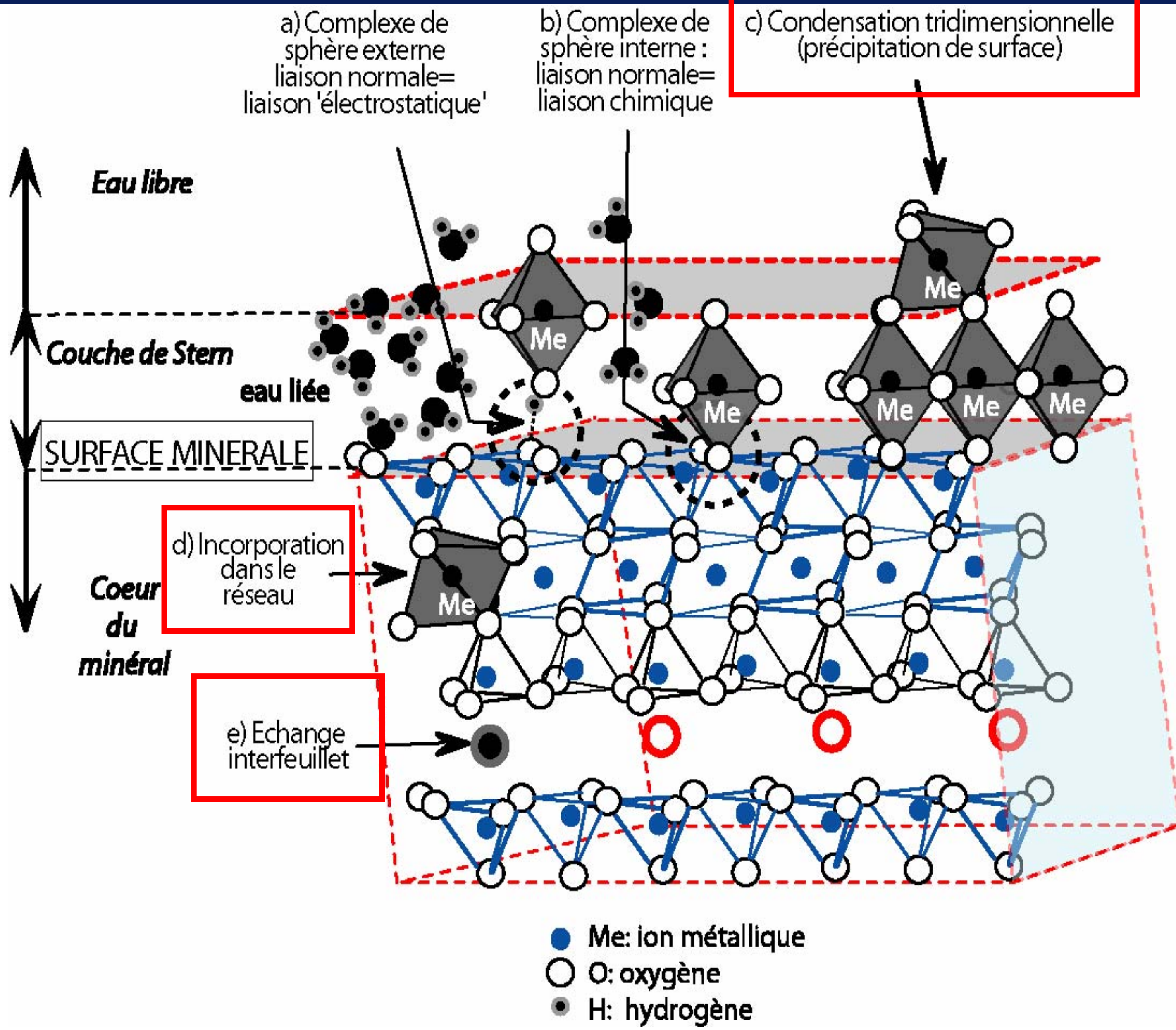
Speciation in the solid phase



Speciation in the solid phase



Speciation in the solid phase

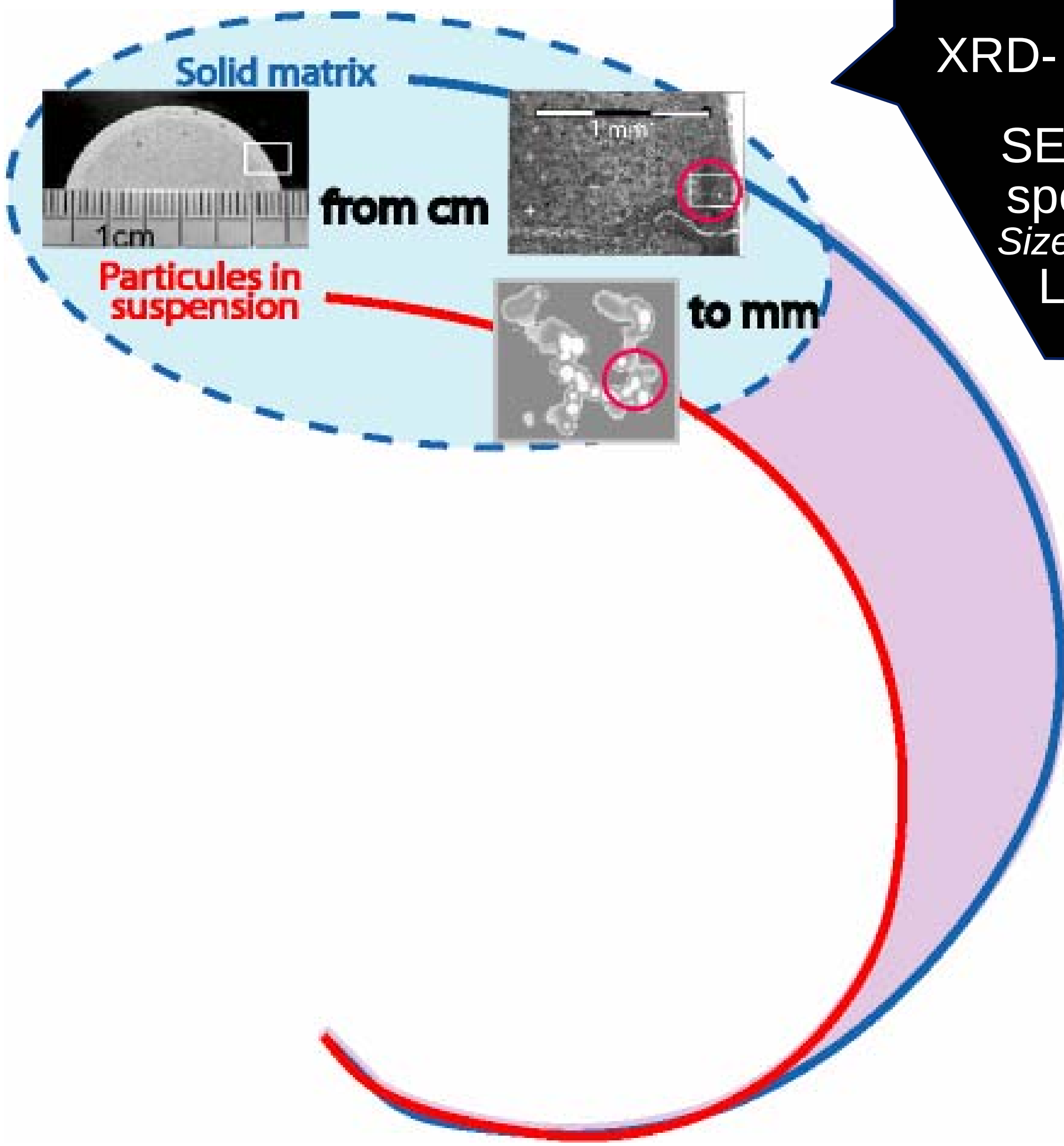


How can we determine the speciation in such complex matrix

- It is almost impossible…

but

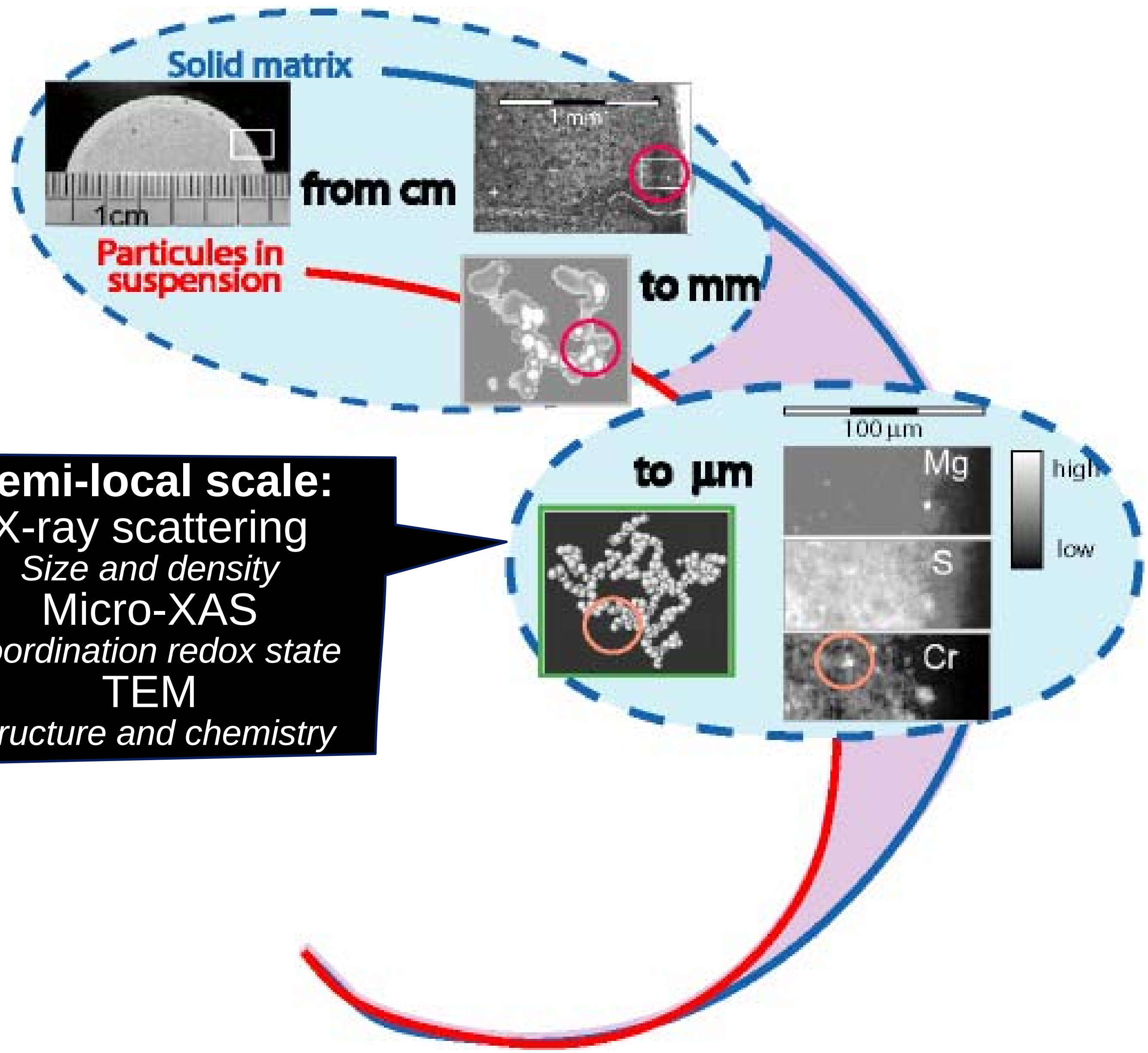
Multi-scale structural study



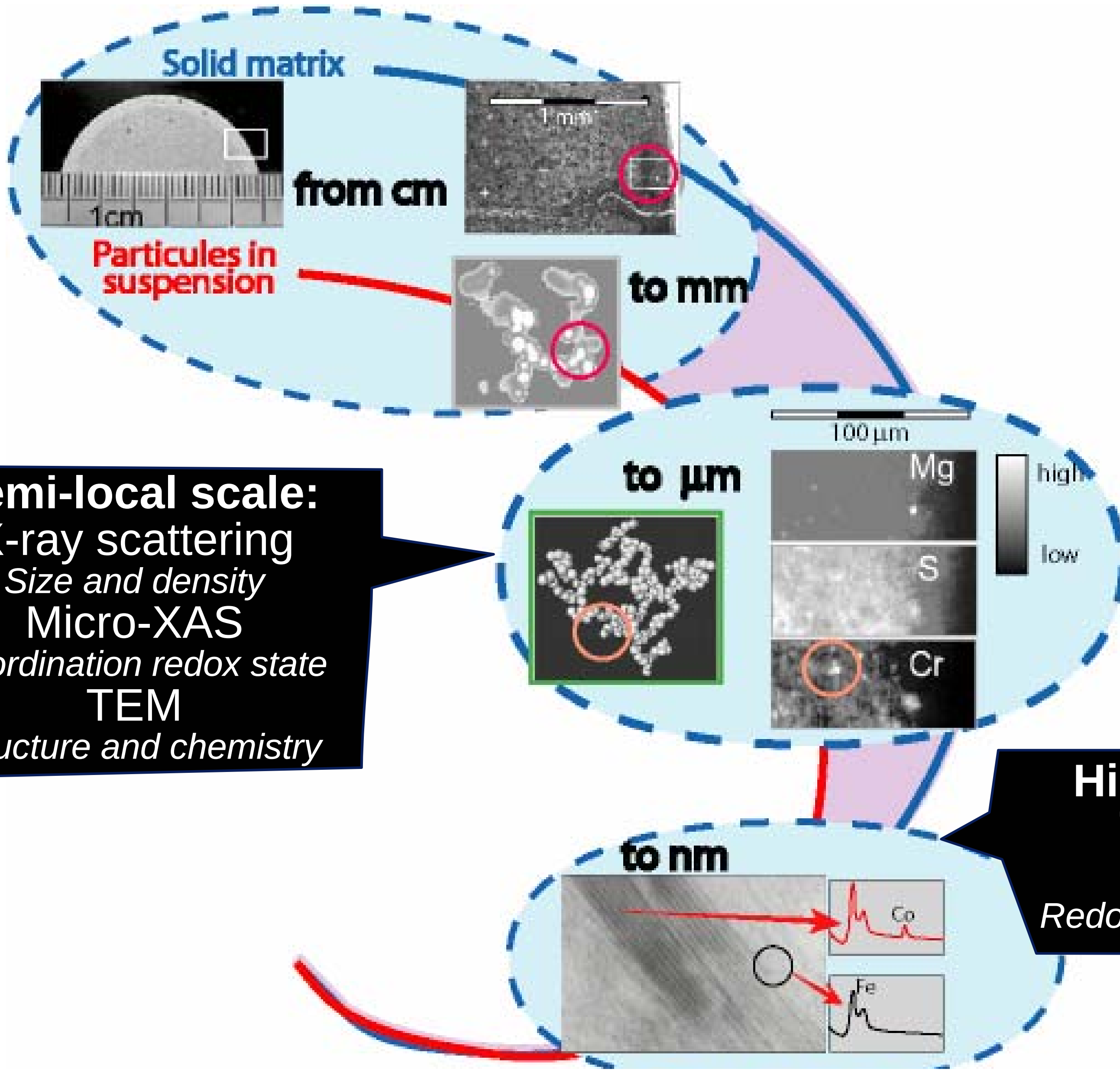
Macro-scale:
XRD- Optical microscopy
Mineralogy
SEM-ESEM+ X-ray spectromicroscopy
Size, structure, chemistry
Light scattering:
Size and density

