2nd Mechanisms and modelling of waste/cement interactions international Workshop

Speciation and role of iron phases in cement to fix heavy metals

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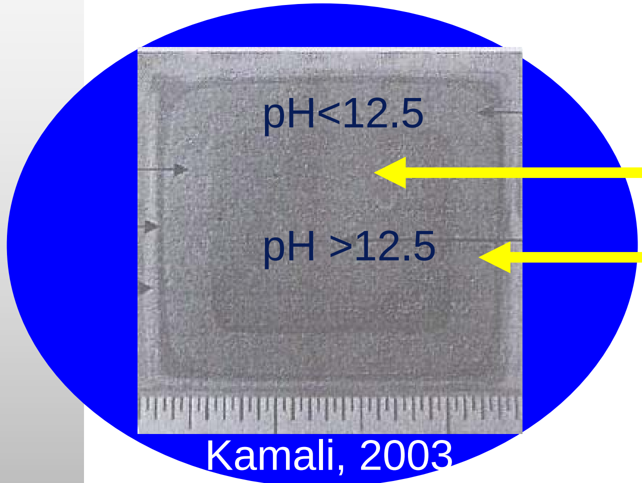
Le Croisic/France

Fixation of heavy metals (HM) in cement (OPC)

- Many OPC mineral phases can fix HM:
- C-S-H : Pb, Zn, Eu…
- AFm : Cr (III, VI),
- Ettringite : almost all !!!
- Other minor phases…. (LDH…)

Leaching of Portland cement (as an example)

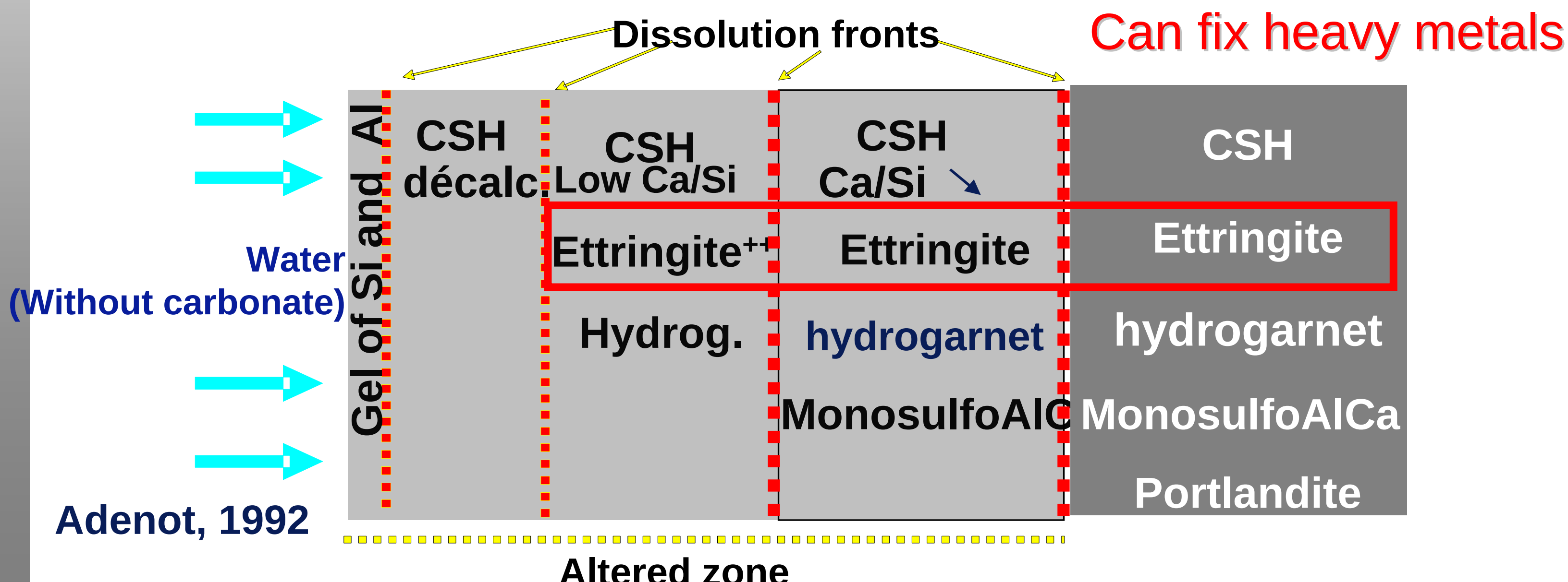


Cement corrosion

Non-Altered zone

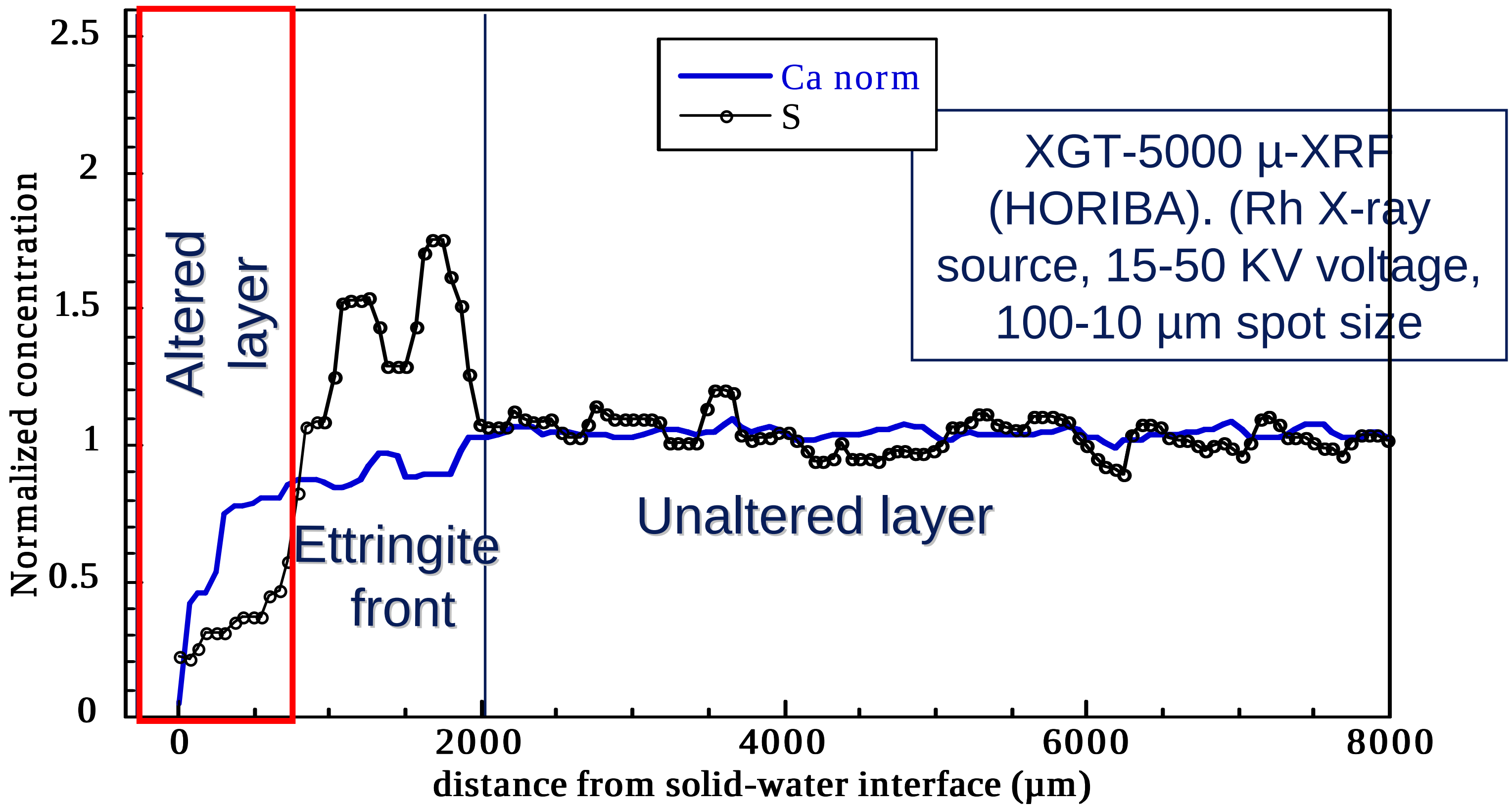
Altered zone

Dissolution / precipitation
pH modification



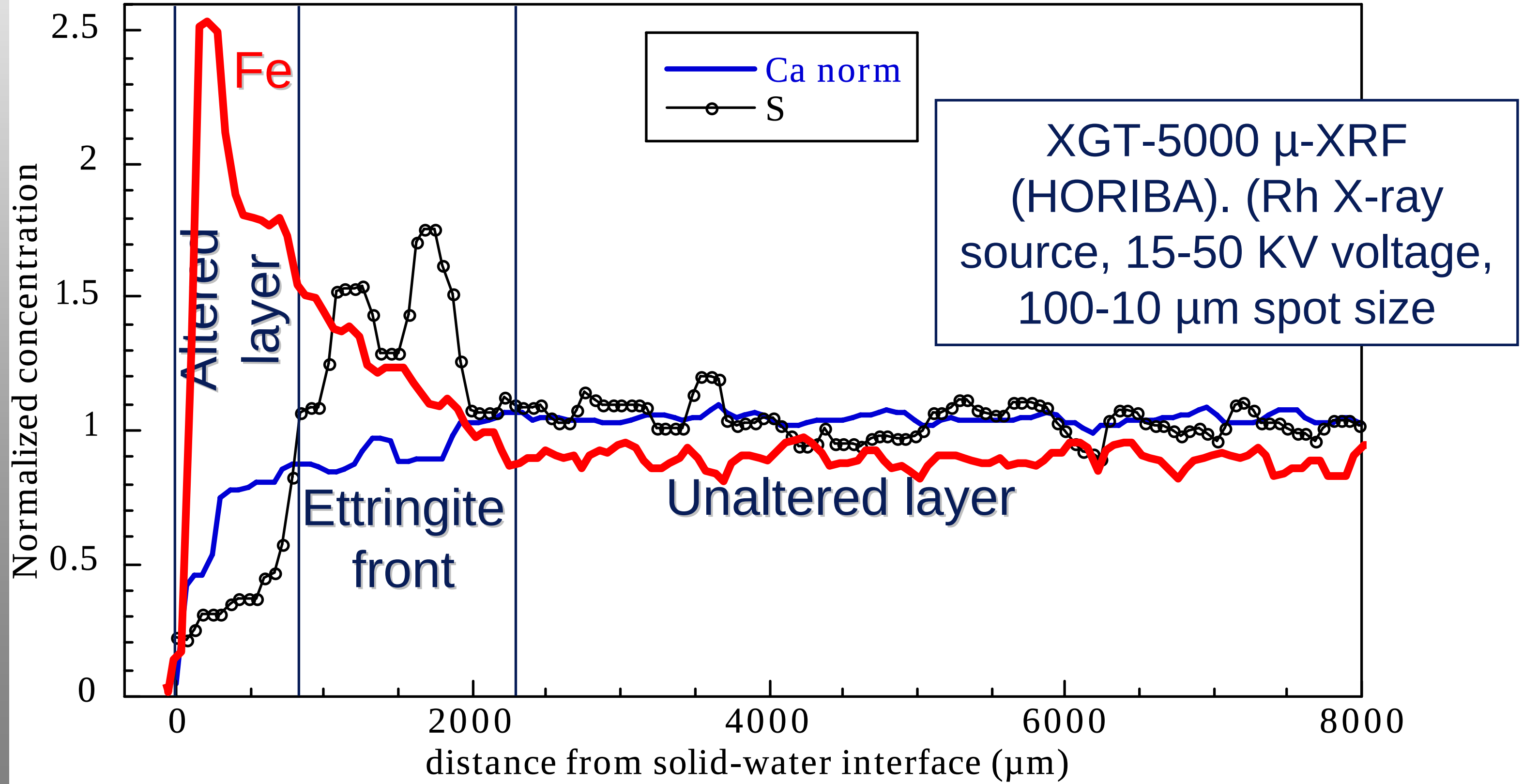
Leaching of Portland cement (as an example (30 days…at 35°C in water)

- What about long term evolution (no ettringite…)