Multi-scale structural study study

Semi-local scale:
X-ray scattering
Size and density
Micro-XAS
Coordination redox state
TEM
Structure and chemistry



Multi-scale structural study

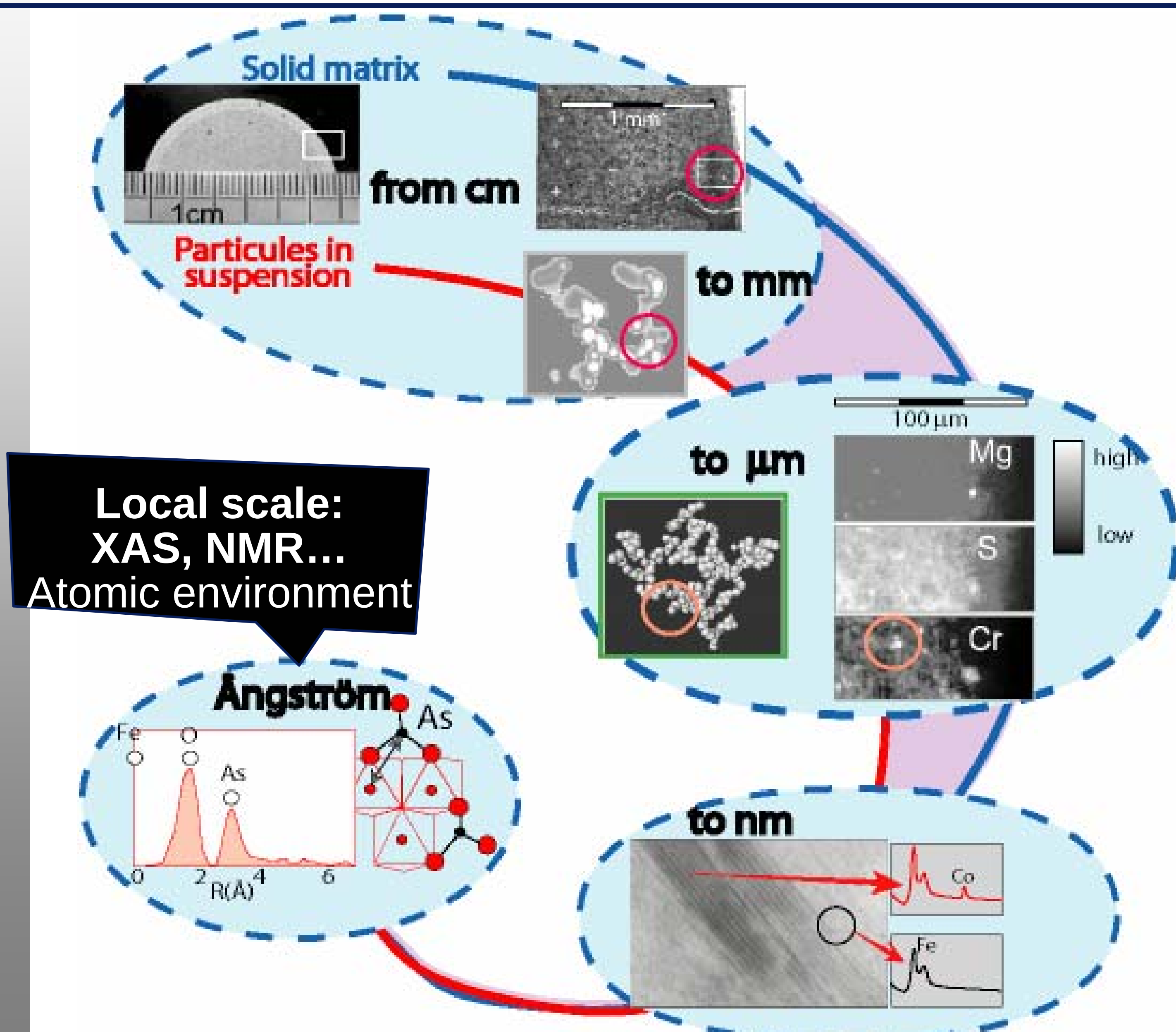


Semi-local scale:
X-ray scattering
Size and density
Micro-XAS
Coordination redox state
TEM
Structure and chemistry

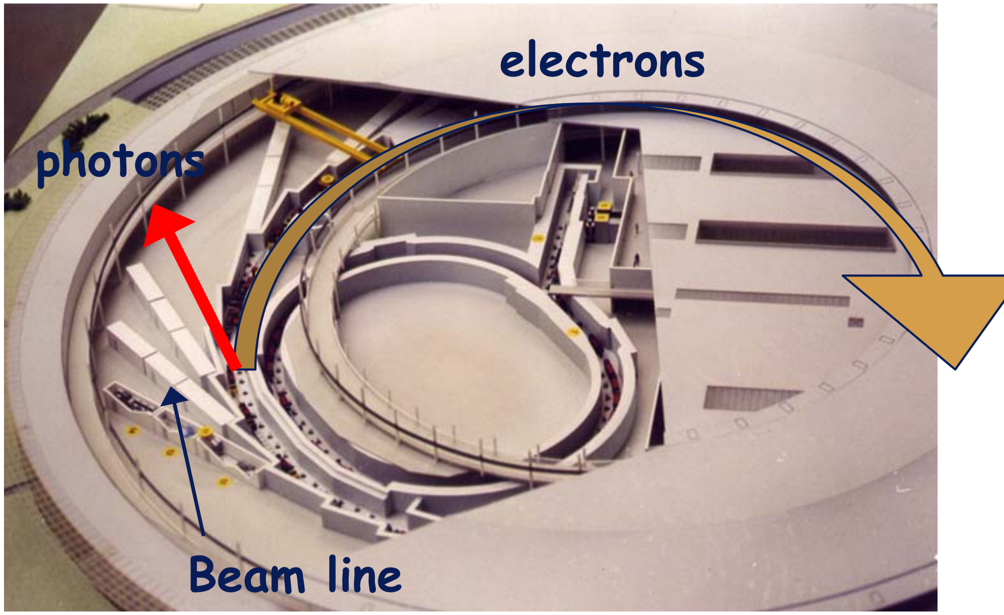
High resolution TEM+EELS

Redox state, coordination

Multi-scale structural study

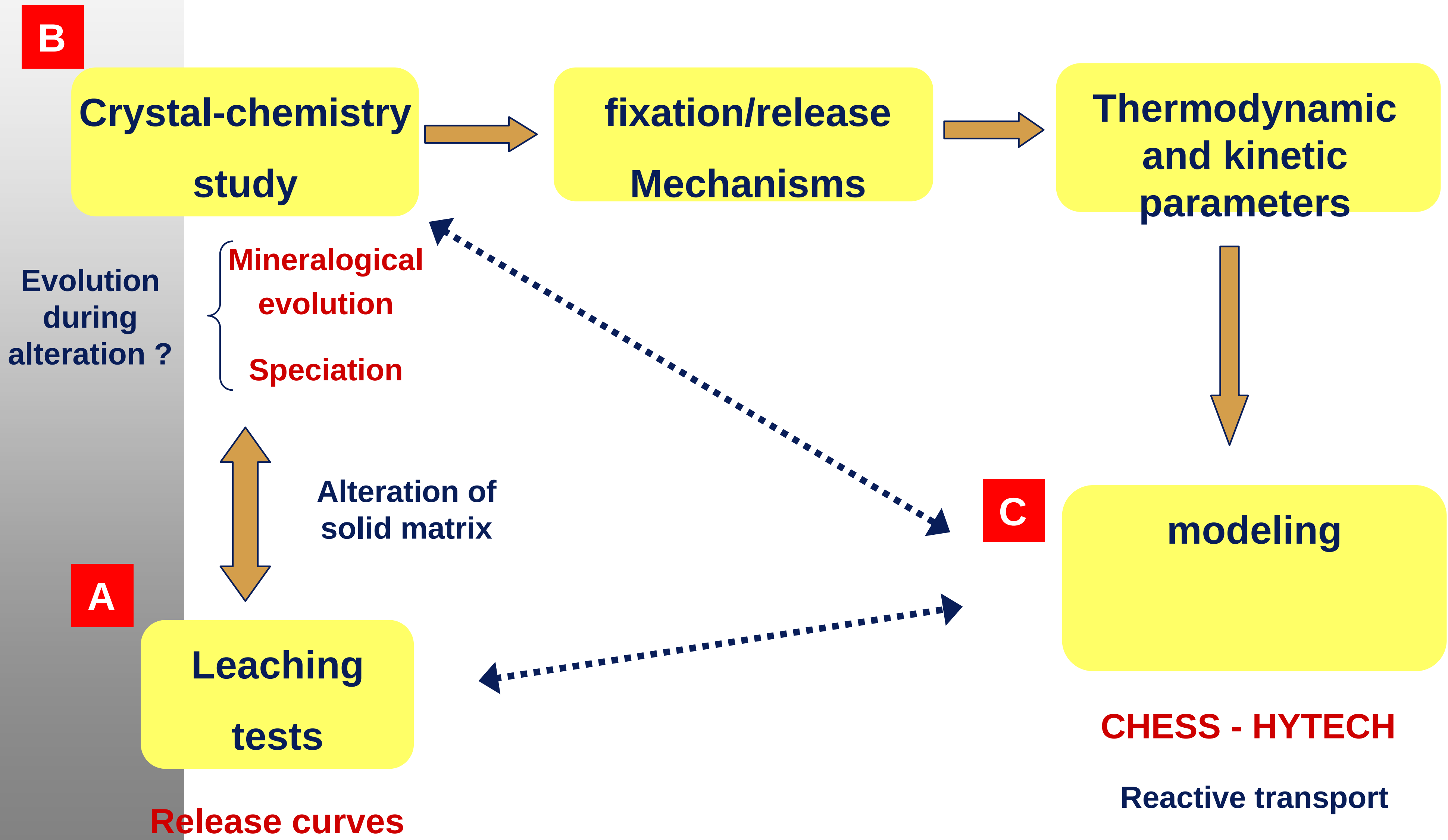


Synchrotron



Projet SOLEIL, Orsay

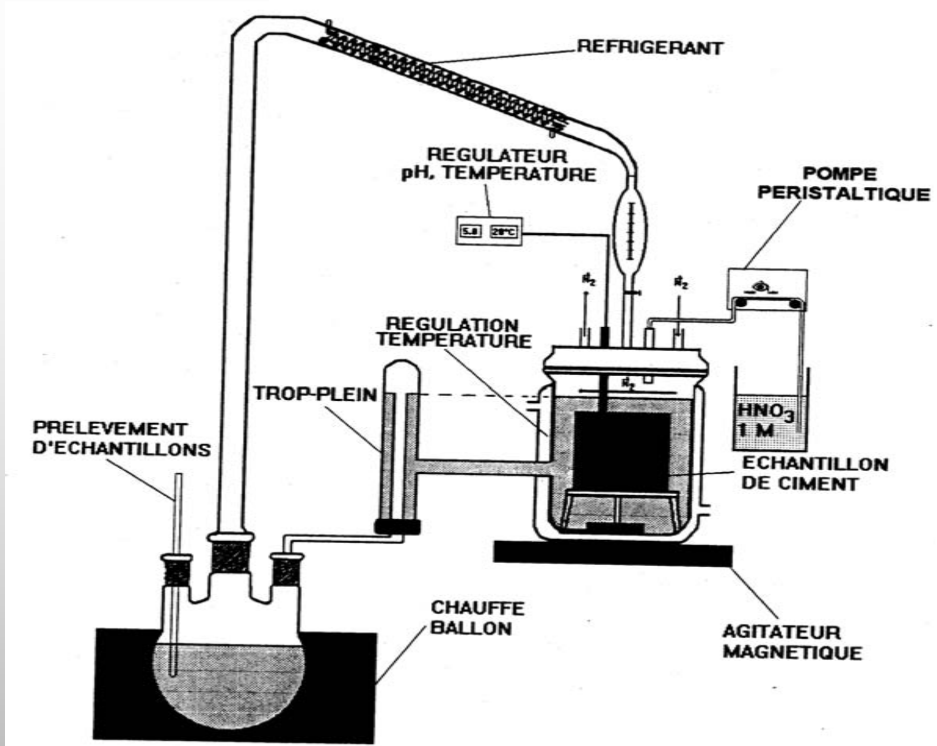
Speciation : not enough…

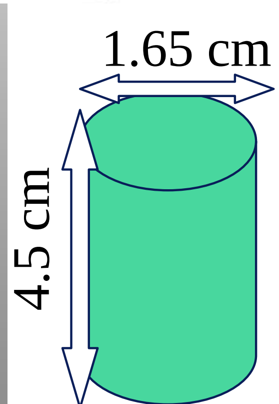


Some examples

- Cr(VI) in cement phases (waste co-firing)…(before Fe(II) treatment)
- Pb in cement phases
- Cr and V in BOF Steel slag (reuse in road making)

Cr in cement: Experimental conditions





1 CEM I
1 CEM III/A

L/S = 0.5
28 days
Cr^6 or Cr^3
0-2000 ppm

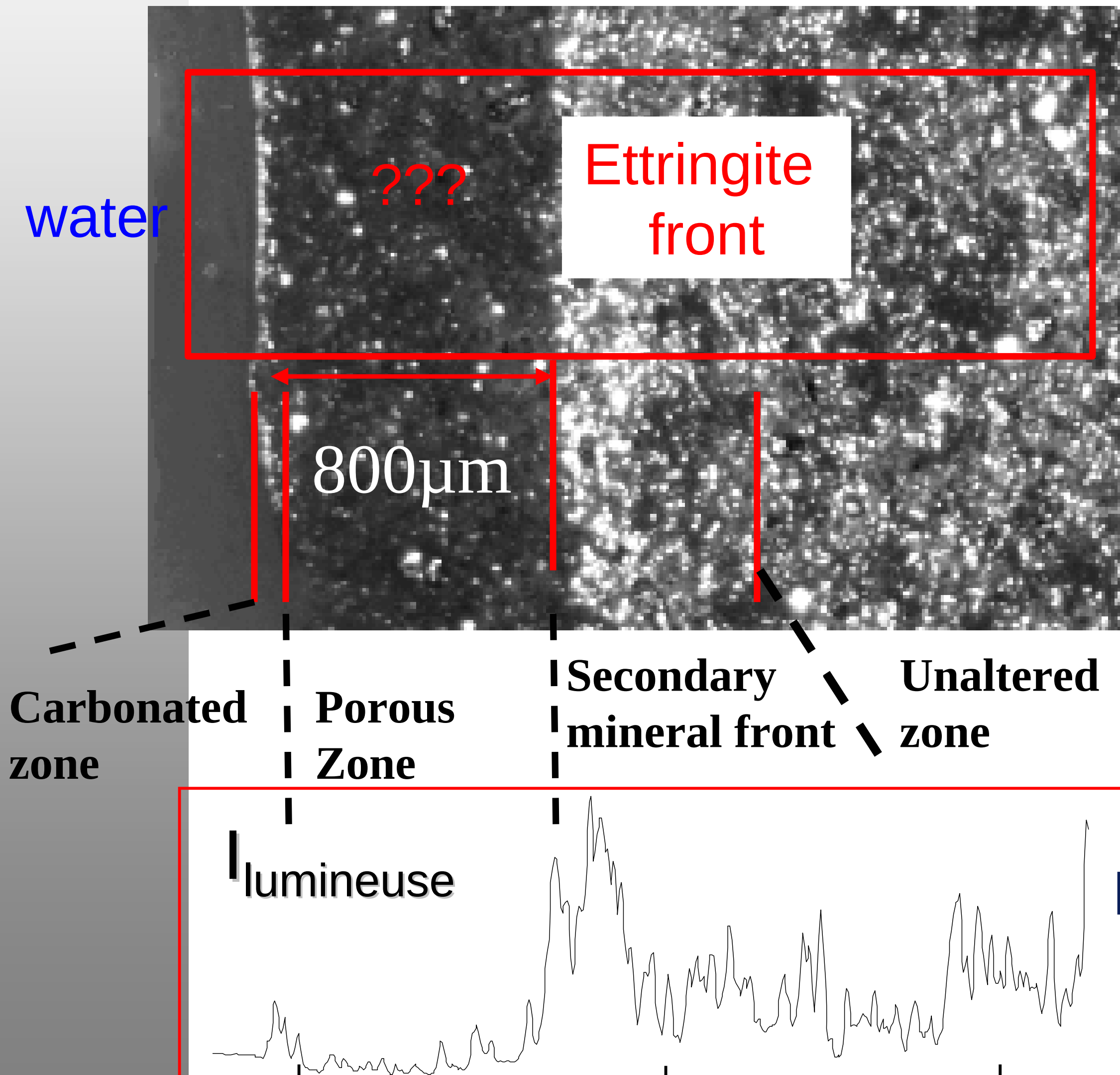
Leaching: 42 days pH = 5 température 40°C

Analyses: liquids and solids

Moudilou, E.; Bellotto, M.; Defosse, C.; Serclerat, Y.; Baillif, P.;Touray, J. C. Waste Manage. 2002, 22, 153-157.

High spatial heterogeneity: chemical, mineralogical, textural: importance of imaging techniques

Image of the surface of altered cements



Polarized light microscope

HM behaviour?
Micro-XRF/XRD
Micro-XAS

Chromium behaviour during leaching

Case of Cr:

Cr(VI)-Cr(III):
Cr(VI) is more soluble (and toxic) and should be released (diffusion). Cr(VI) should be absent in the altered layer after the ettringite front? (predicted by models)

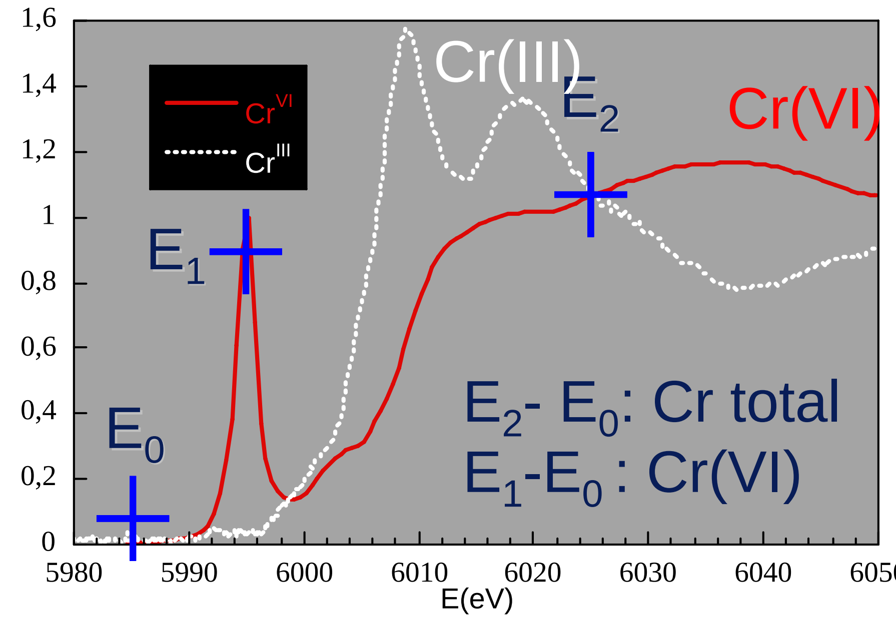
Prediction: analysis of the solid matrix is needed

Chromium behaviour during leaching

µ-XANES-µ-SXRF (ESRF)