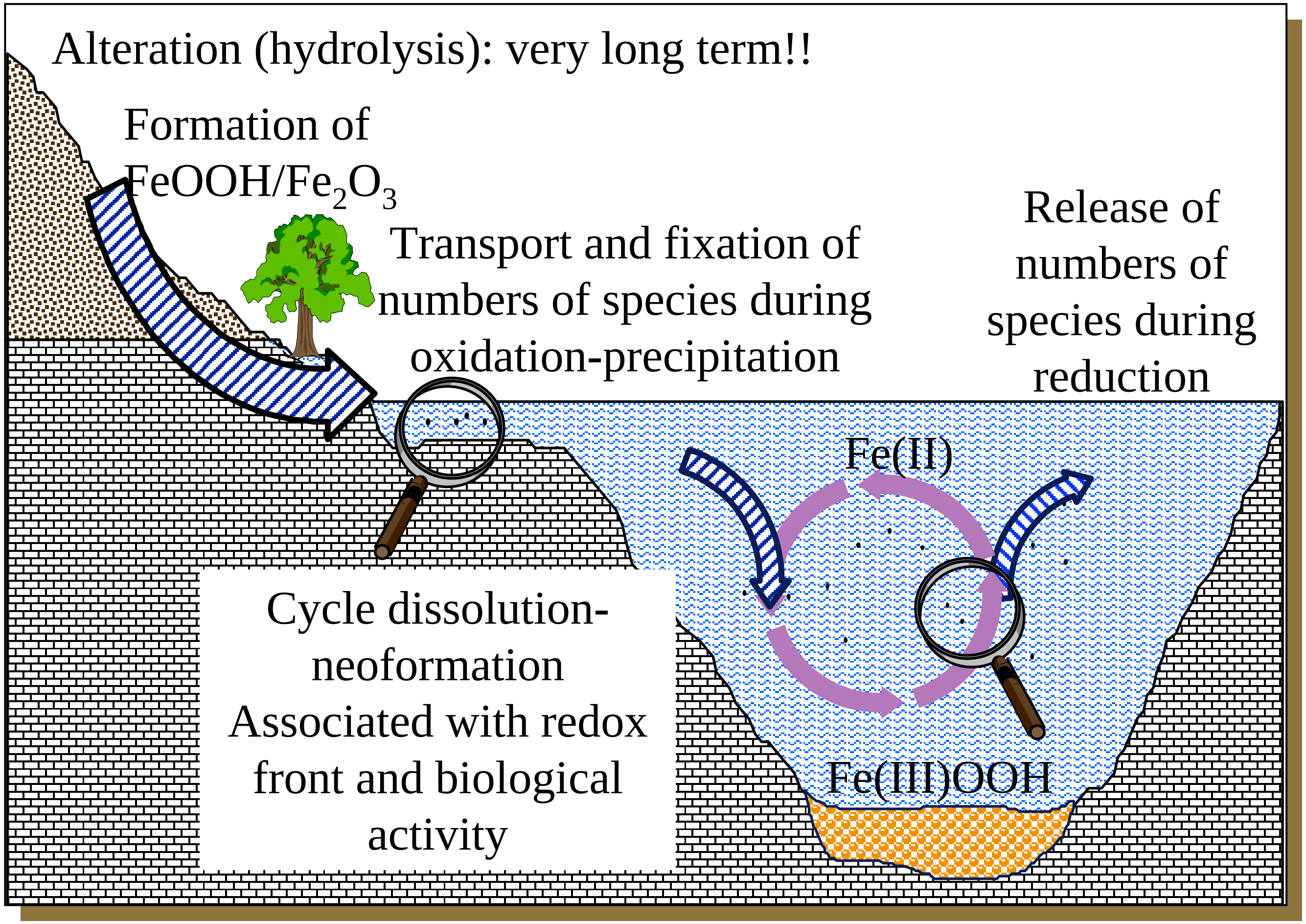


Leaching of Portland cement (as an example)

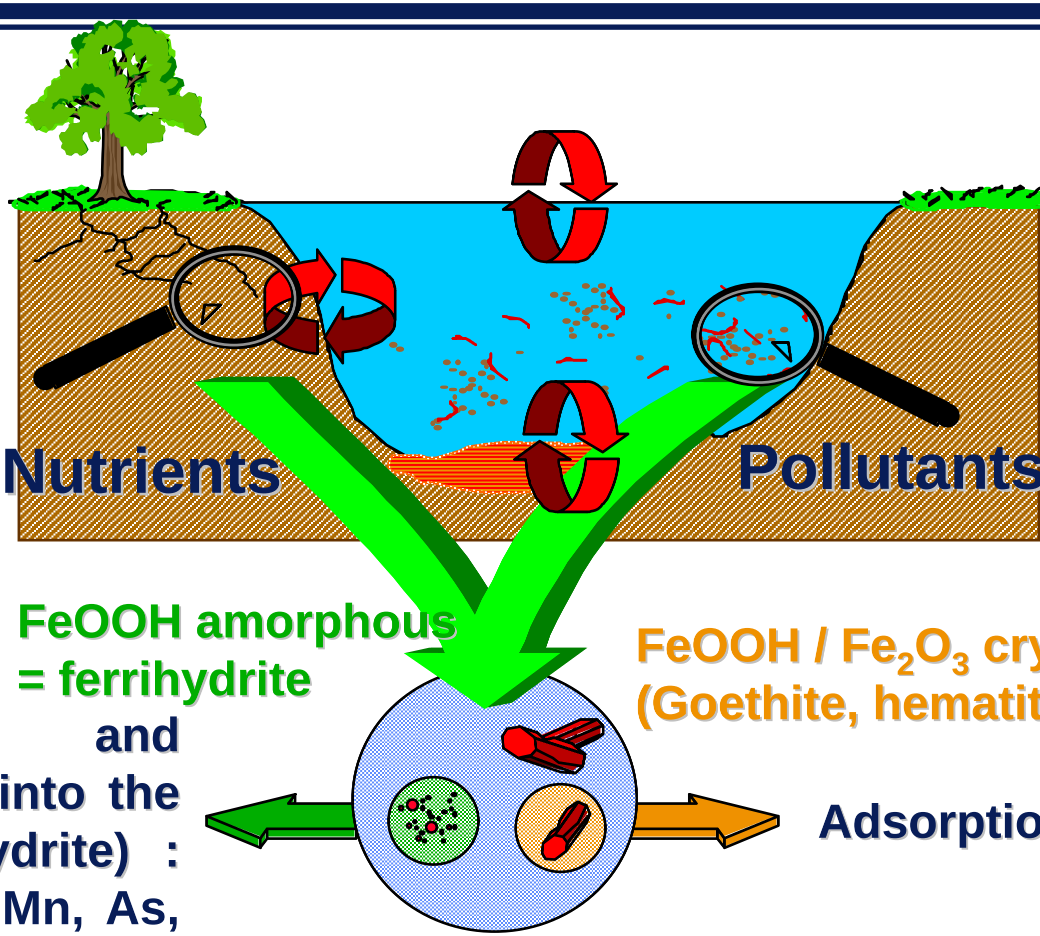
- What about long term evolution (no ettringite…)
- Iron ? Iron (III) is highly insoluble.



Iron (oxyhydr-)oxide in natural systems



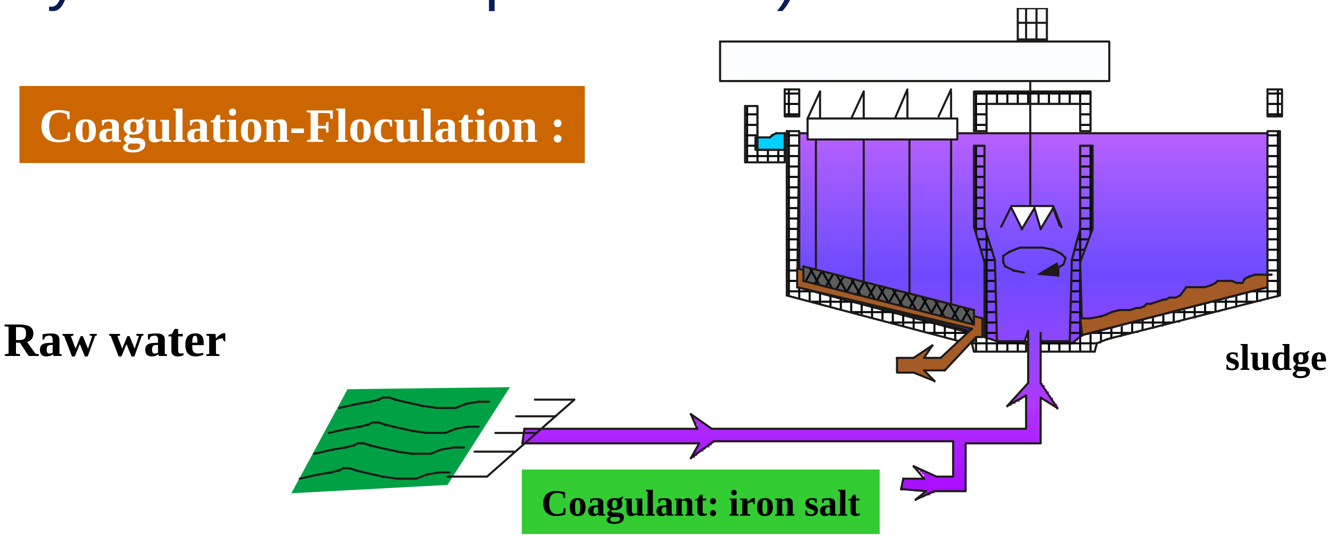
Natural system:
(in oxic zones, near neutral pH)



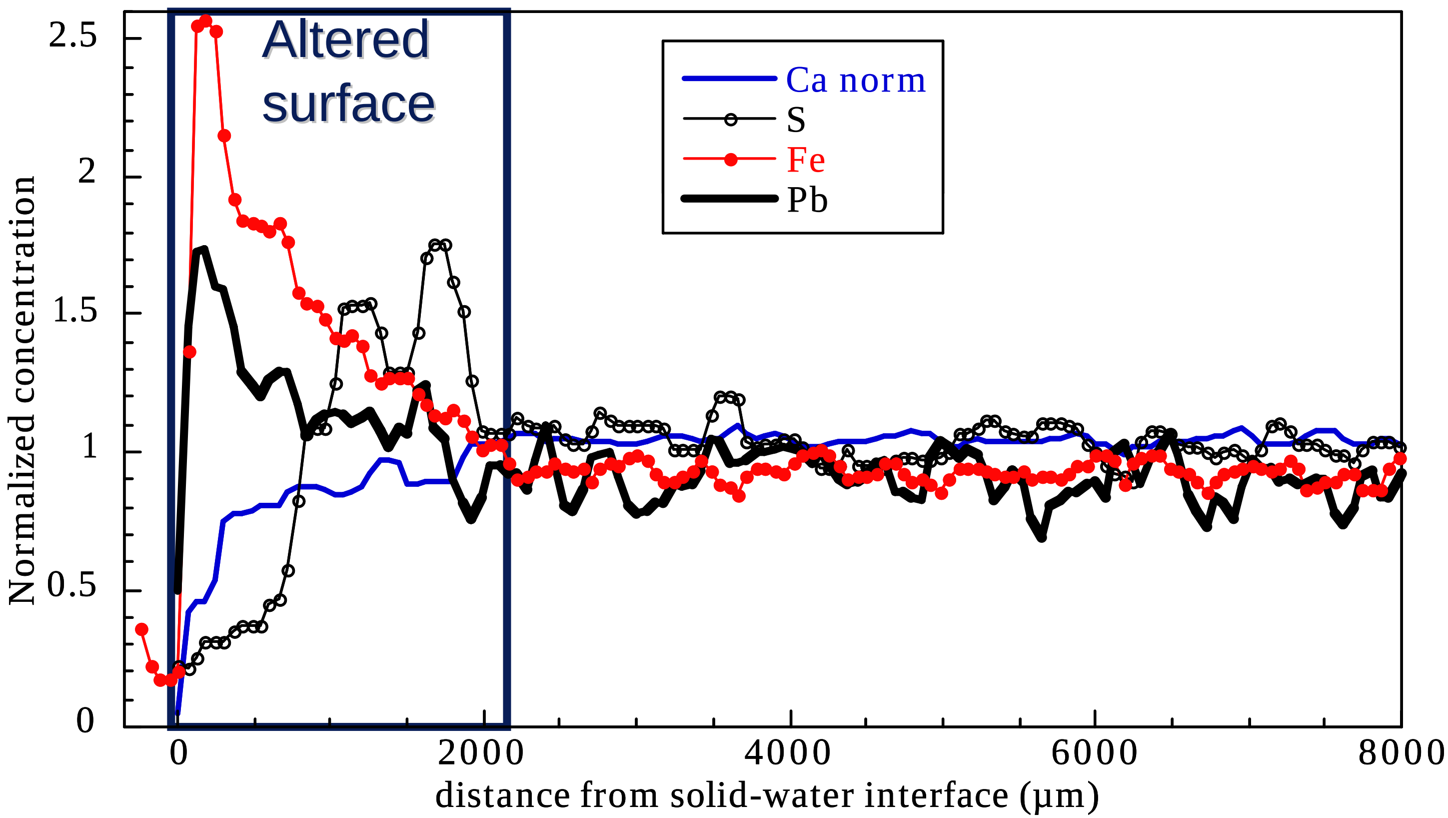
Adsorption and incorporation into the matrix (ferrihydrite) : U, Cr, Co, Ni, Mn, As, Se, Pb, U…)

Iron (oxy-hydr-)oxides for waste treatment

- Highly reactive minerals
- Many metals and metalloïds can be adsorbed or incorporated
- They are used as adsorbants (water treatment, physico-chemical processes)



Iron phases in cement?? µ-XRF profiles



After long term leaching : one of the only remaining phase?