- Beam size : 1x1µm
- Detection limit : few 10 ppm
- Enable speciation of Cr

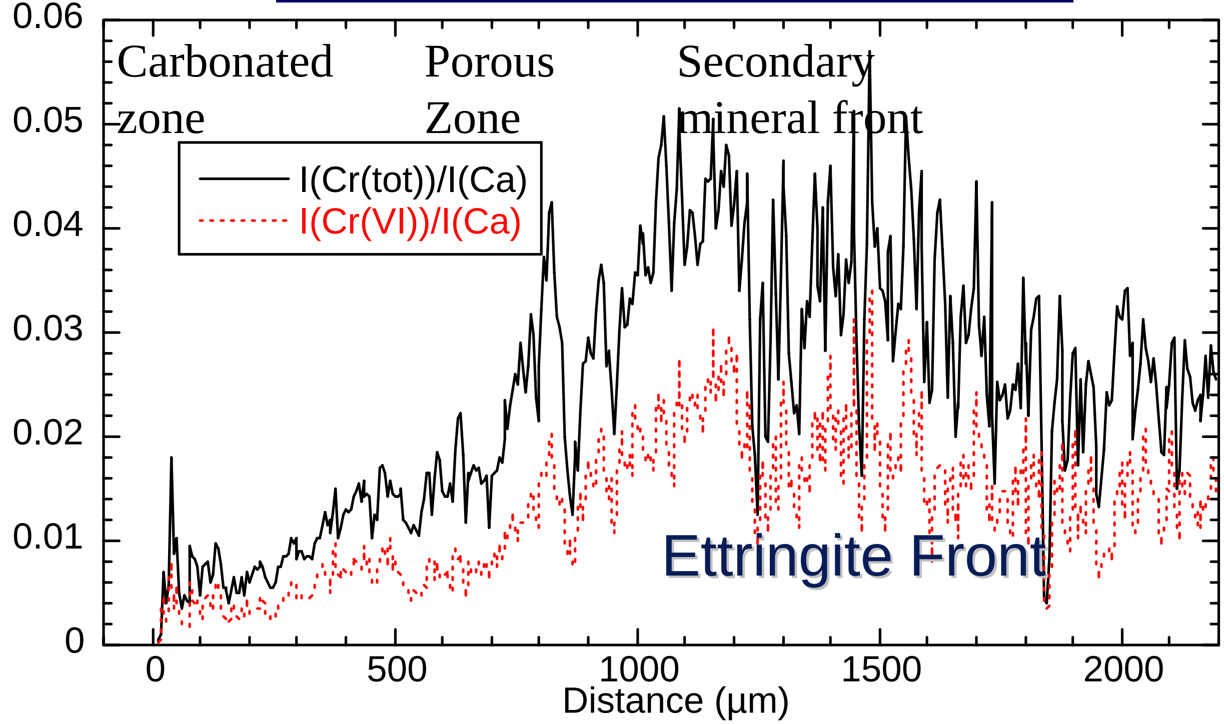
ID 21 Beamline ESRF-Grenoble France

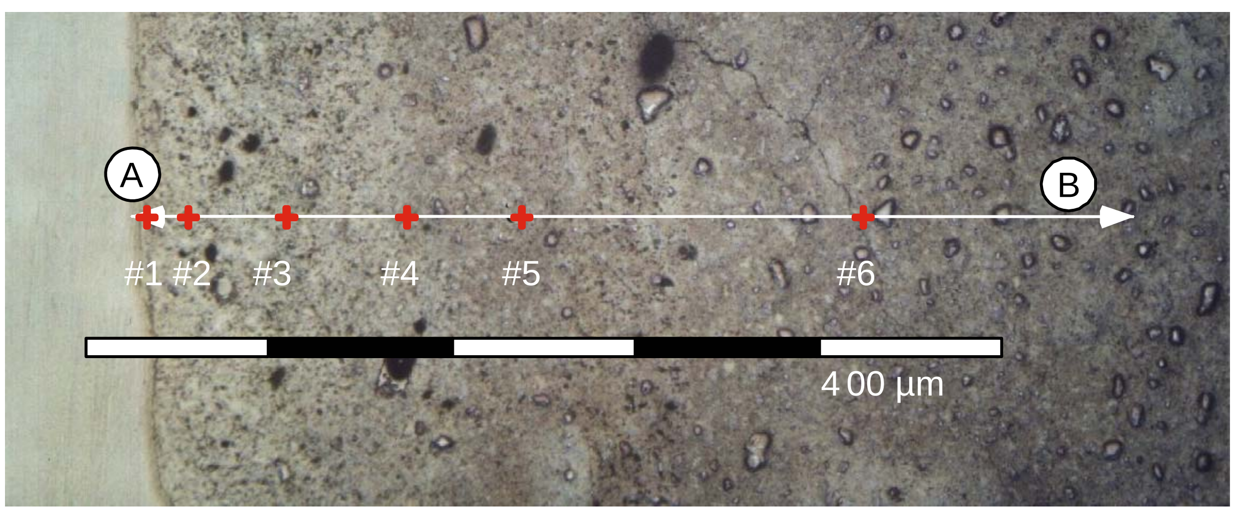


Cr (tot) and Cr(VI) line scans high spatial heterogeneity

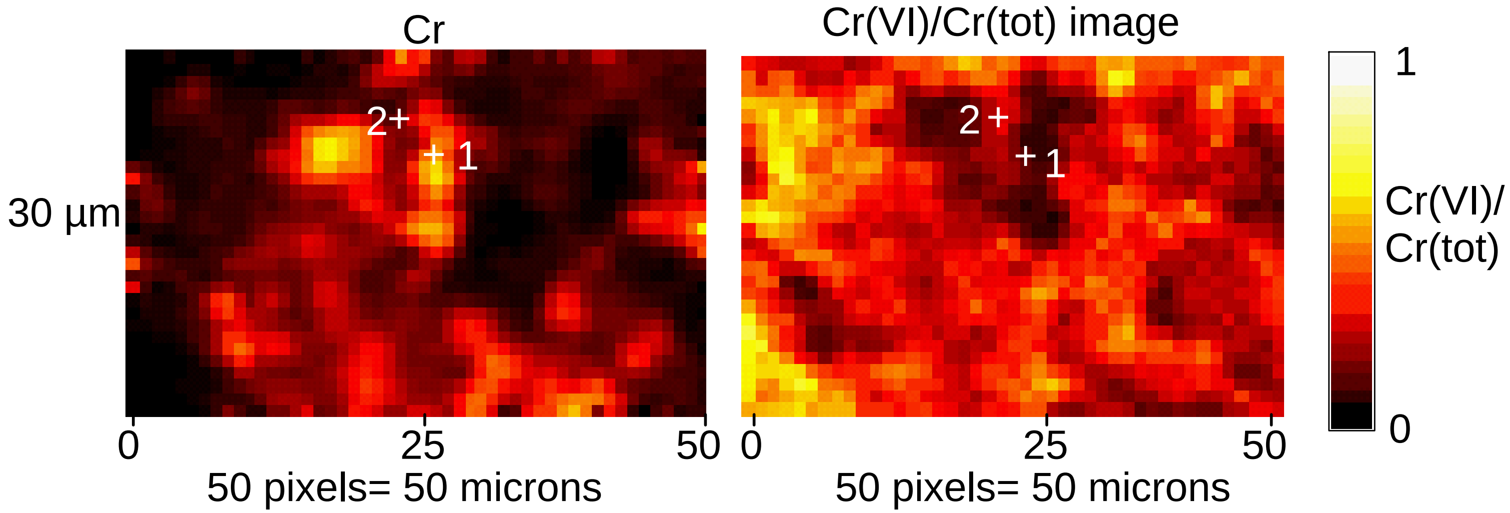
Surface layer

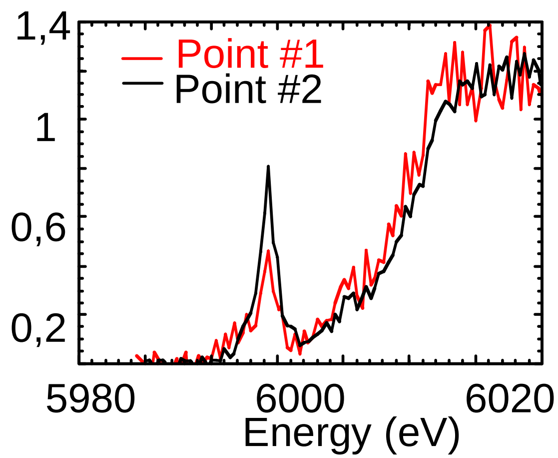
Unaltered zone

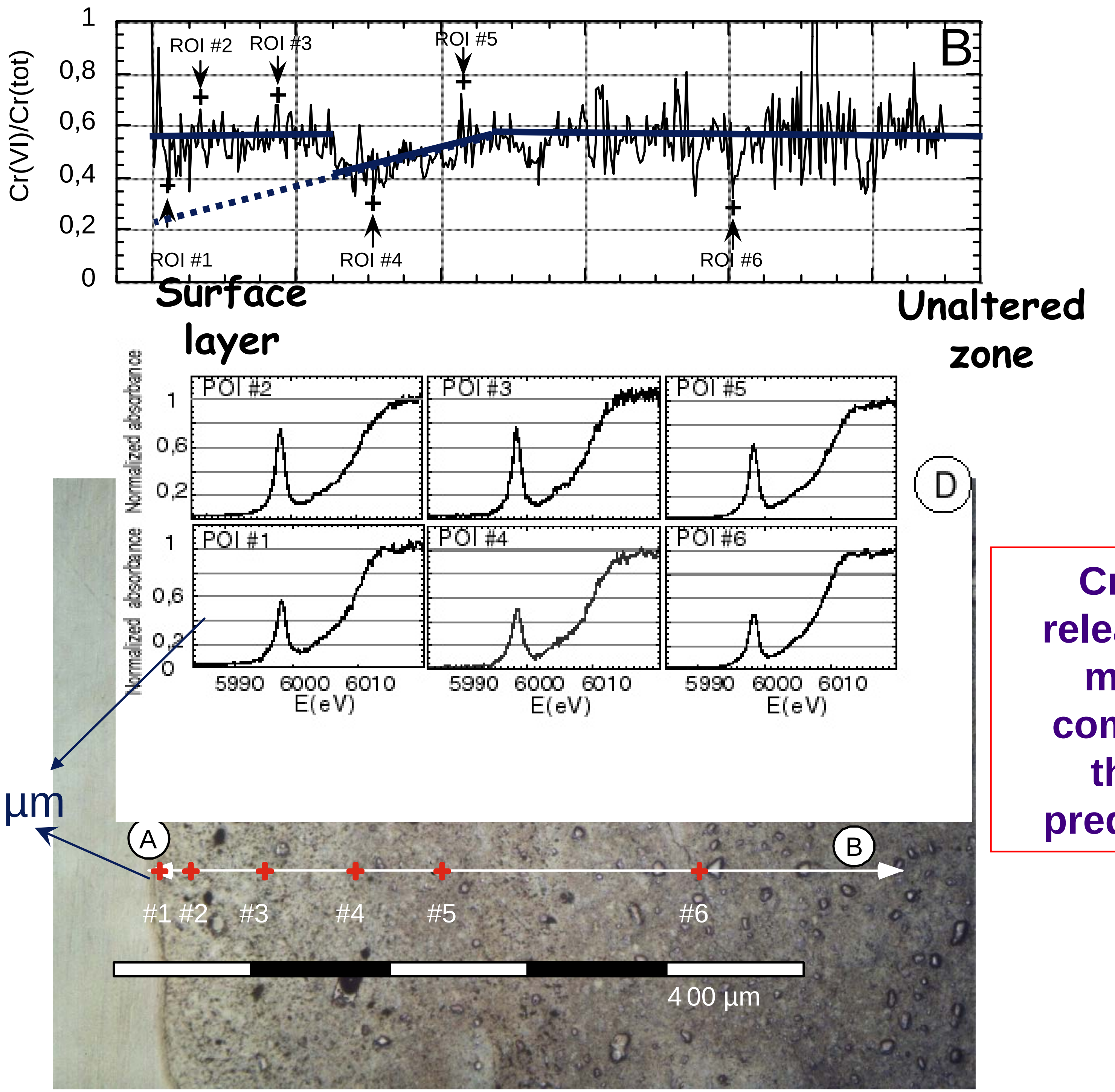




Cr (tot) and Cr(VI) images: high spatial heterogeneity







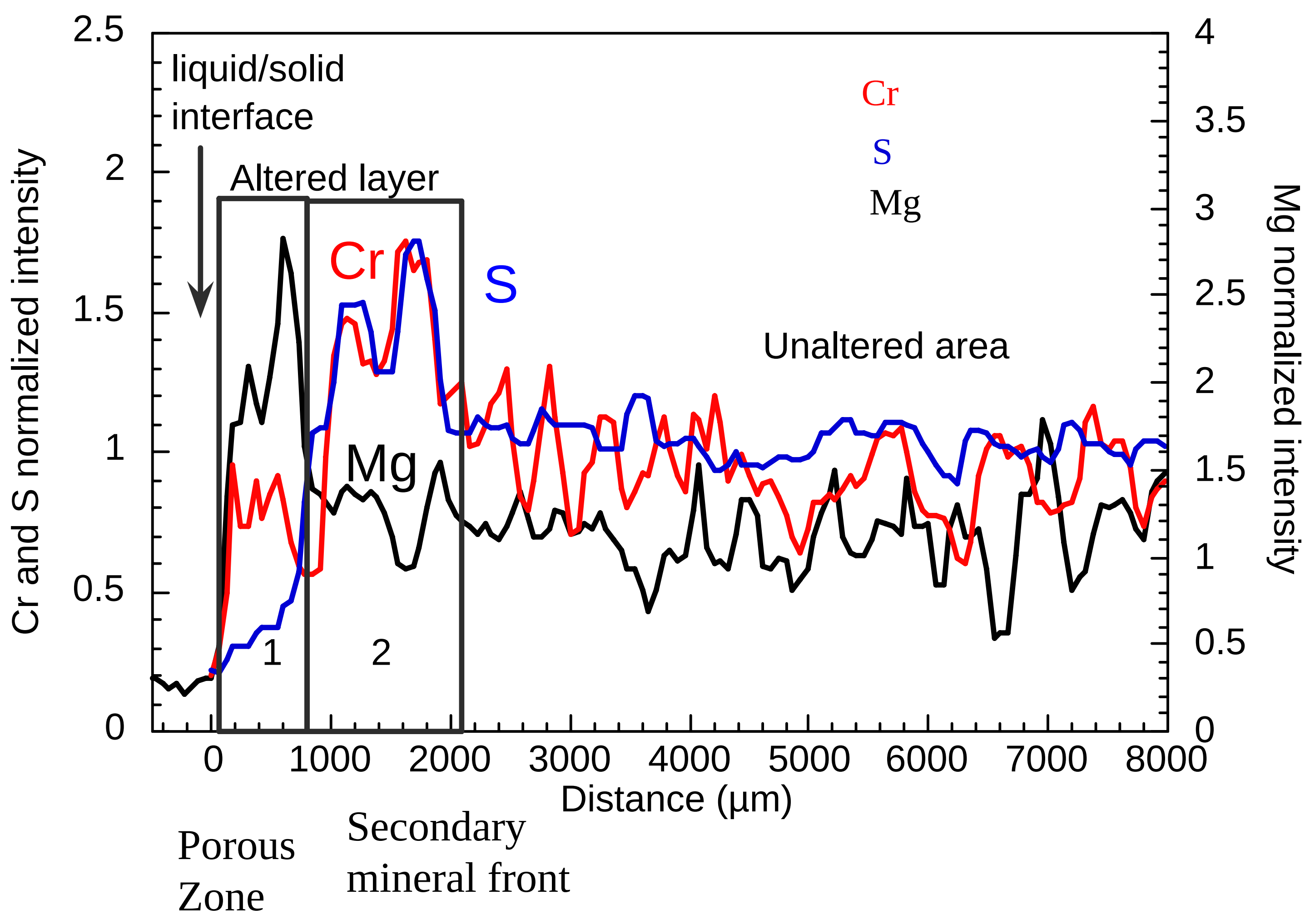
Cr(VI) release is more complex than predicted

Rose, et al, 2003, *Environ.Sci. Technol.*; *37*(21) 4864 – 4870.

Chromium behaviour

- Cr(VI) less mobile than predicted by models.
- Which mineral can fix Cr(VI) after the ettringite front ?

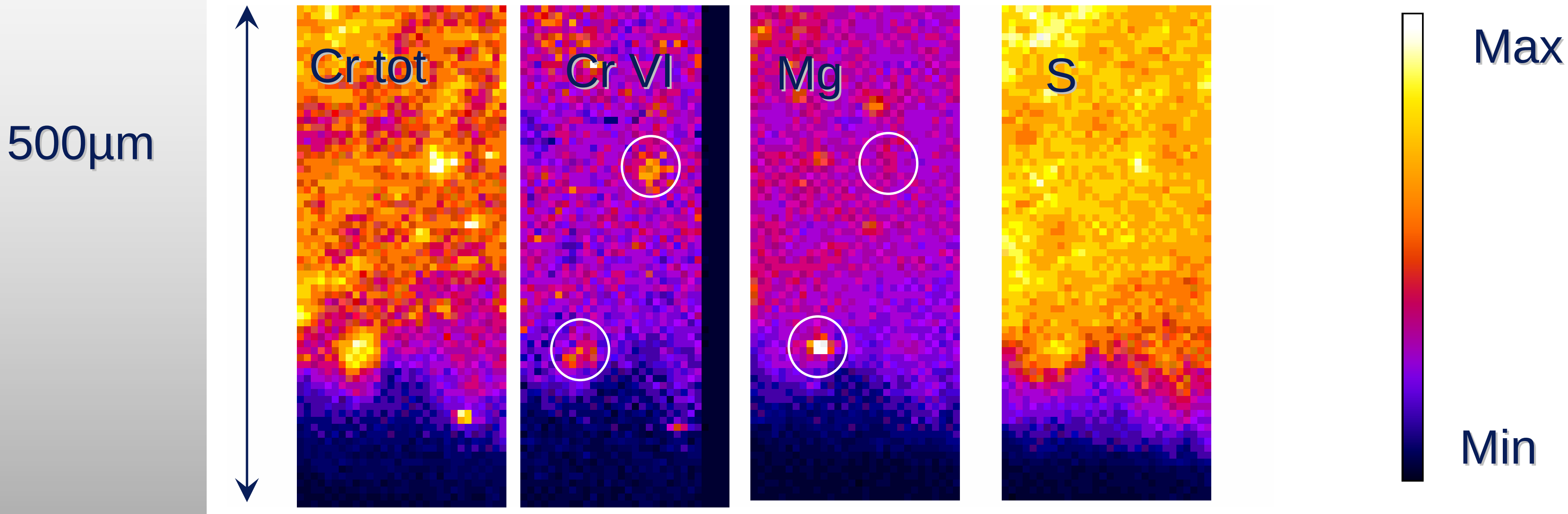
μ-XRF



Cr and S normalized intensity
Mg normalized intensity
Distance (µm)
liquid/solid
interface
Altered layer
Cr
S
Mg
1
2
Unaltered area
Cr
S
Mg
Porous
Zone
Secondary
mineral front

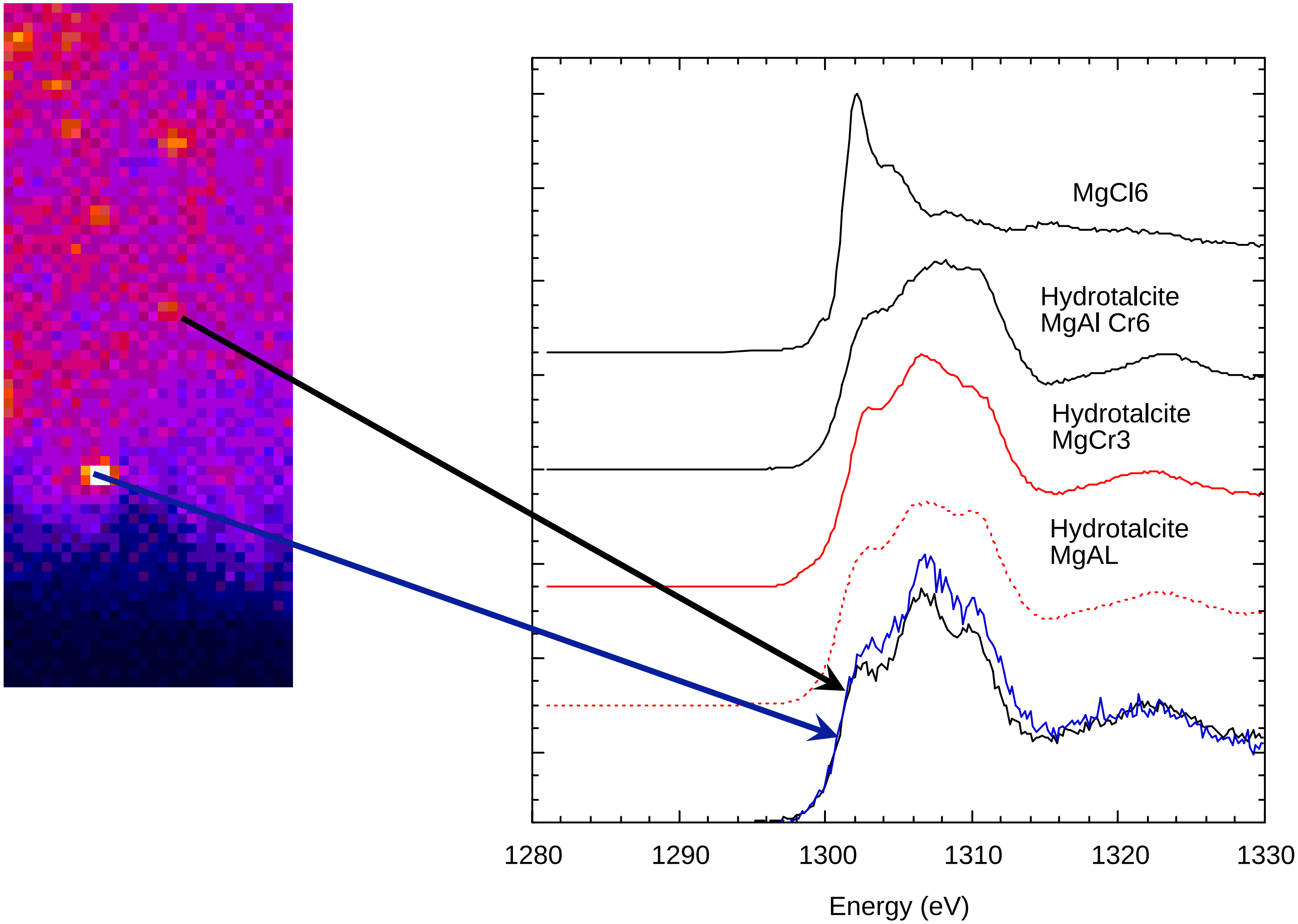
µ-XANES

LUCIA beamline
SLS-Villigen



Cr and Mg are correlated in the altered layer

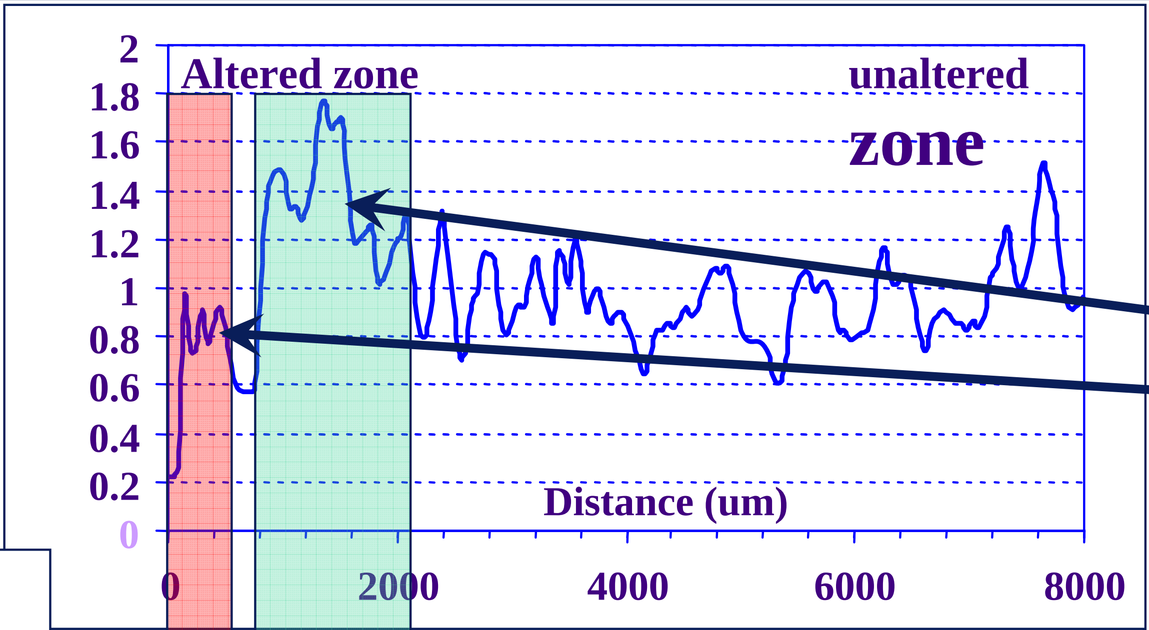
Mg K edge XANES



Rose at al, *Cem & Conc Res*. In prep

Porous Zone
Secondary mineral front

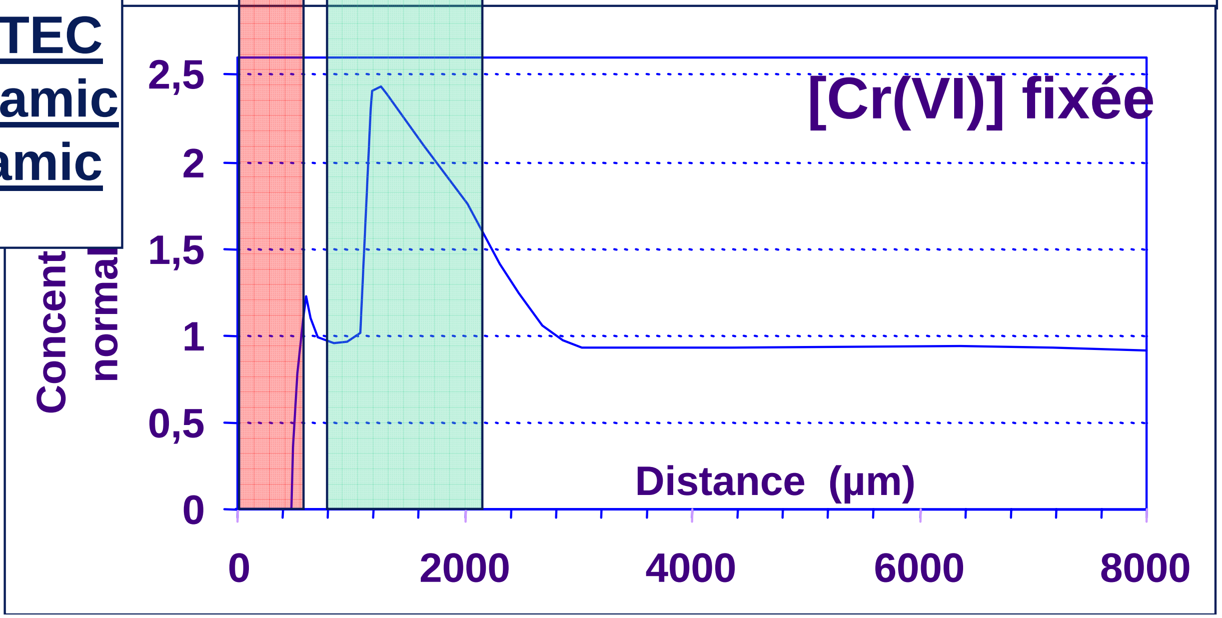
Exp.



Ettringite
and
hydrotalcite

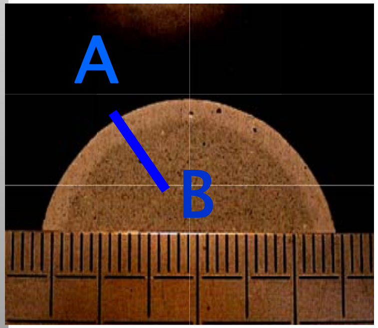
Ph'D A. Benard

Model
CHESS+HYTEC
Thermodynamic
+hydrodynamic

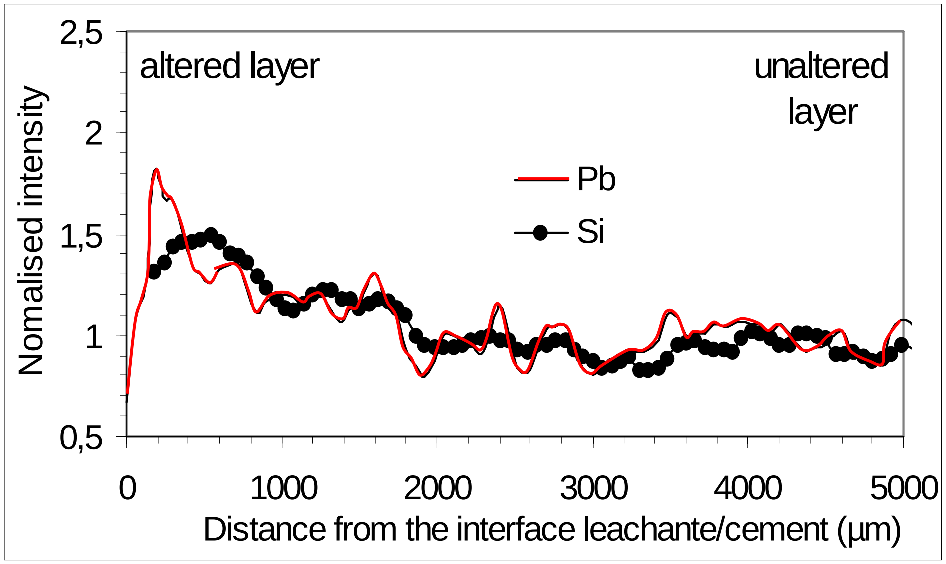


Case of Lead in cements

Pb behaviour through
Altered cement matrix



Lead and C-S-H

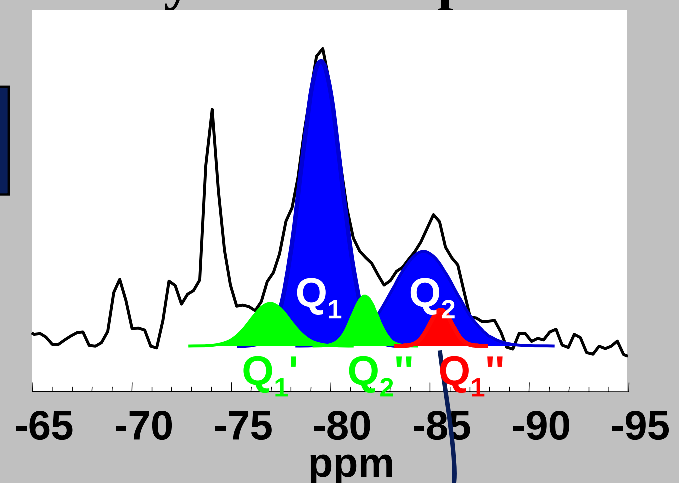


2,5
2
1,5
1
0,5
Nomalised intensity
altered layer
unaltered layer
Pb
Si
0
1000
2000
3000
4000
5000
Distance from the interface leachante/cement (µm)

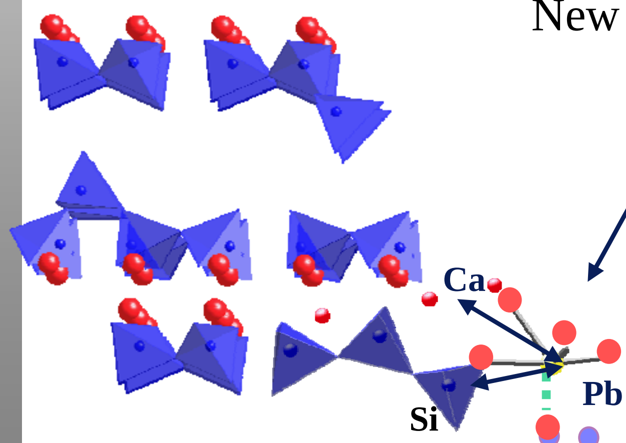
Lead and C-S-H

CSH hydrated in presence of Pb

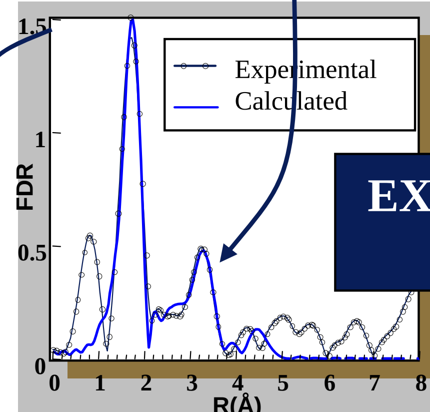
^{29}Si NMR



New peak at +85.6 ppm



CSH structure



EXAFS at the Pb LIII edge

~1 Si at 3,75Å de Pb

~0,8 Ca at 3,58Å de Pb

Rose et al, *langmuir*, 2002

Modeling

Calculation:

Translation into a chemical-transport model code (CHESS-HYTEC)

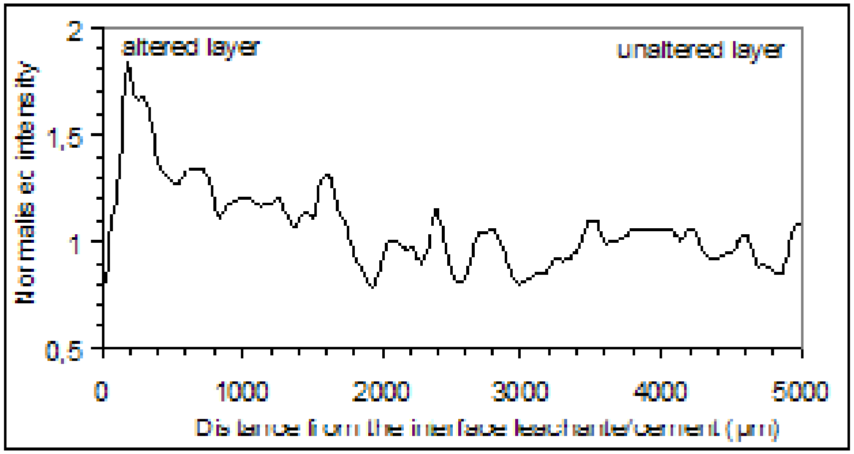
- **Translation of experimental data into thermodynamic data**

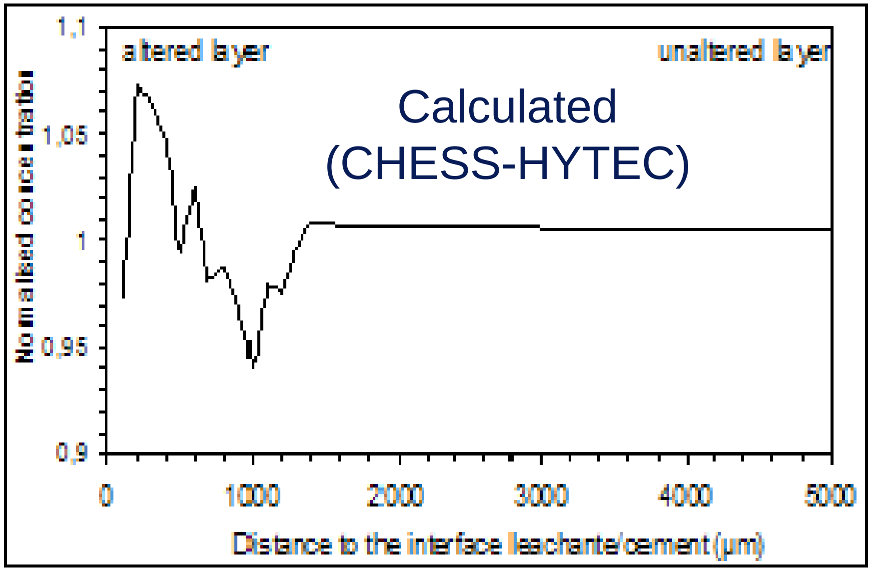
For Pb retention sites (Nonat C-S-H model (Nonat et al, 01, Pointeau ,01)

$SiOH + Ca^{2+} + Pb^{2+} + 3H_2O - 4H^+$ <==> $SiOCaPb(OH)_3$ log K(25°C) = -33.4

$SiOH + SiOH + SiO_{2(aq)} + Ca^{2+} + Pb^{2+} - H_2O - 4H^+$ <==> SiOH-CaSiOPb-SiOH log K(25°C) = -23.3

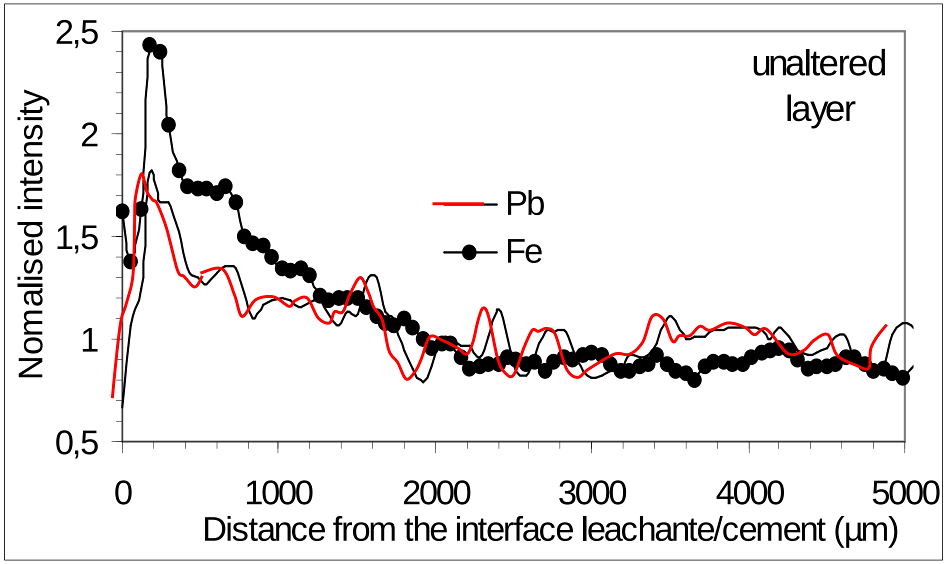
Experimental (µ-XRF)





Benard, Rose et al., *Waste Management*, in press

Iron phases in cement…



What is the speciation of iron in cement?

Fe in ettringite, AFm? Formation of FeOOH?
Pb adsorption to FeOOH or coprecipitation?

Hydration of C4AF

calcium ferroaluminates
C4AF?

calcium aluminates
C3A

↓

Ettringite

AFm

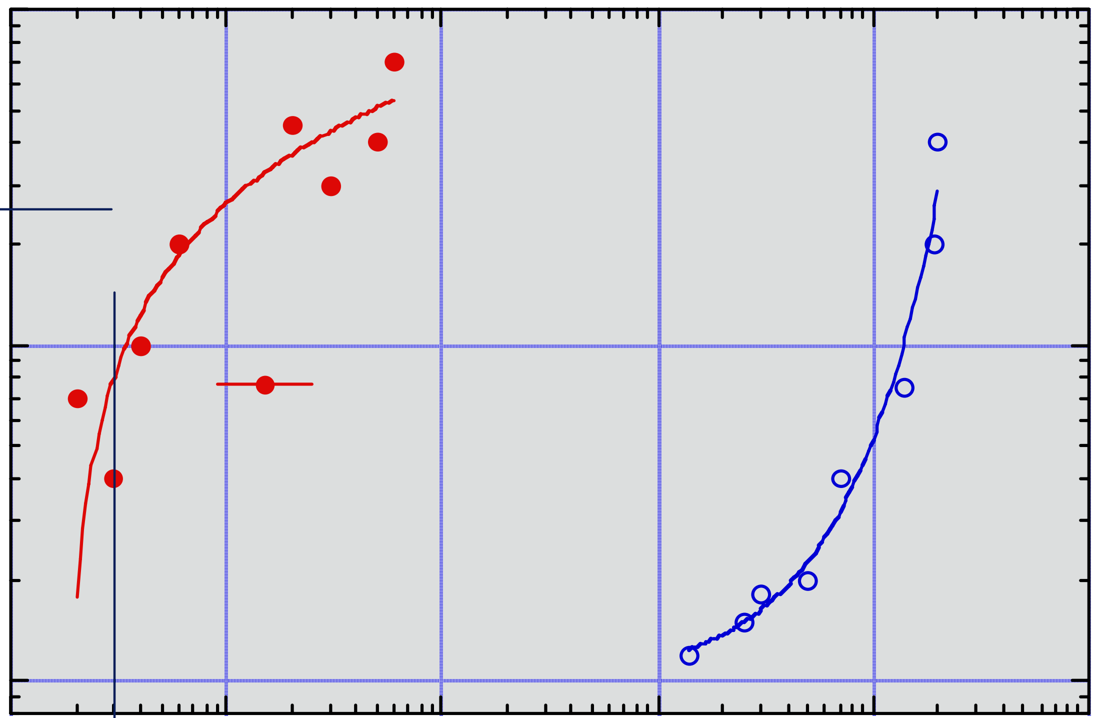
↓

C3(A,F)H6+
amorphous FeOOH
(highly reactive phase)

Rose at al, waste management, 2006
Möchner et al, GCA, submitted

Fe and Pb in cement

Everything fixed by the solid



“Nothing” in solution

Environmental impact of waste reuse:

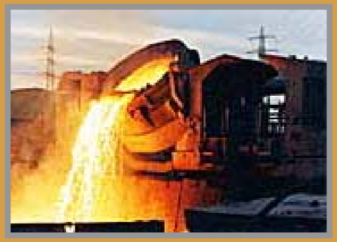
Cr and V in BOF steel slag

❖ **Basic Oxygen Furnace** (BOF) **slag** is a **residue** from the **converter** in steel-making operations.

❖ In Europe, a significant portion of BOF slag is **reused** as aggregates in **road constructions** (unbound layers).

Release of pollutants

Environmental impacts ?