Iron in Portland cement

Anhydrous phase

calcium silicates
C_3S, C_2S
$3\ CaO.SiO_2$
$2\ CaO.SiO_2$

Calcium Aluminates
C_3A
$3\ CaO.Al_2O_3$

calcium-ferric aluminate
C_4AF
$2\ CaO\ (Al_2O_3,\ Fe_2O_3)$

CaSO4

Cement hydration
=
dissolution + precipitation

Hydrated phases

C-S-H
$xCaO.SiO_2.yH_2O$

$C_3(A,F)H_6$
$3CaO.(Al_2O_3,Fe_2O_3).6H_2O$

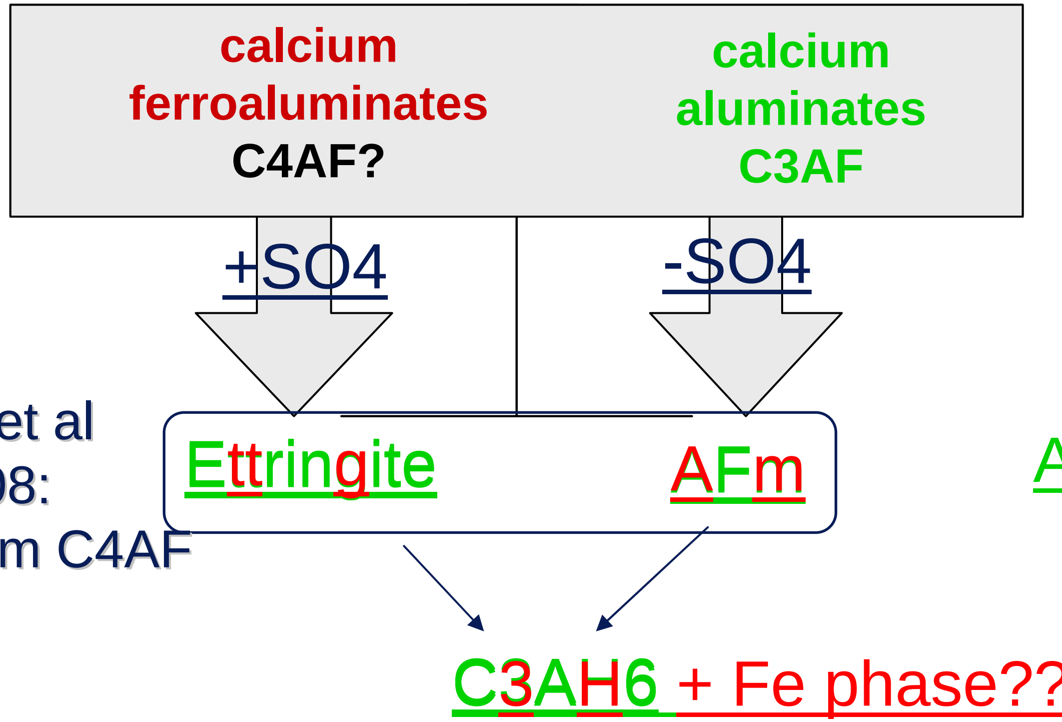
$Ca(OH)_2$

AFm
AFt (ettringite)

Möschner et al, GCA, 2008

"ferric" phase ('hydrated phase: FeOOH)?)

Hydration of C4AF what do we know?



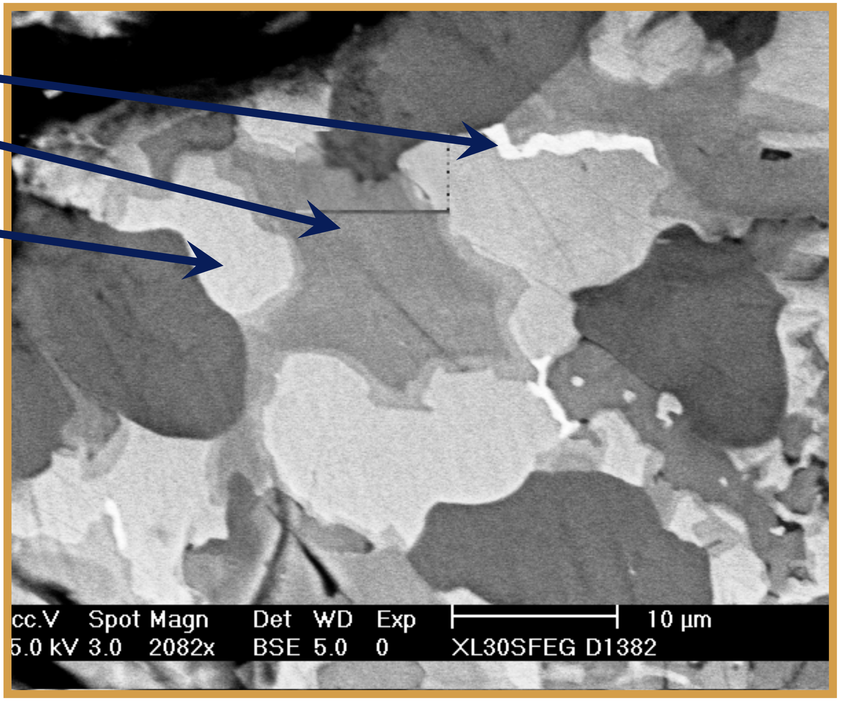
Möschner et al GCA 2008:
Not starting from C4AF

Al<=>Fe?

Teoreanu et al. (1979), Fukuhara et al. (1981), Rogers and Aldrige (1977), and Brown (1987) :
amorphous FeOOH phase can exist
No molecular scale investigation

Iron in other cements: slag,…

- Fe
- C2F/C4AF
- FeO
- Fe3O4

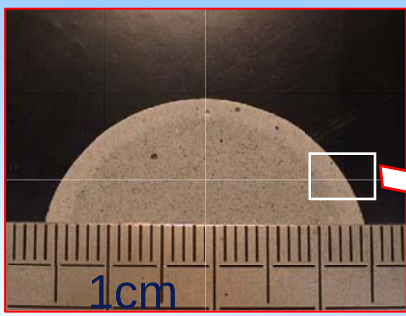


Aim of the work

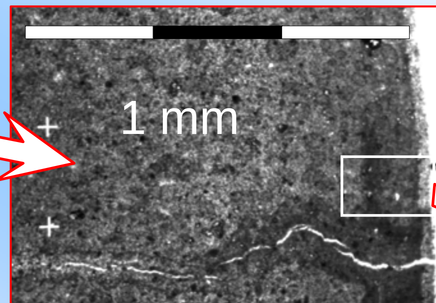
- To determine the speciation of iron on synthetic system (C4AF…)
- To determine the speciation of iron on OPC… (still ongoing research)
- To determine the interaction with heavy metals on synthetic system
- …. To determine the speciation on leached OPC…?

Molecular scale approach: determination of the iron speciation in cement phases

Polarized light microscope
XRD…

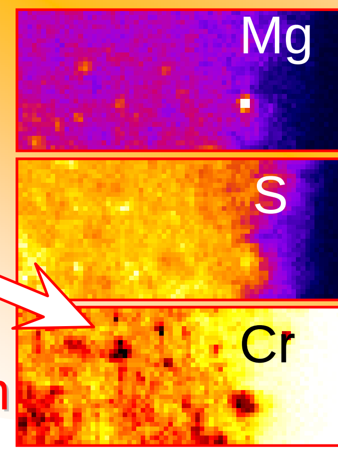


From cm



mm

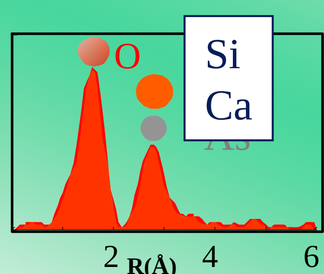
100 µm

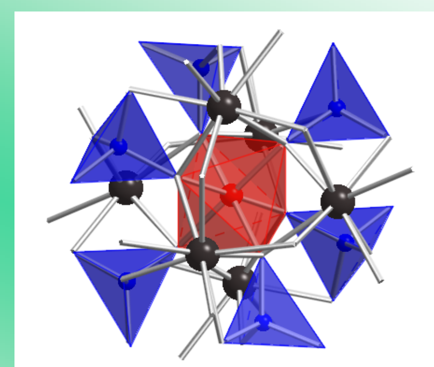


µm

SEM-EDX
µ-XRF
(fragile samples)
(synchrotron
(small spot size,
sensitive))

XAS
Micro-XAS
(synchrotron)

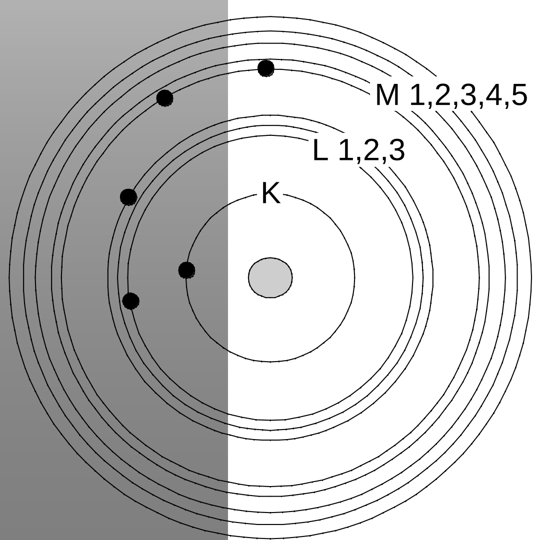


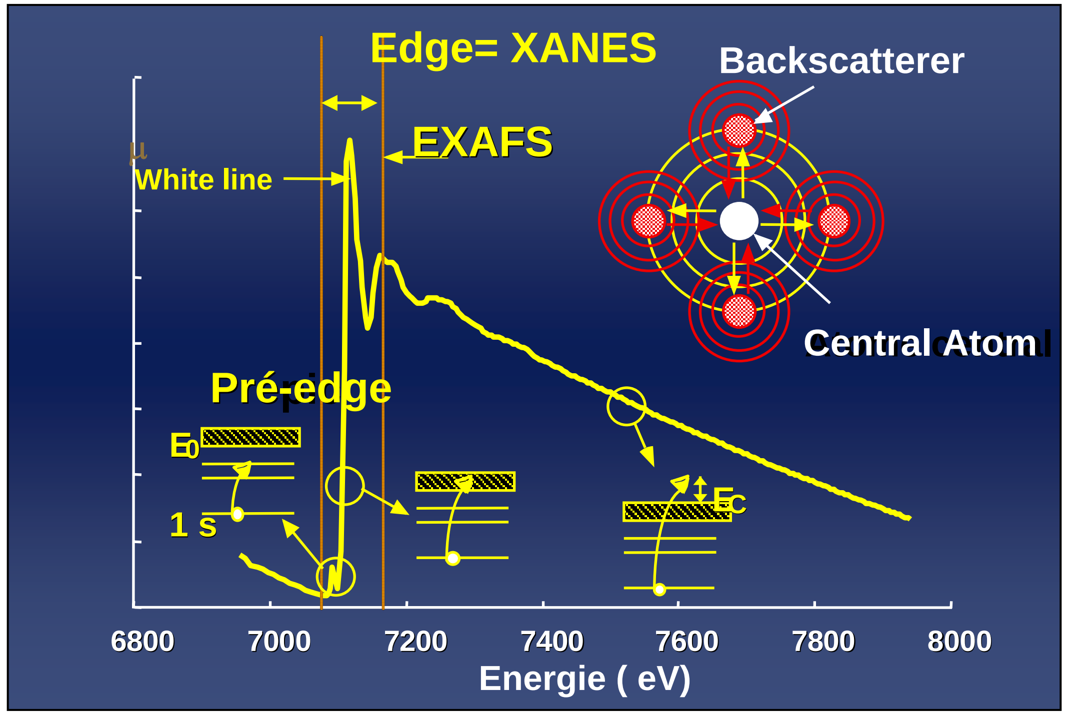


Å

Structure at the local scale : X-ray Absorption Spectroscopy

Element	K1S	L_1 2S	$L_2 2p_{1/2}$
H	13.6 (eV)		
….			
Ar	3205.9	326.3	250.6
K	3608.4	378.6	297.3
Ca	4038.5	438.4	349.7
…			
Ti	4966	560.9	460.2
V	5465	626.7	519.8
Cr	5989	696	583.8
Mn	6539	769.1	649.9
Fe	**7112**	844.6	719.9