Oxygen converter

Pig iron

BOF steel slag

12 millions tons/an (Europe)

Steel (300 tons)

Environmental impact of waste reuse

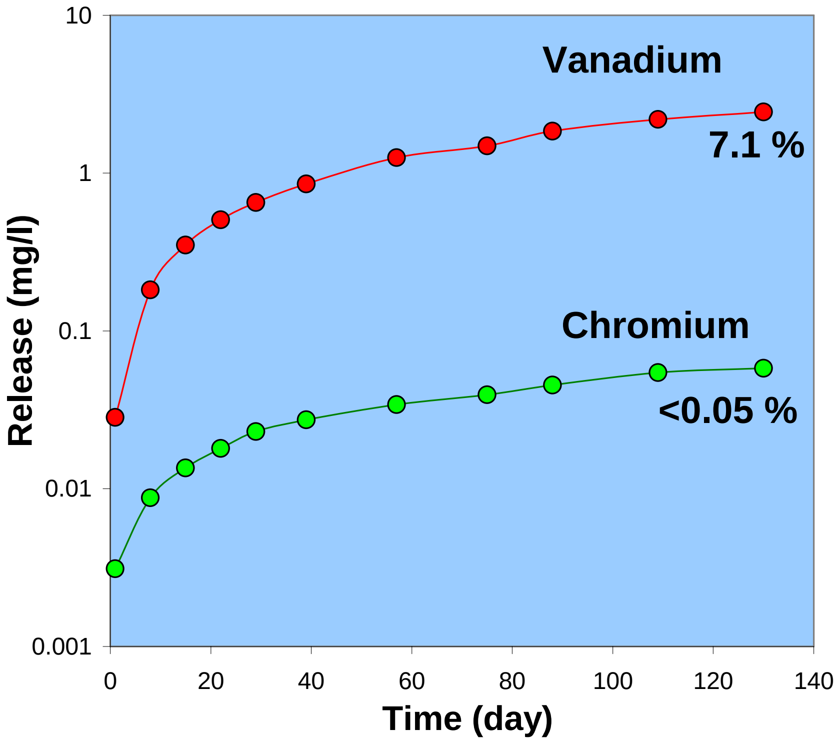
Traces elements in BOF slag

❖ BOF slag contains trace amounts of **potential toxic** element which can be released : **Chromium** (Cr, **2400 mg/kg**) and **Vanadium** (V, **690 mg/kg**).

❖ **Dynamic leaching tests** at a laboratory scale (*modified soxhlet extractor*[1]):

Leaching conditions

130 days, leachate = UPW, pH = 8.5 – 9, L/S = 20, recirculation flow = 5 ml/min.



❖ **Field test: Lysimeter 1M³: 2 years:**

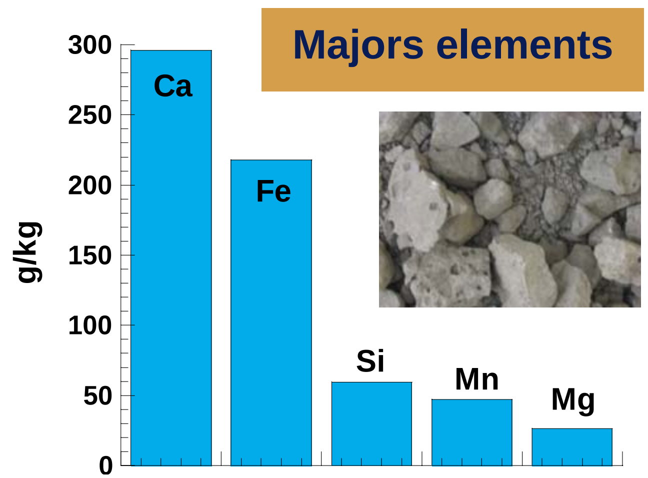
❖**Cr not detected,**

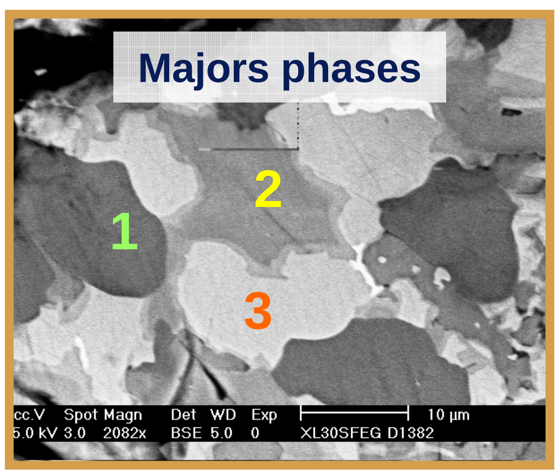
❖**V: below 0.1 % of the initial total fraction**

Environmental impact of waste reuse

Majors phases in BOF slag

❖ BOF slag **solid matrix** was well defined by using complementary techniques: **ICP-AES, DRX, MEB-EDS, µ-XRF**.





SEM photography of a polished BOF slag section

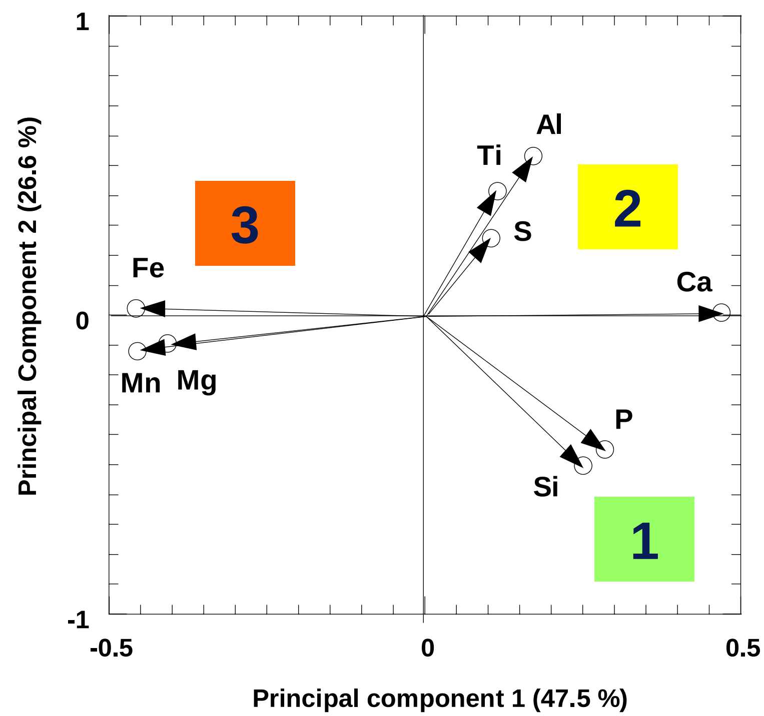
1. Ca_2SiO_4 + P (larnite)

2. $Ca_2Fe_{2-x}AlO_5$ (brownmillerite) + Ti, S

Cr and V bearing

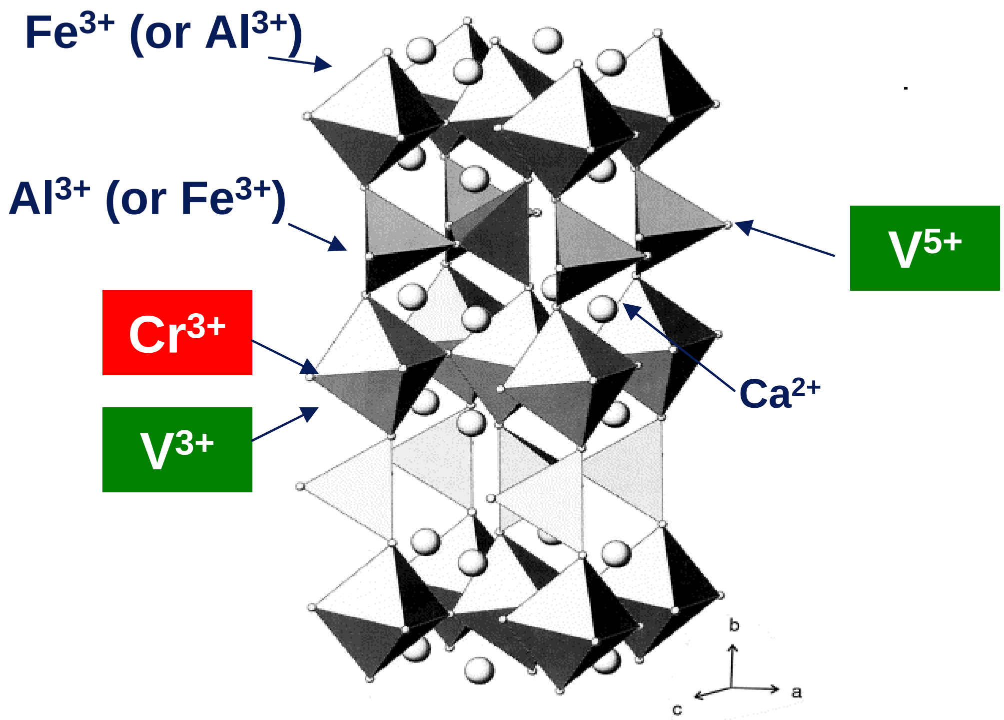
3. (Fe, Mn, Mg)O (solid solution, wustite)

PCA loading plot from 143 µ-XRF spectra (10 µm, 15 kV, 1000 s)



$Ca_2Fe_{2-x}Al_xO_5$:

Cr and V bearing phase



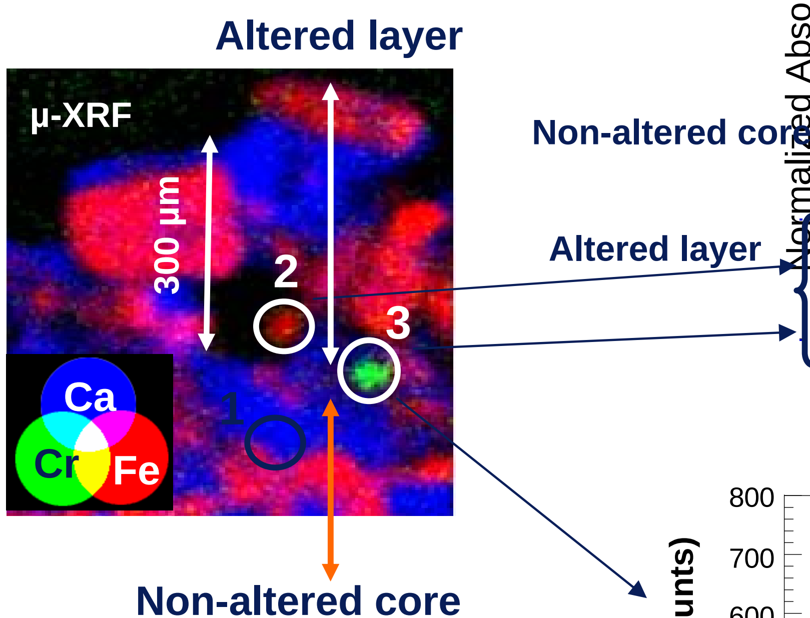
Chromium speciation under leaching conditions

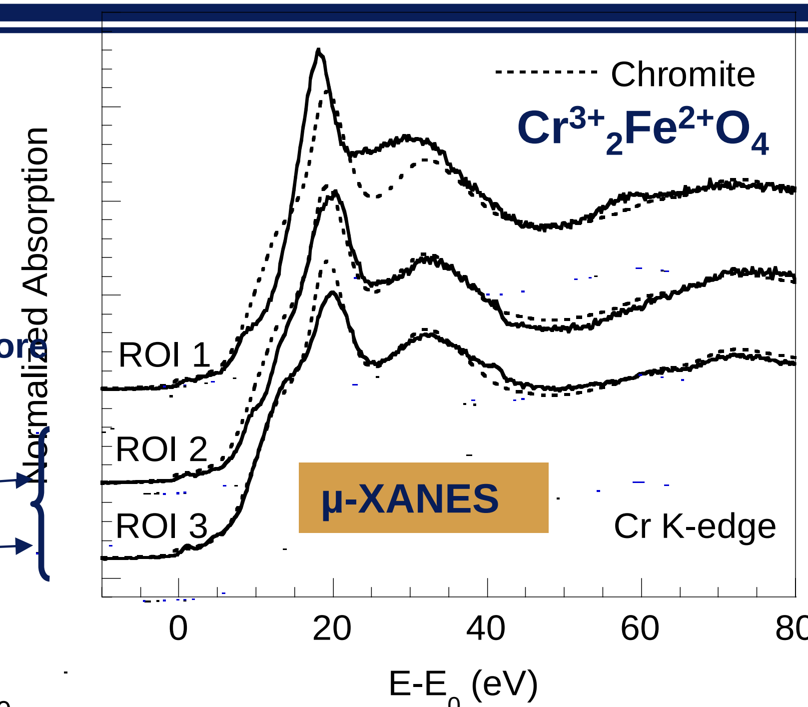
Techniques :

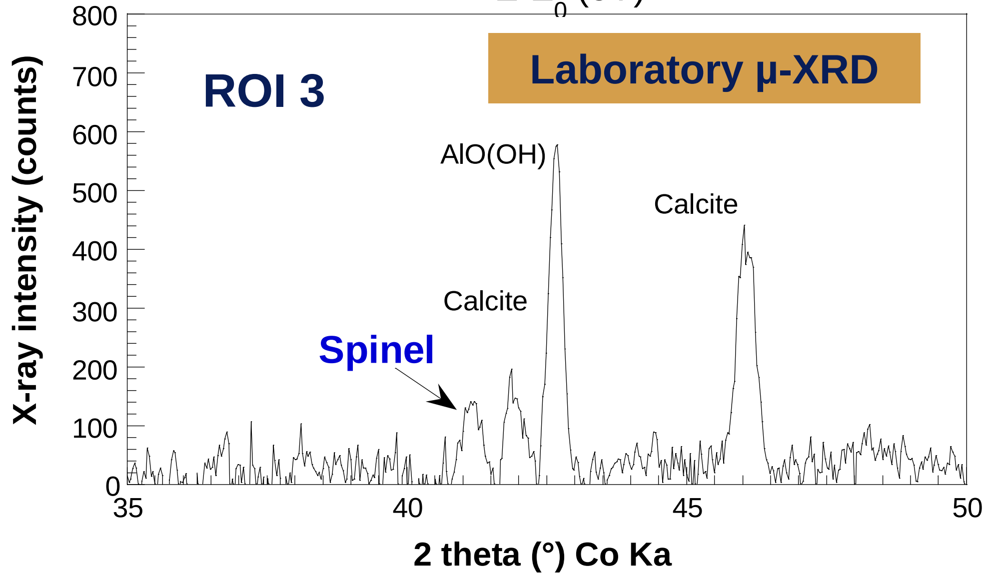
μ-XRD

μ-XANES

Spinel-type phase : $A_2^{3+}B^{2+}O_4$







(X'Pert Pro MPD, Panalytical)

100 μm spot size

Chaurand, Rose et al, *ES&T*, submitted

4. Results on V speciation

Vanadium oxidation state

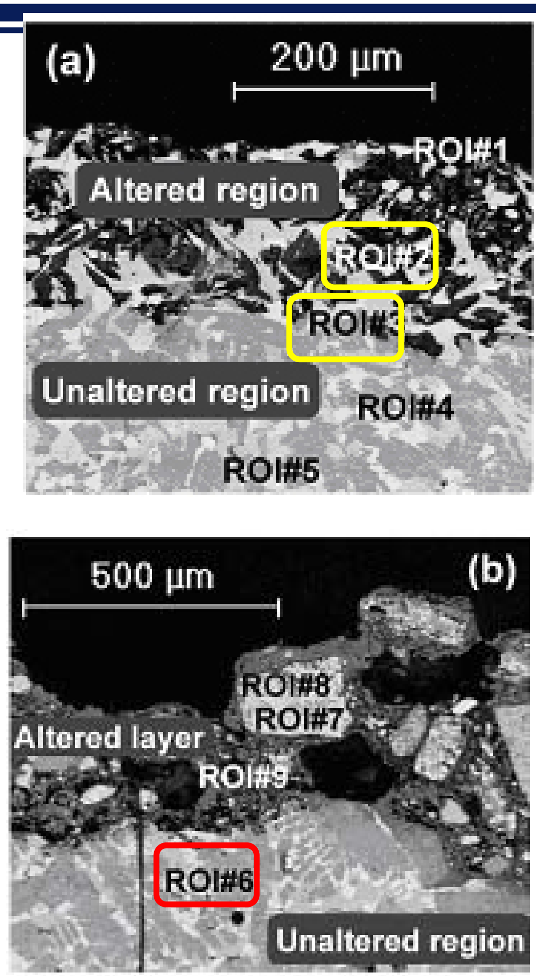
Techniques :

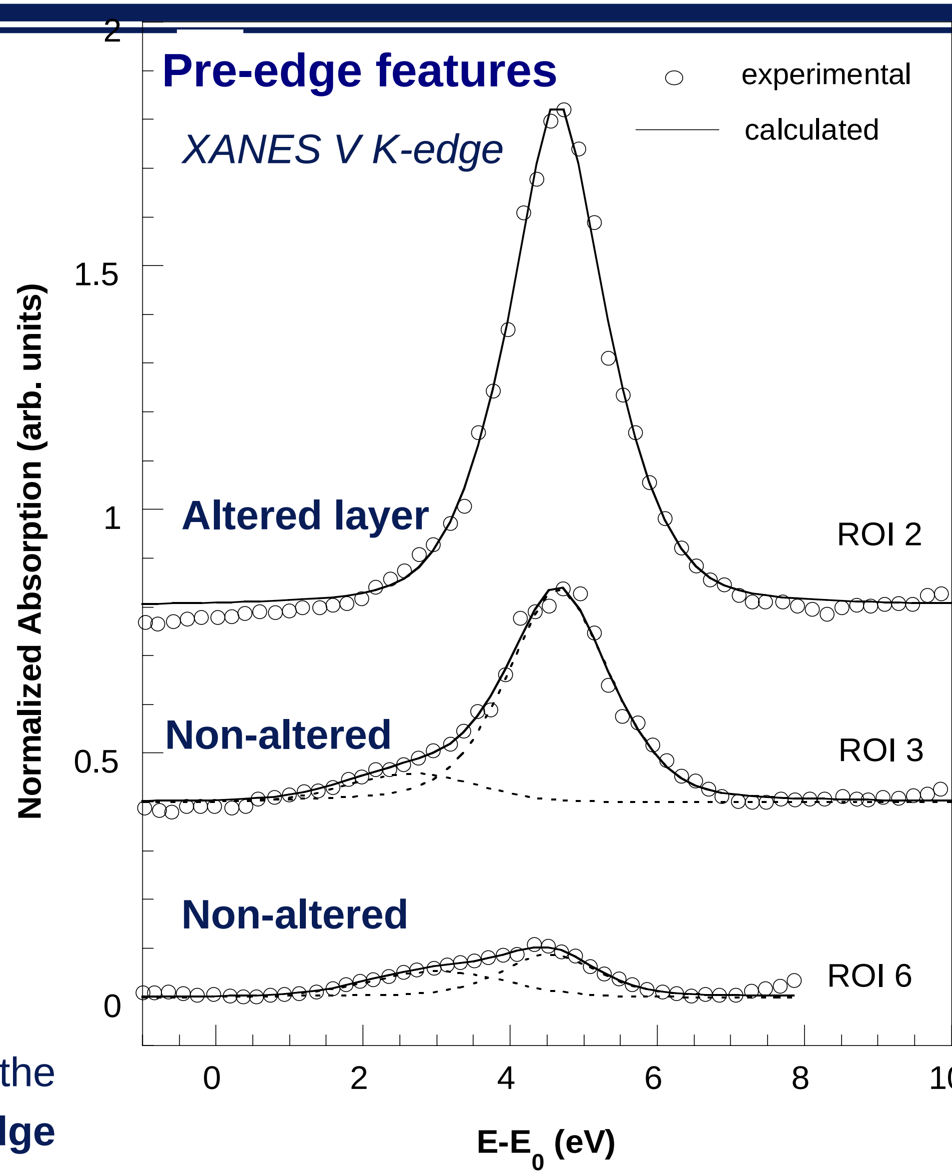
XANES and

µ-XANES

Lab

Field (Lysimeter Upper part)



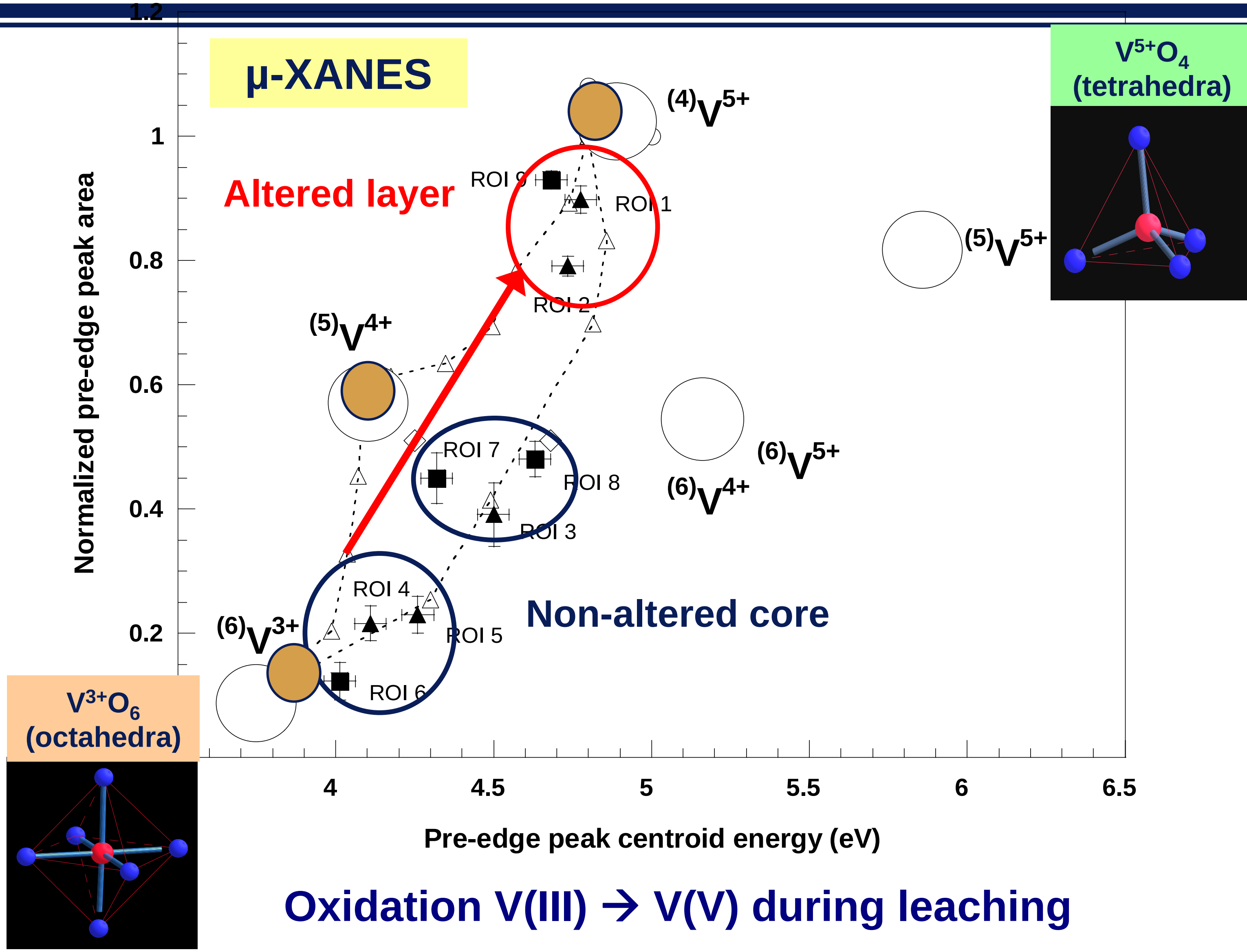


From the non-altered core to the altered layer : changes in the **pre-edge peak position and intensity.**

Vanadium oxidation state

Techniques :

µ-XANES



Chaurand, Rose et al., J.Phys.Chem, accepted

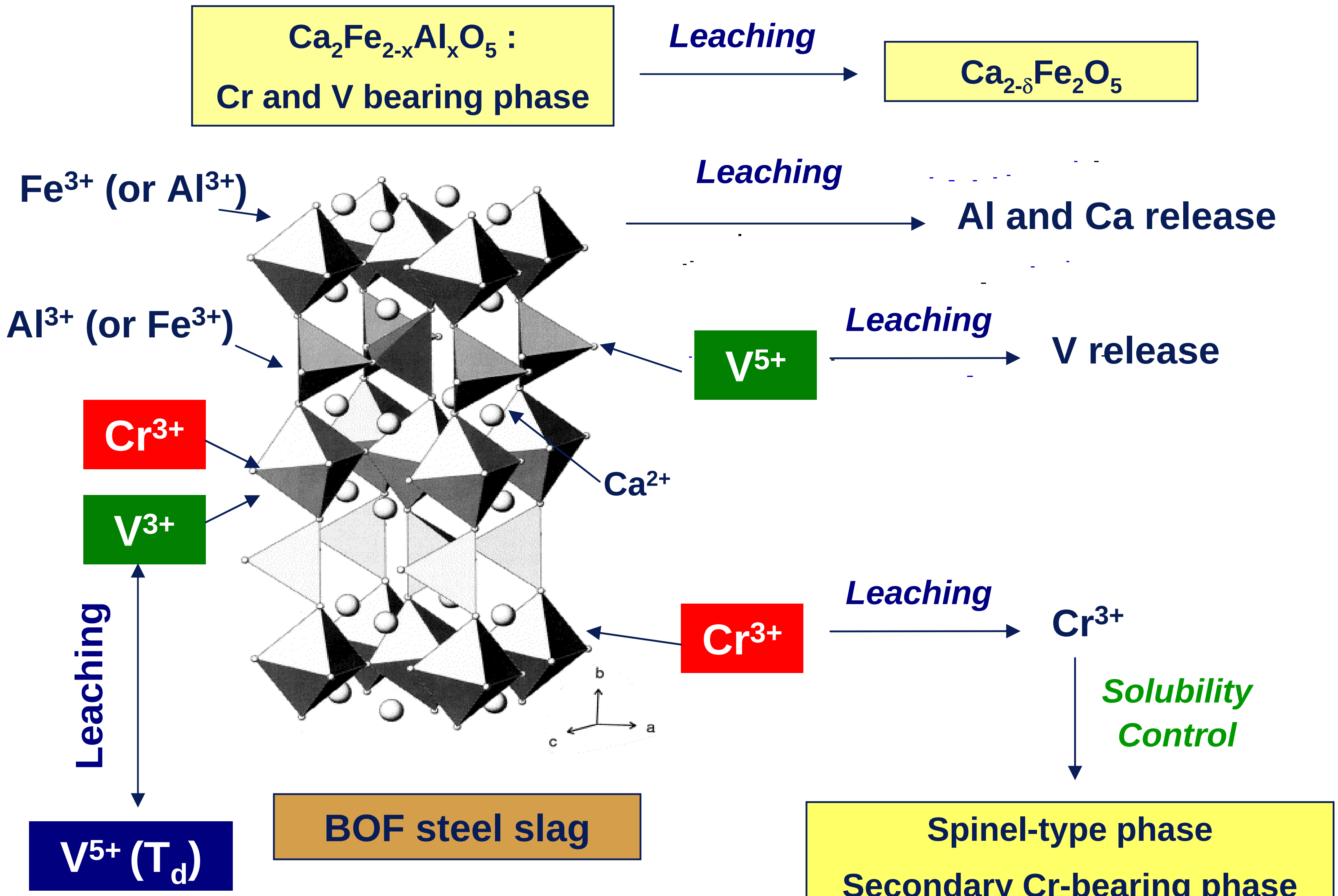
Oxidation V(III) → V(V) during leaching

+ loss of symmetry Oh → Td

Summary

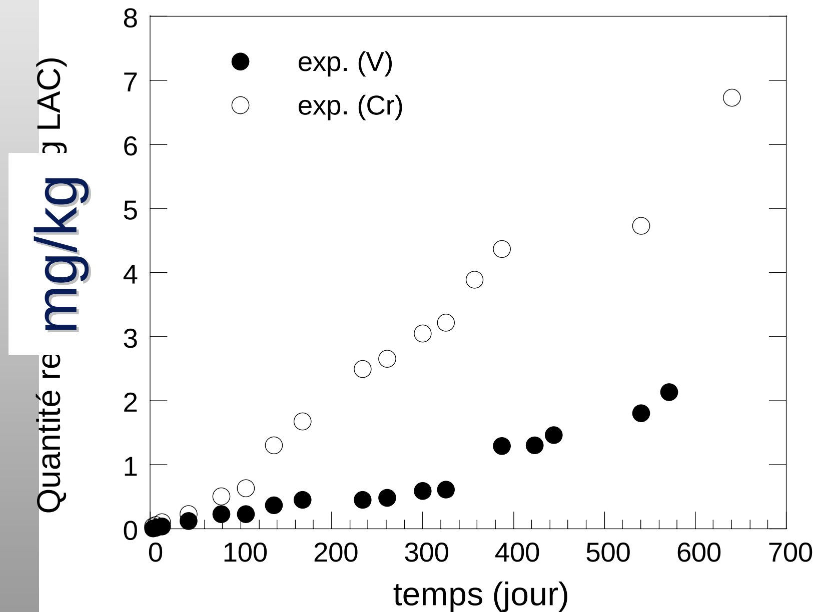
Molecular mechanisms of release

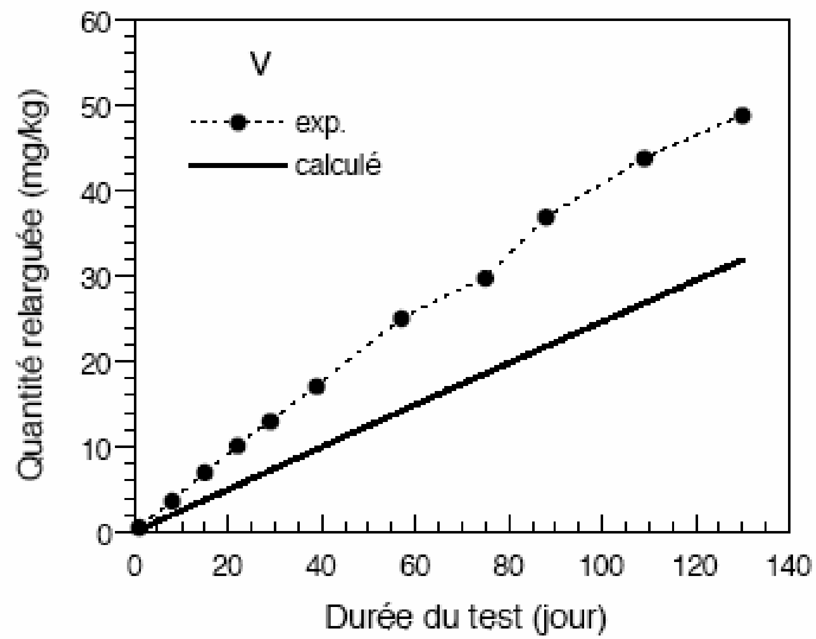
❖ Objective : to explain the **leaching behavior** of **Cr** and **V** present as traces in steel slag



Out of the lab…

Role of CaCO3 (protective layer)?
Accumulation front (porosity)?