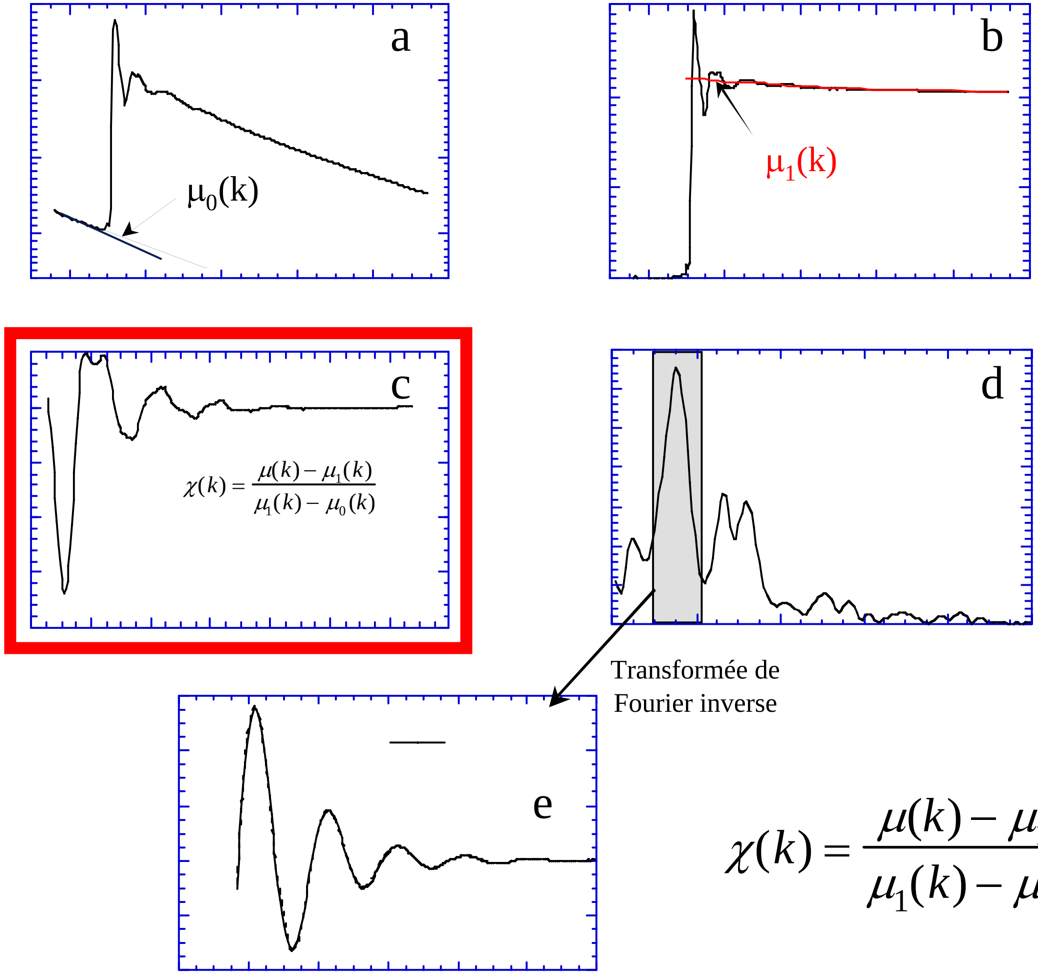


XANES = **X**-ray **A**bsorption **N**ear-**E**dge **S**pectroscopy : REDOX STATE

EXAFS = **E**xtended **X**-ray **A**bsorption **F**ine-**S**tructure : ATOMIC ENVIRONMENT

EXAFS

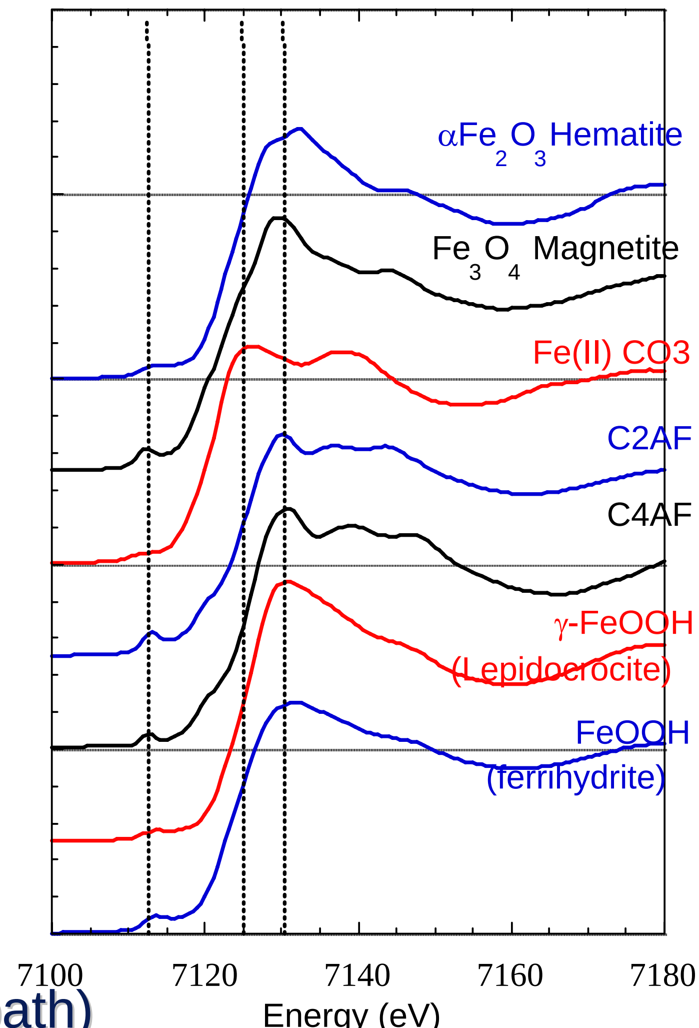
EXAFS curve = Fingerprint of the atomic structure



$$\chi(k) = \frac{\mu(k) - \mu_1(k)}{\mu_1(k) - \mu_0(k)}$$

XANES = fingerprint
EXAFS = fingerprint

- Reference spectra :
- Redox state
- Symmetry



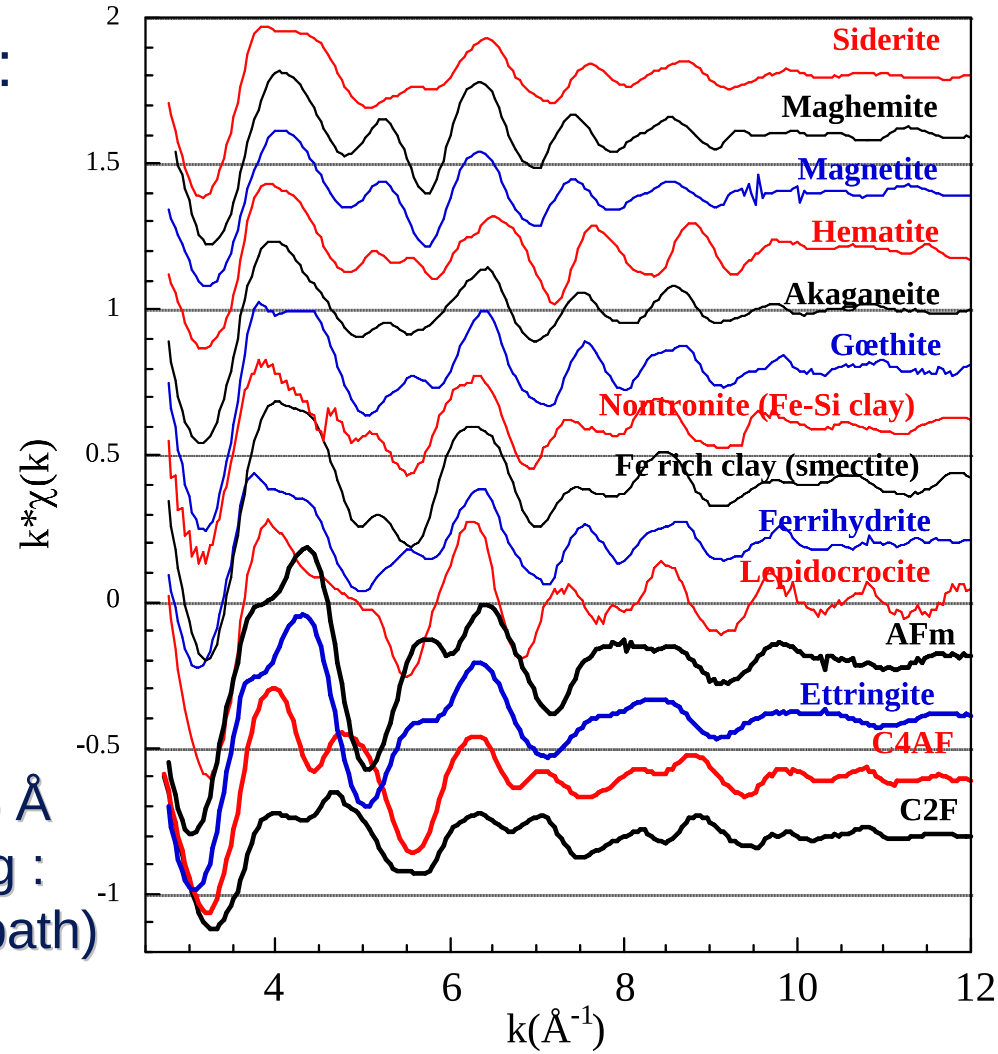
From 0 to … 6-10 Å
(multiple scattering : high e^- mean free path)

XANES = fingerprint
EXAFS = fingerprint

- Reference spectra :
- Redox state
- Nature, number

And distance of neighboring atoms

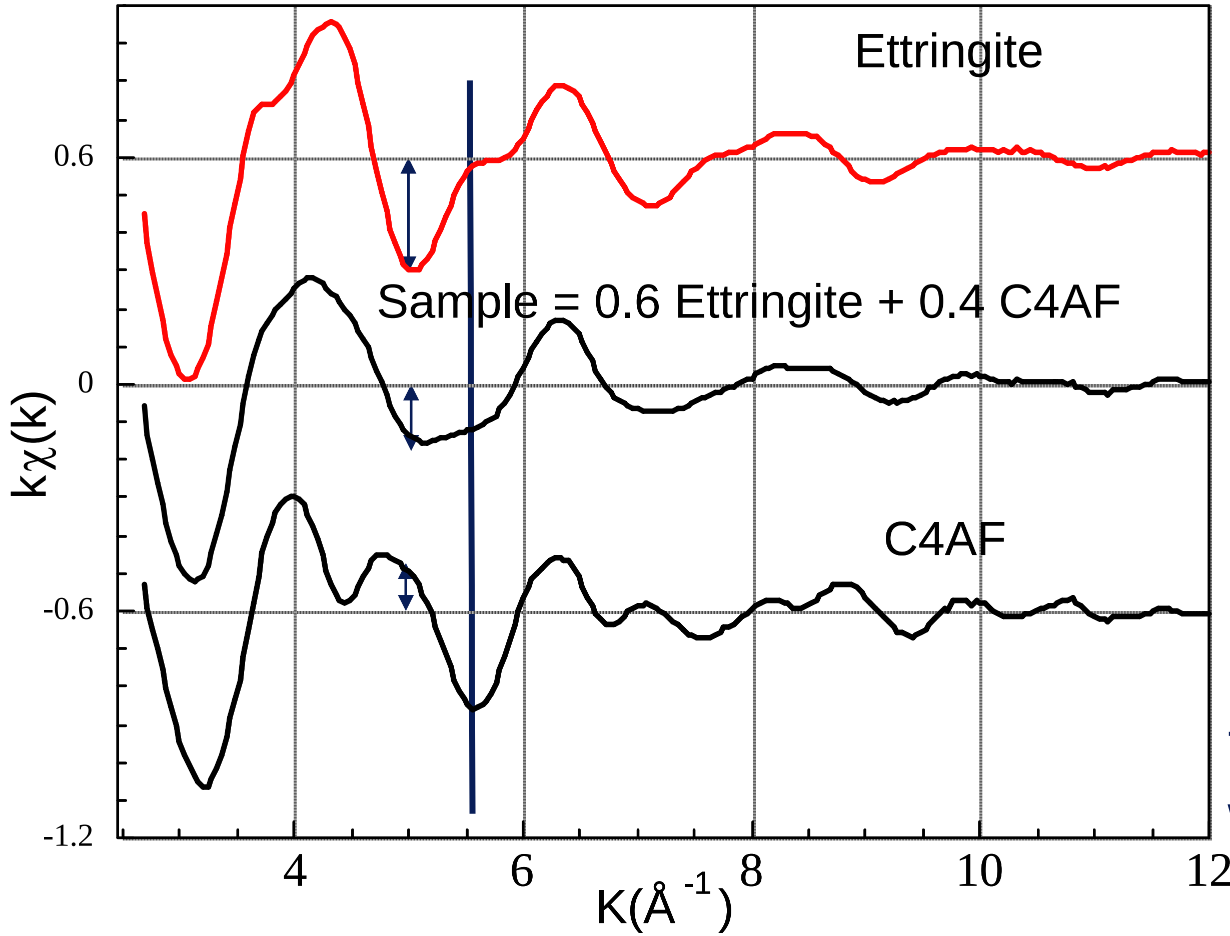
From 0 to … 4-5 Å
(single scattering :
low mean free path)