1 m^3 lysimeter (field experiment)
2 years under atmospheric condition

Soxhlet

Conclusion - perspective

- Mechanistic approach can be performed at the molecular level
- Necessity of large scale leaching experiment
- Effect of under - saturated conditions (CO_2…)
- Role of iron phases.
- Effect of organic matter and living organisms

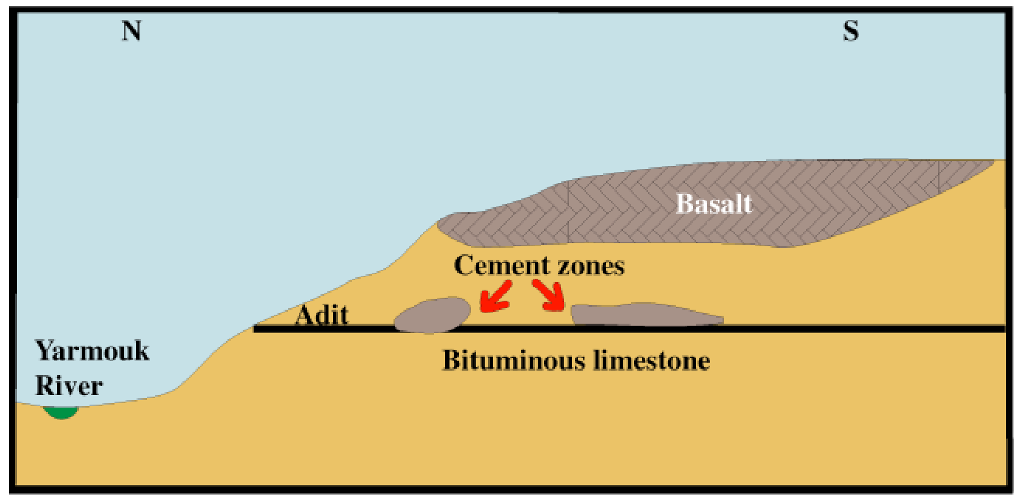
Technological development…

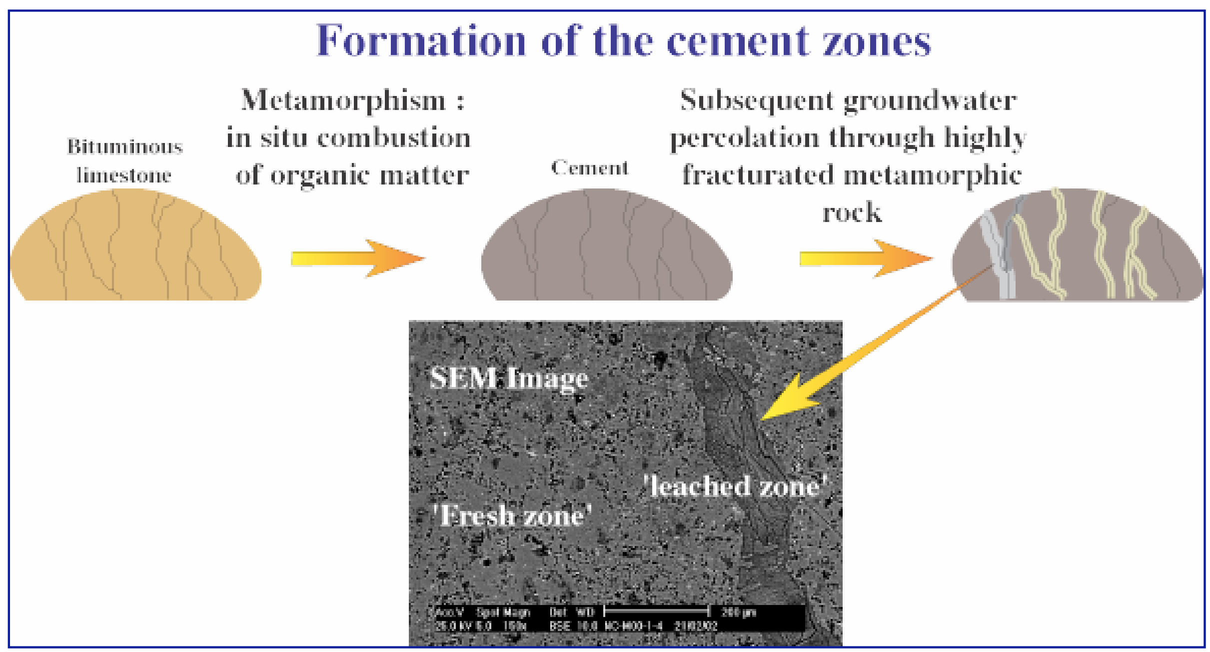
- XRF scanner (beam resolution 200 µm) for large samples (1.8 m : cores from lysimeter…)
- Redox state for core samples (high energy resolution XRF (inelastic X-ray fluorescence))
- …

Chromium behaviour in natural cement analogue: MAQARIN site

QuickTime™ et un décompresseur
TIFF (non compressé) sont requis pour visualiser
cette image.

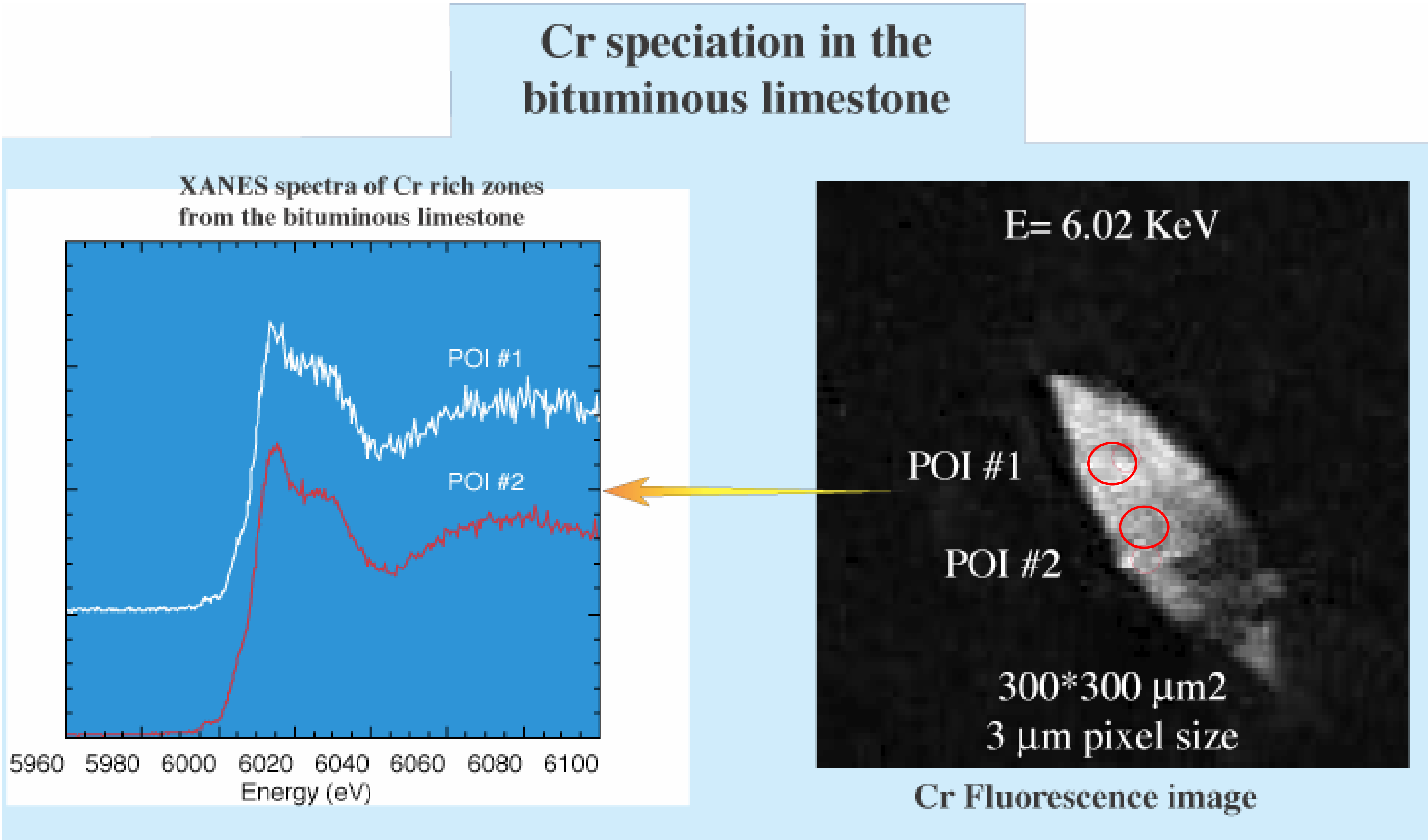
Geological section along the adit





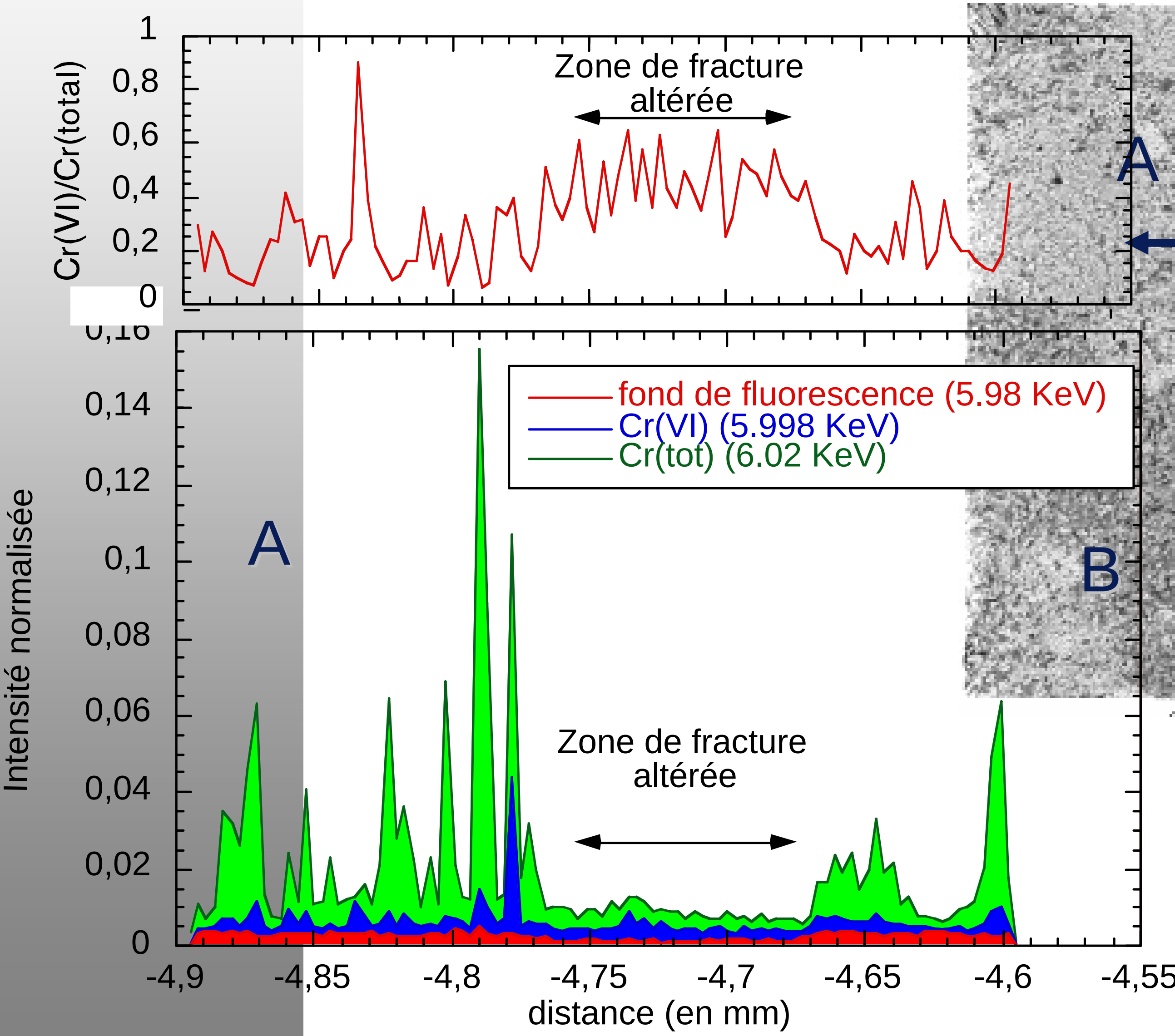
300 ppm Cr

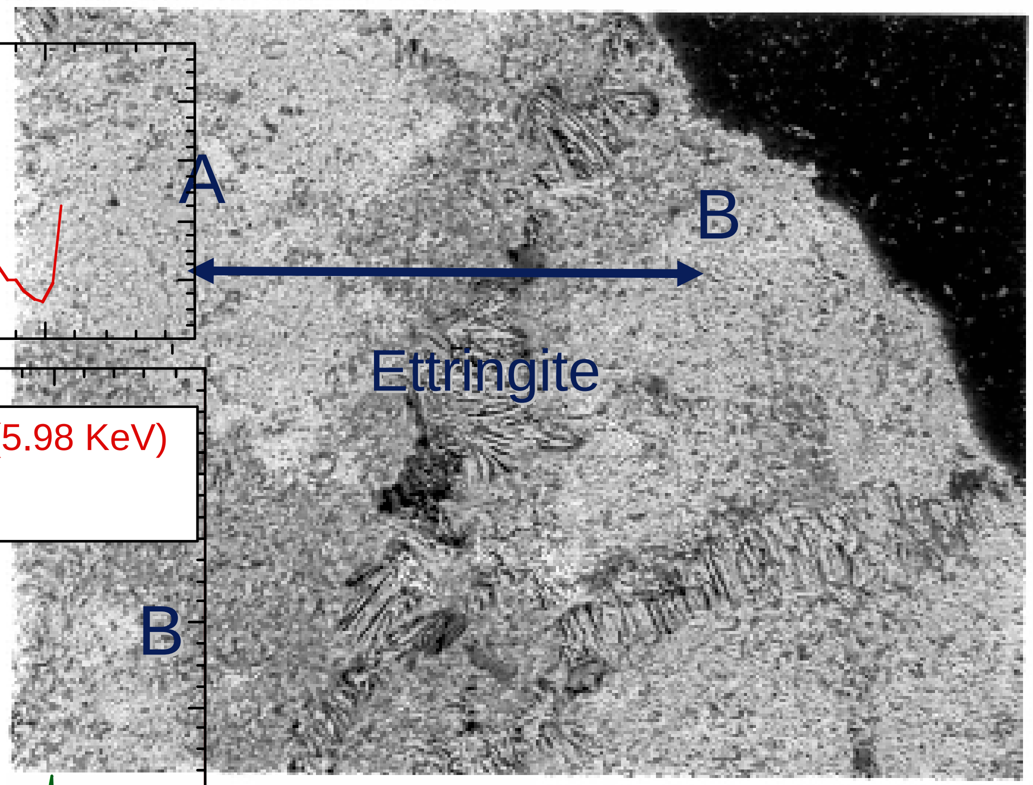
Chromium behaviour in natural cement analogue: MAQARIN site



Rose J., N.Crouzet, L.Trotignon, S. Grimal , J. Susini, H. Khoury , E. Salameh, , A. Milodowski, F.Mercier, 2003, 'Effect of leaching on the crystallographic sites of trace metals associated with natural cements (site of Maqarin, Jordan): case of Cr', J. Phys. IV, 104, 447-450

Chromium behaviour in natural cement analogue: MAQARIN site





Oxidation of Cr(III) to Cr(VI) in the fracturated zone