EXAFS

- In a sample :

  Fe is in C4AF (40%) and Ettringite (60%)



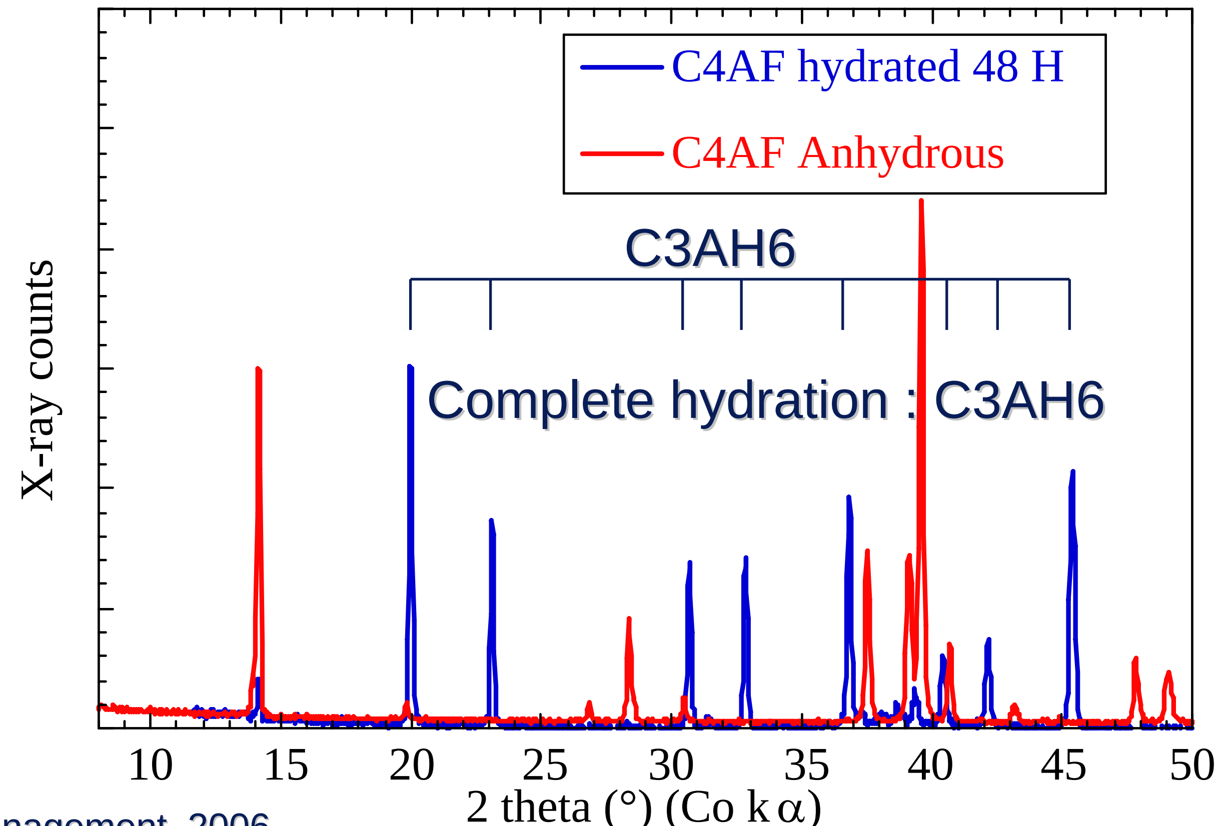
The same with XANES

Local scale study

- Procedure :
  - PCA, then linear combination… (XANES and EXAFS)
  - EXAFS modelling (XANES : still difficult on heterogeneous sample)
- With XAS : the fit does not indicate that the mineral exist: it reflects a similar atomic structure
- XAS does not require long range order.

RESULTS :
Hydration of C4AF in LW (without sulfate)

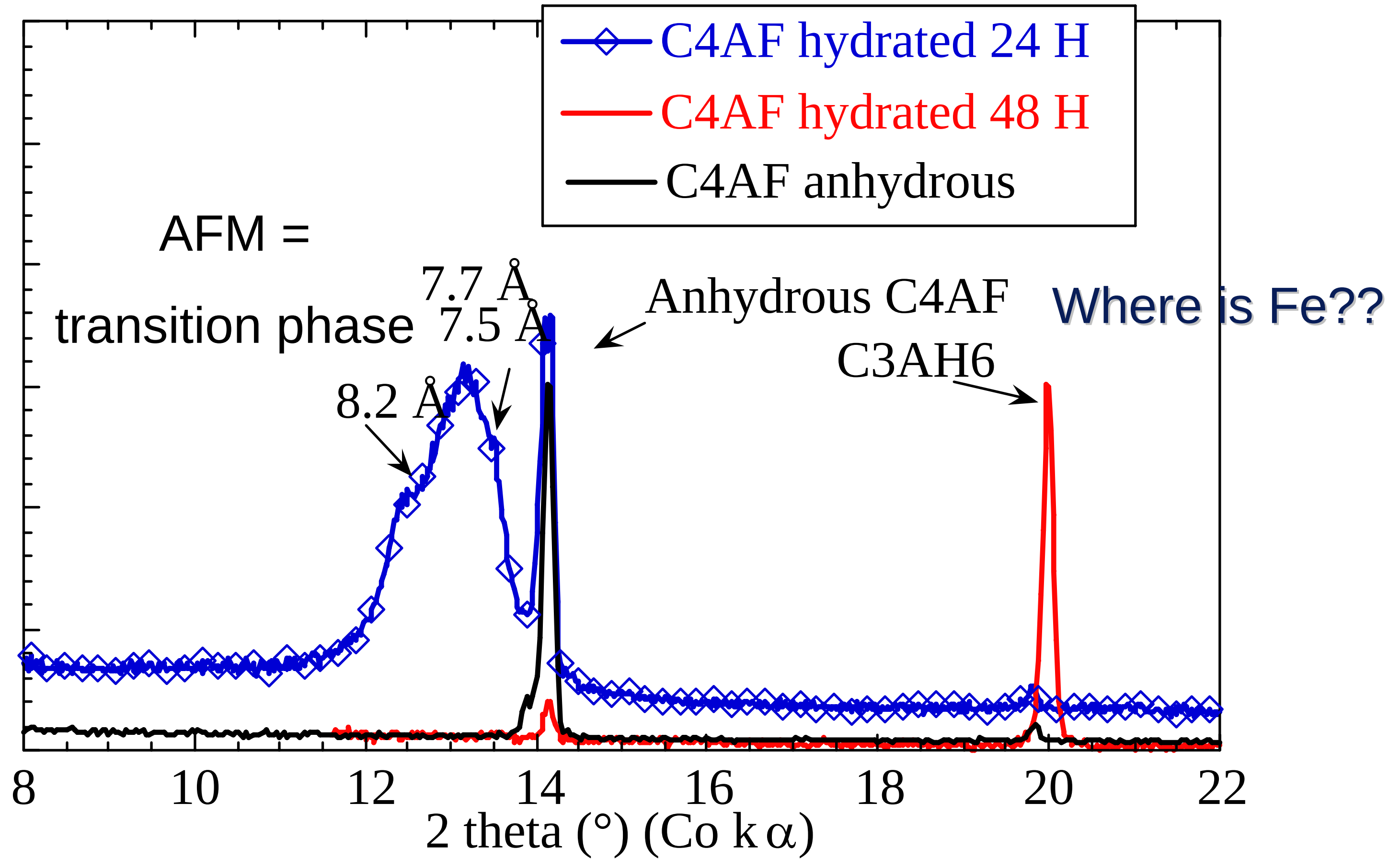
- Hydration liquid/solid ratio of 0.5, 10, 60.



Rose et al, Waste Management, 2006

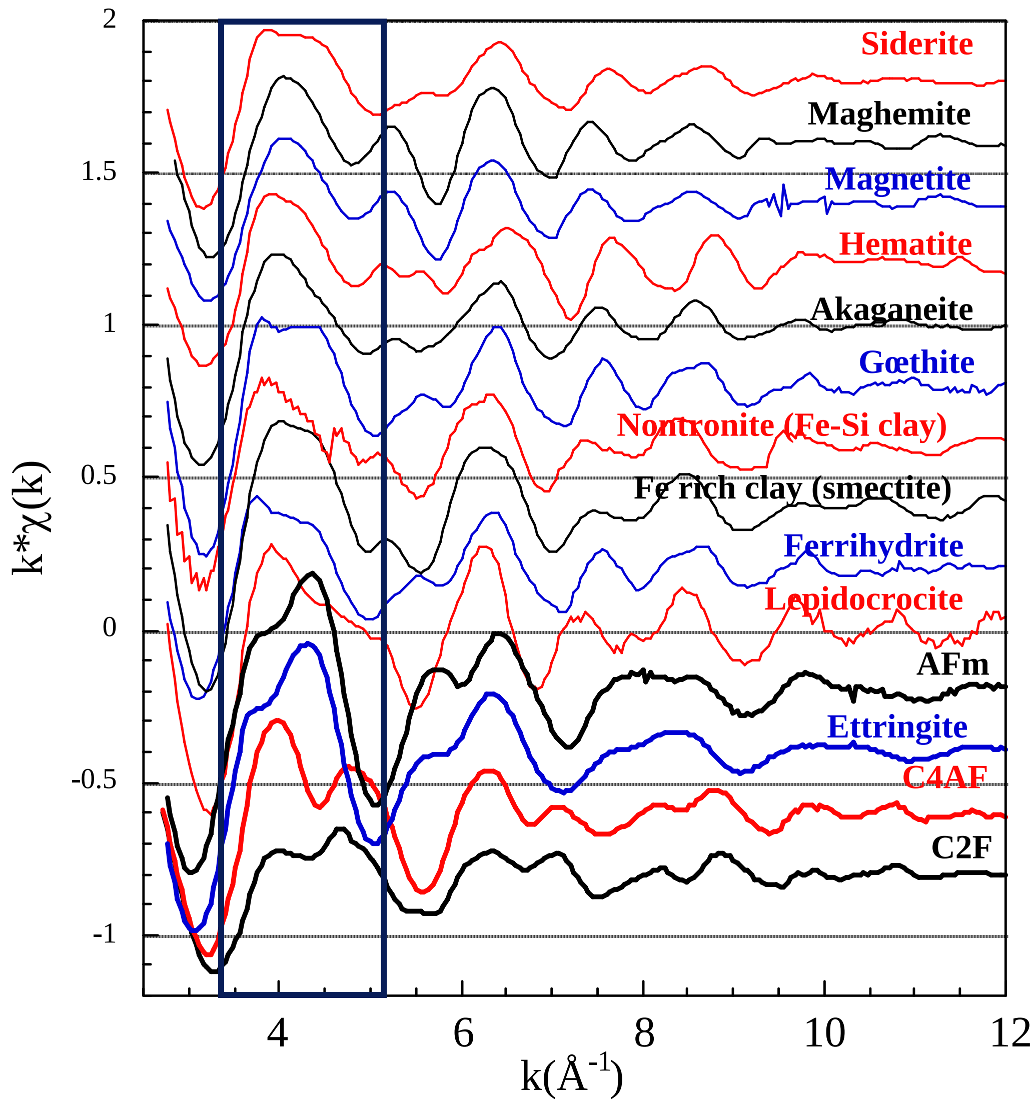
Hydration of C4AF in LW (without sulfate)

- Hydration liquid/solid ratio of 10



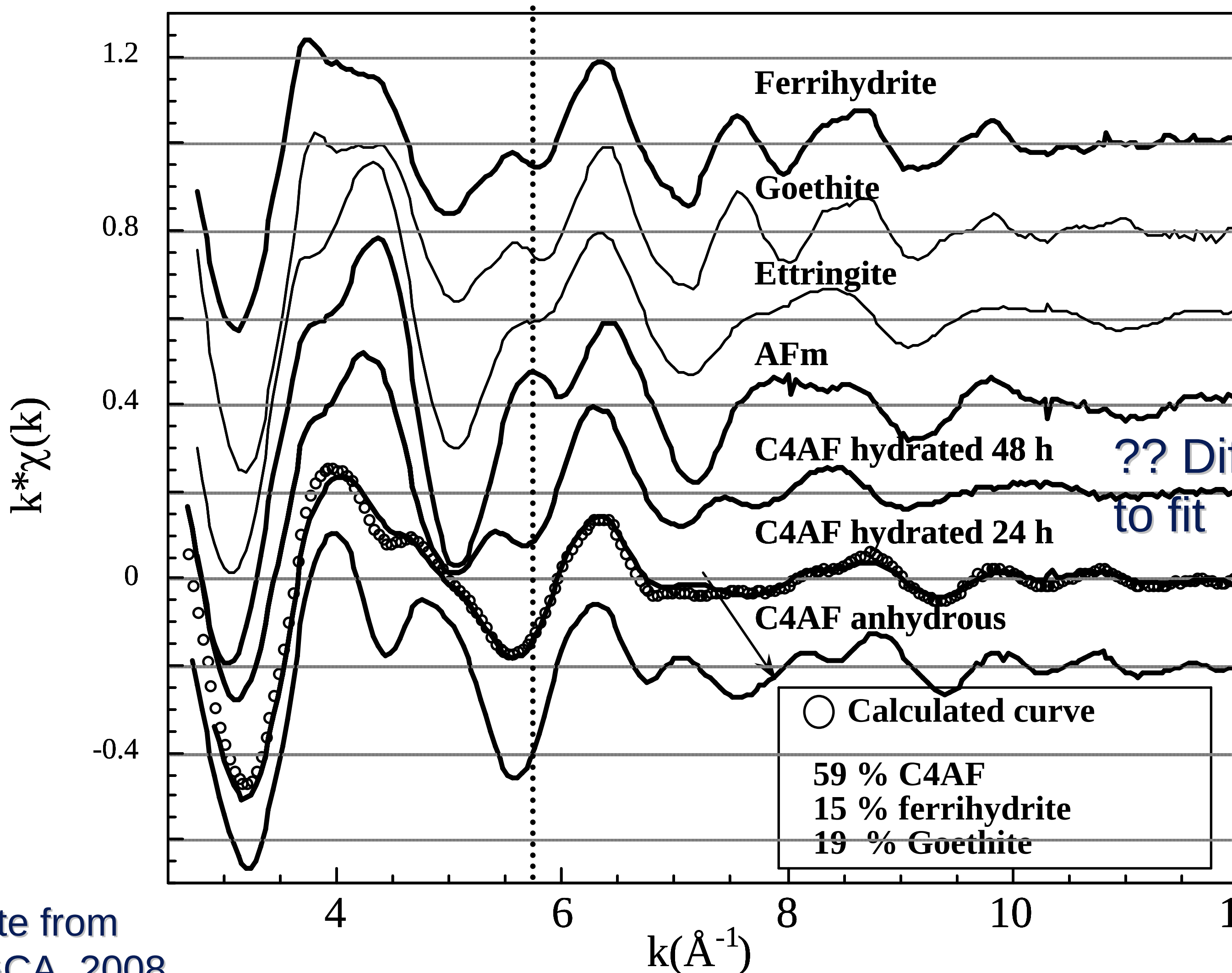
EXAFS results at the Fe K edge

- Comparison with FeOOH, Fe-oxides; carbonates, AFm, Ettringite, C4AF, C2F



AFm and Ettringite from Moschner et al GCA, 2008

EXAFS results at the Fe K edge



?? Difficulty to fit

±10-15%

AFm and Ettringite from Moschner et al GCA, 2008

EXAFS results at the Fe K edge

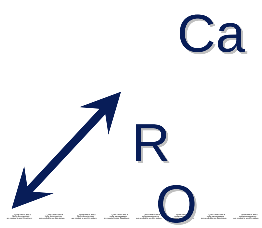
- EXAFS modelling

amplitude — phase

$$\chi(k) = -\sum_{i=1}^{N} \frac{N_i S_0^2}{kR_i} \left|f_i(\theta, k, R_i)\right| e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)} \sin\left(2kR_i + \phi_i(k) + 2\delta_c(k)\right)$$

$N_{Fe\text{-}O} = 6$

$N_{Fe\text{-}\text{-}Ca} = 8$

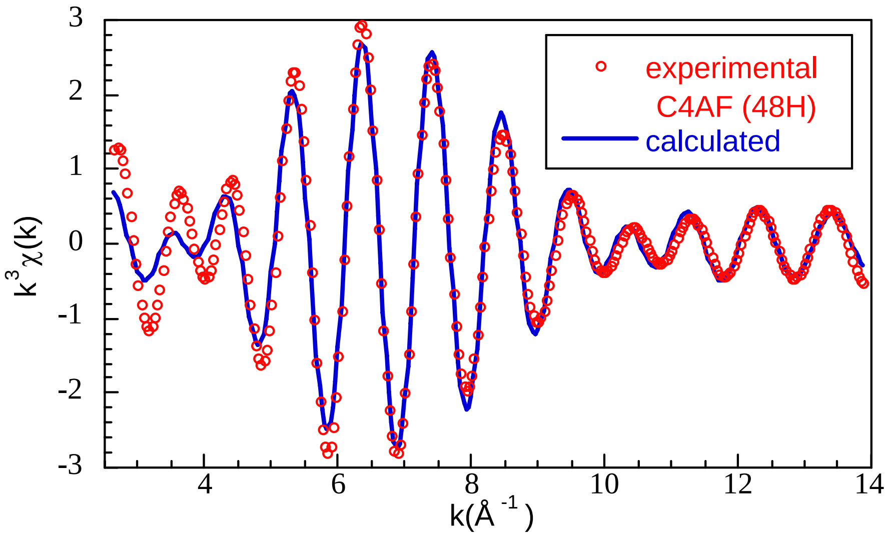


$R_{Fe\text{-}O} = 2$ Å

$R_{Fe\text{-}\text{-}Ca} = 3.4$ Å

EXAFS results at the Fe K edge

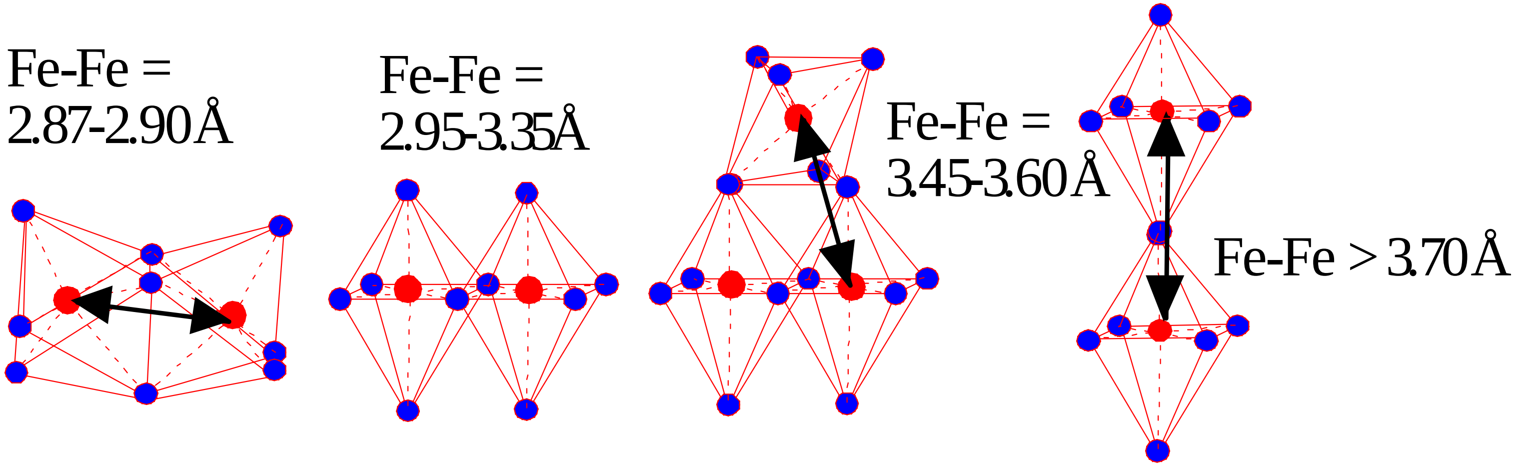
- EXAFS modelling



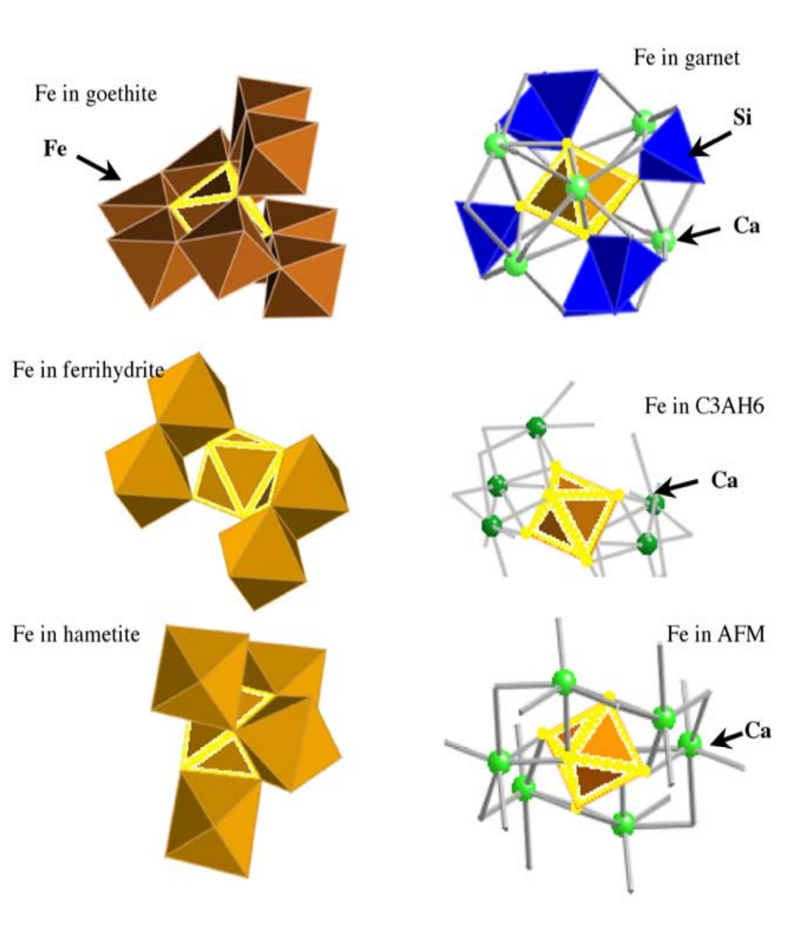
Sample	Atomic pair	R (Å)	σ (Å)	N	Residue
C_4AF, **48 H**	Fe–Fe	3.03	0.104	2.1	0.0389
	Fe–Fe	3.45	0.070	0.2	
	Fe–Ca	3.59	0.091	2.1	

Fe - Fe distance : how can we go further?

Structural approach



Structural approach



	Atomic pair	Distance (Å)	Number of Fe neighbours
Goethite (α-FeOOH)	Fe--Fe	3.01	2
	Fe--Fe	3.28	2
	Fe--Fe	**3.46**	4
Ferrihydrite (amorphous-FeOOH)	Fe--Fe	3.01	4.5
	Fe--Fe	**3.43**	**3.9**
Hemathite (α-Fe2O3)	Fe--Fe	2.90	1
	Fe--Fe	**2.97**	**3**
	Fe--Fe	**3.36**	**3**
	Fe--Fe	3.70	6
C3AH6	Fe-Ca	3.51Å	6
AFm	Fe-Ca	3.35 Å	6

Hydration of C4AF (in LW)

Sample	Atomic pair	R (Å)	σ (Å)	N	Residue
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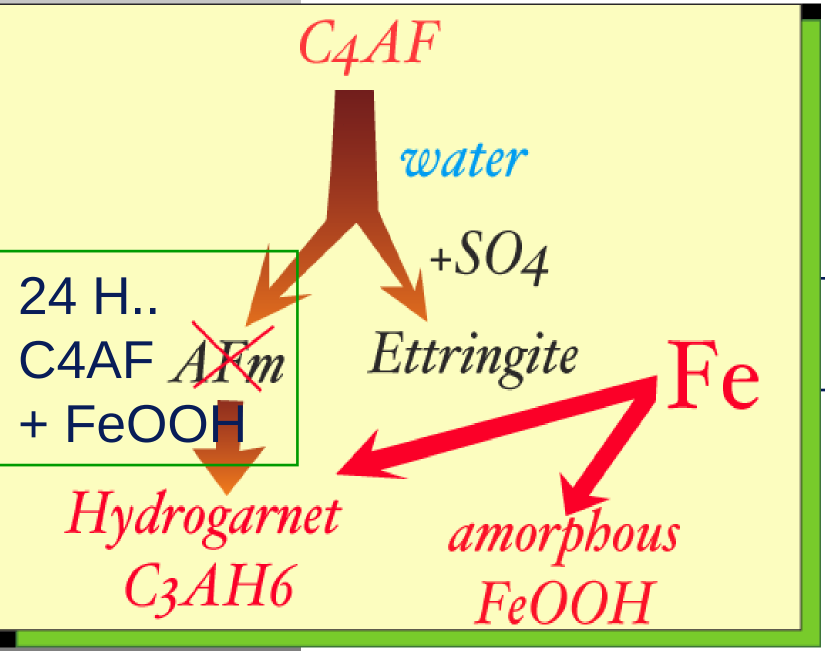
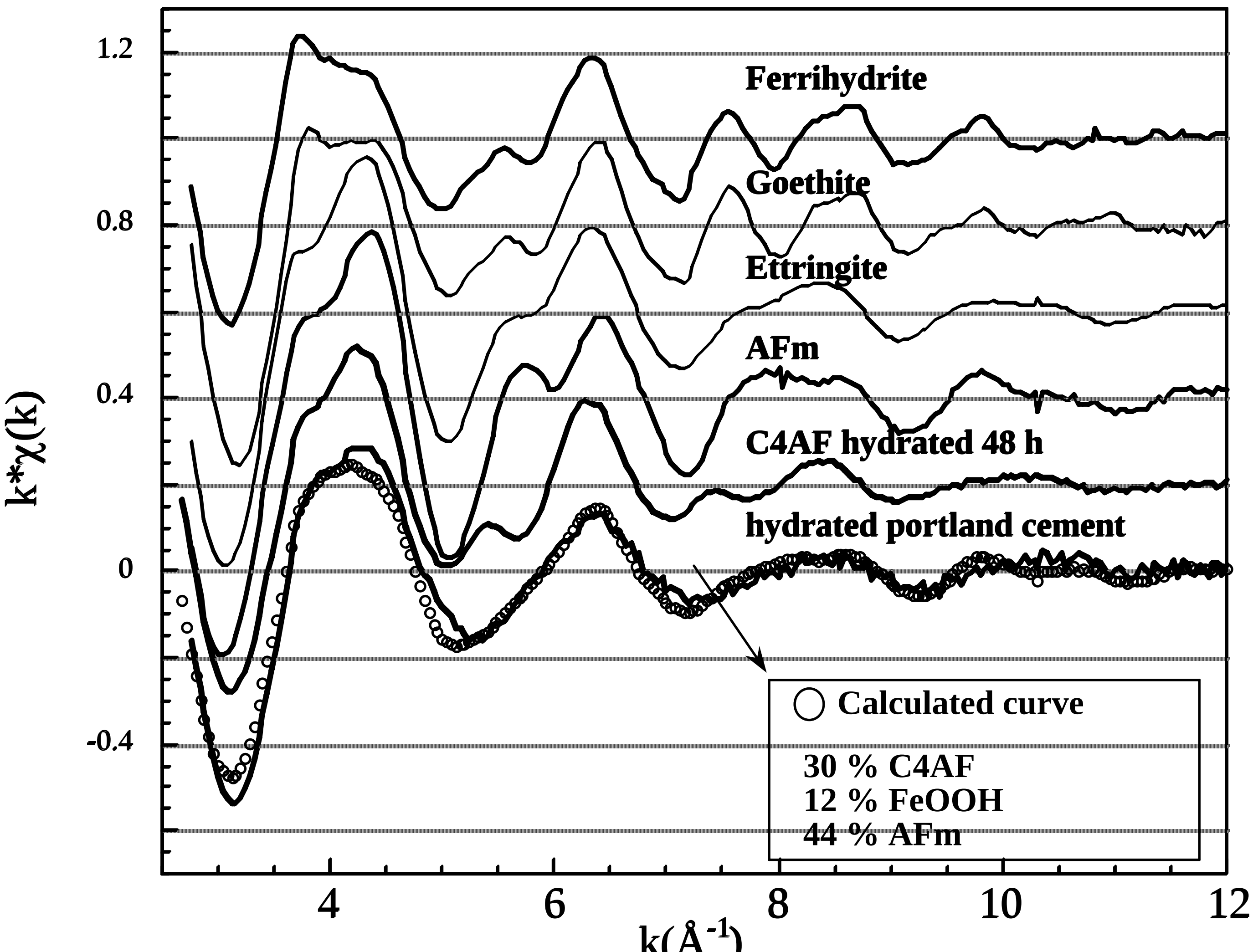


FeOOH + hydrogarnet

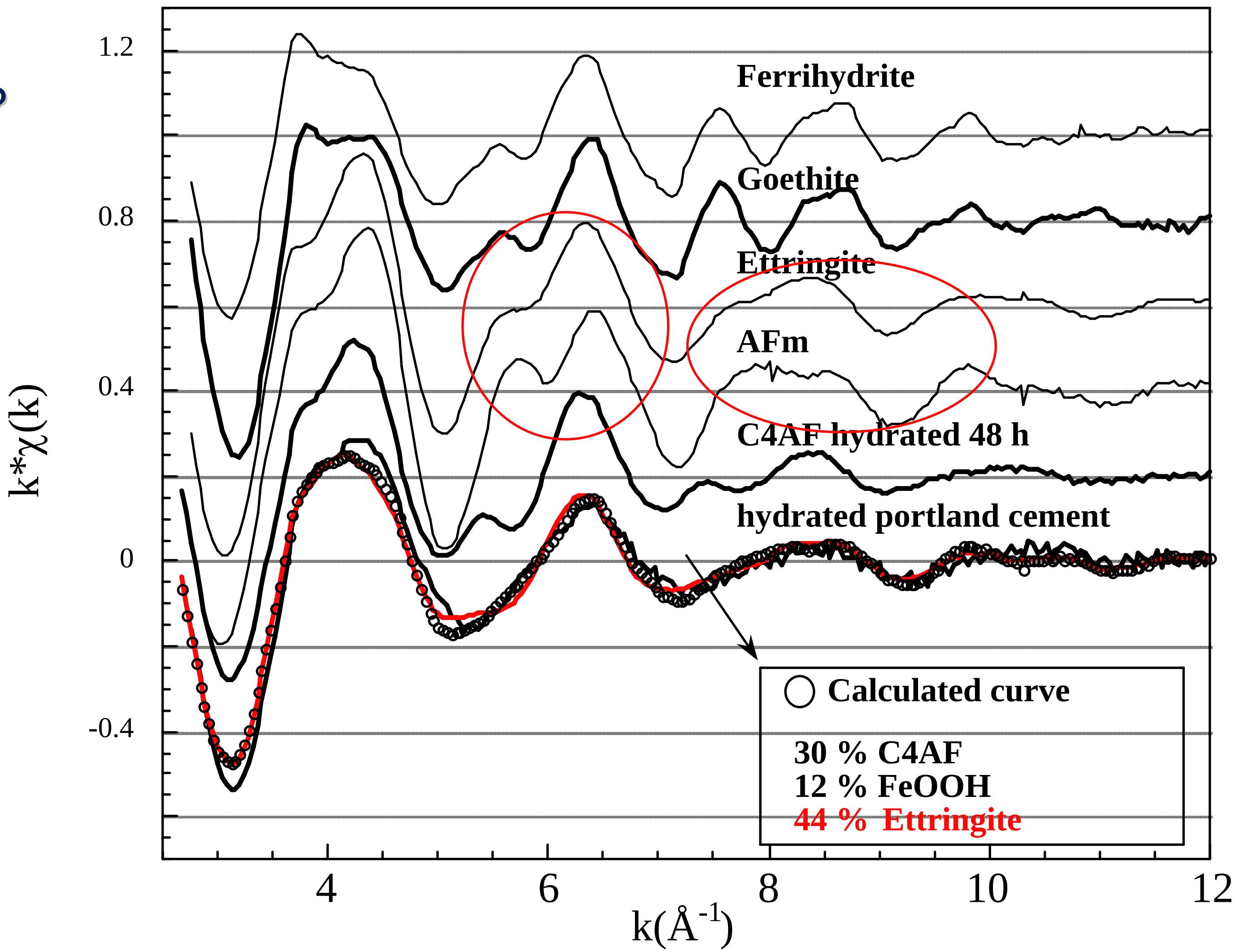
What about Portland cement??

Iron in hydrated Portland cement

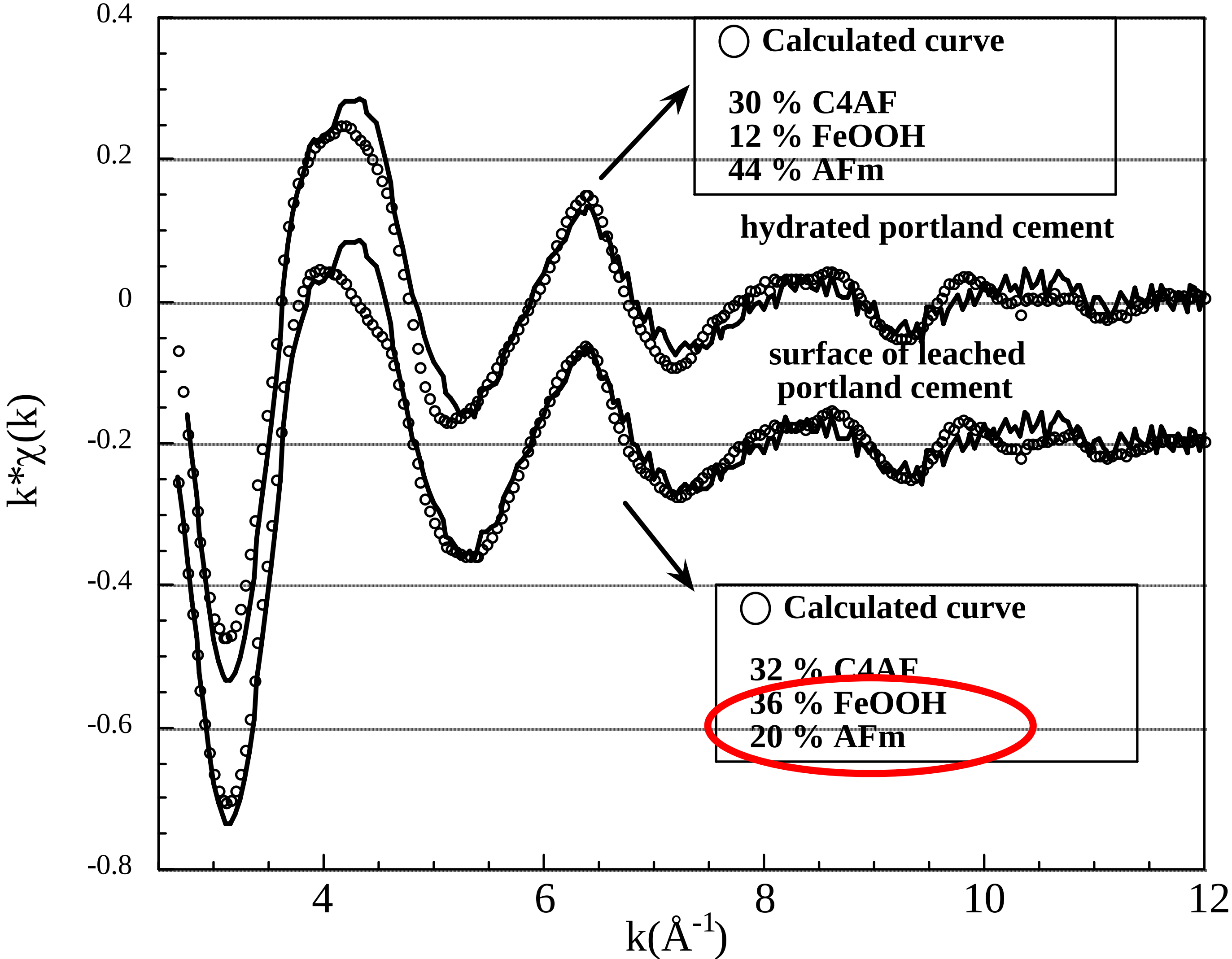


Iron in hydrated Portland cement

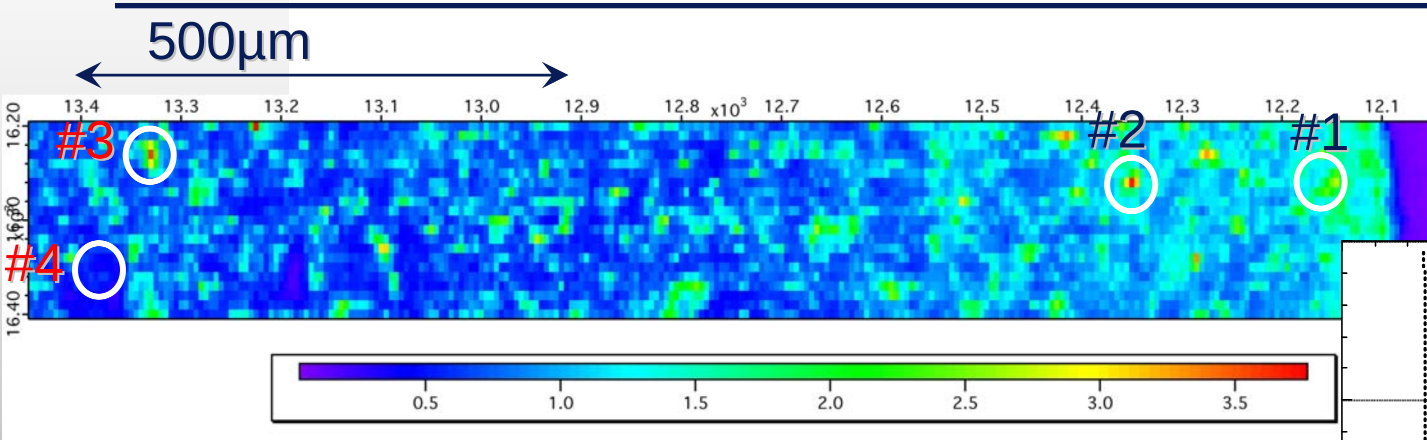
AFm
Ettringite??



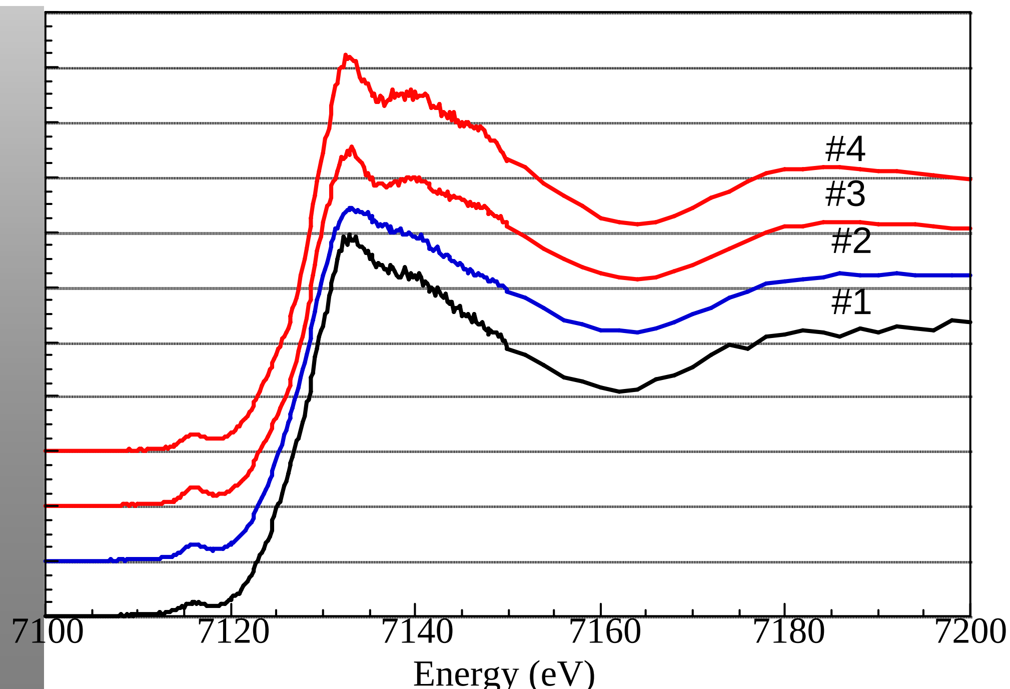
Iron in hydrated Portland cement

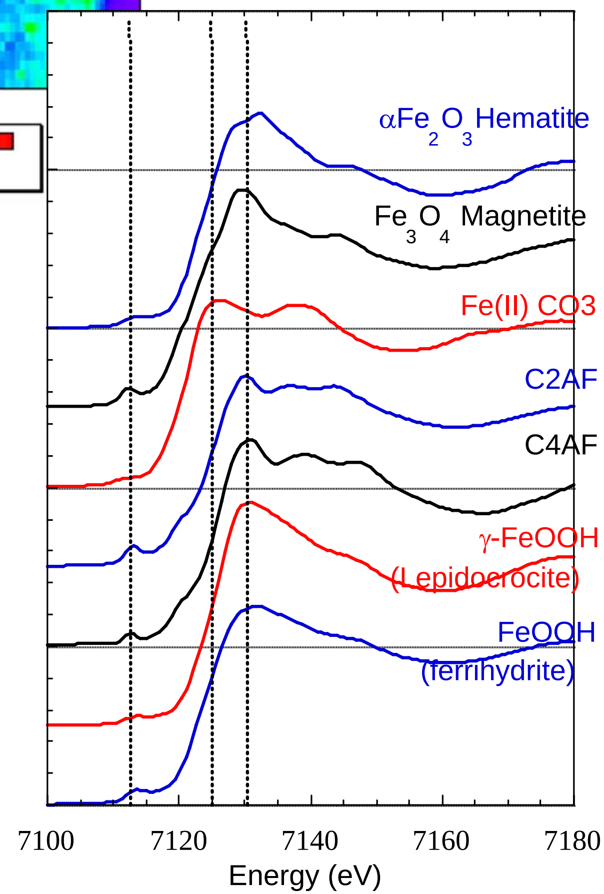


In OPC at the micro scale



μ-XRF (Fe)
Lucia (SLS)
(μ-XANES + μ-EXAFS)





Summary

- Hydration of C4AF (-SO_4) : FeOO + Fe in hydrogarnet (No Fe and AFm??)
- In presence of SO4 (CaSO4) : ettringite (Mochner et al, 2008)

- In OPC : remaining C4AF (local scale) + FeOOH + AFm (??). More amorphous Fe at the surface.

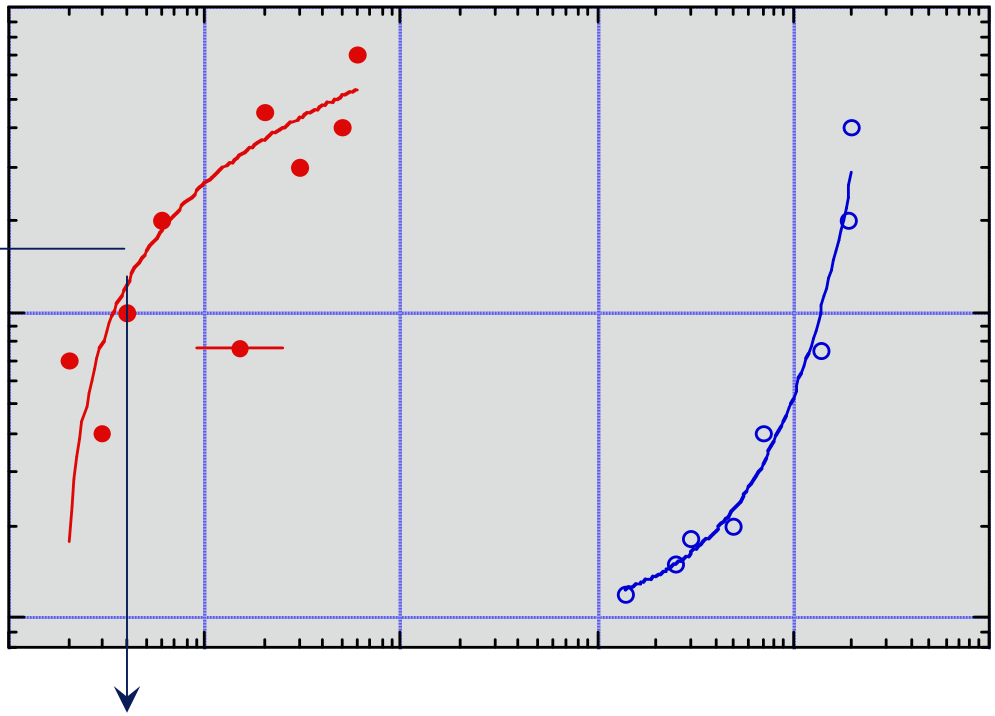
What is the role of iron phases in heavy metal fixation

- Stage 1: C4AF + Heavy metal interactions…
- Stage 2 : on ‘real’ system…

C4AF hydrated in presence of metals

- Fe and lead : isotherms: (L/S ratio (0.5 to 60); with LW, $[Pb]_{initial}$ from 10^{-3} to 8.10^{-3} mol/l)

“Everything” fixed by the solid

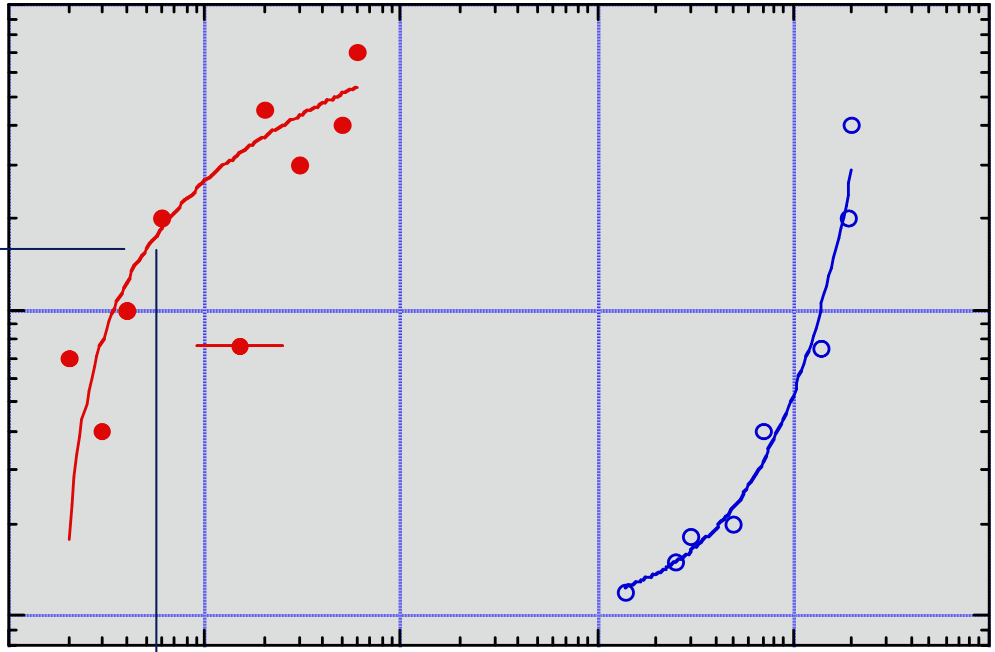


“Nothing” in solution

Reactivity between iron phases and metals (pure system)

C4AF hydrated in presence of metals

- Fe and lead : isotherms: (L/S ratio (0.5 to 60); with LW, $[Pb]_{initial}$ from 10^{-3} to 8.10^{-3} mol/l)



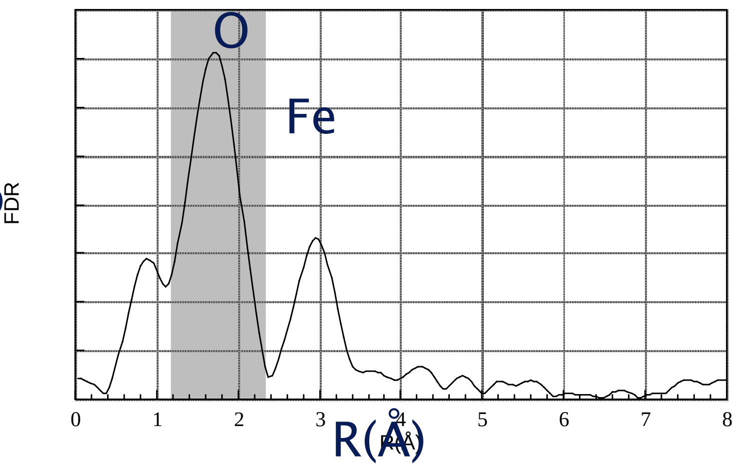
<u>"Everything" fixed by the solid</u>

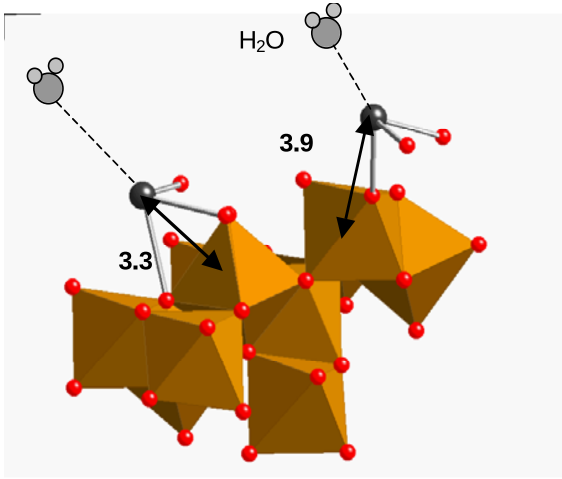
<u>"Nothing" in solution</u>

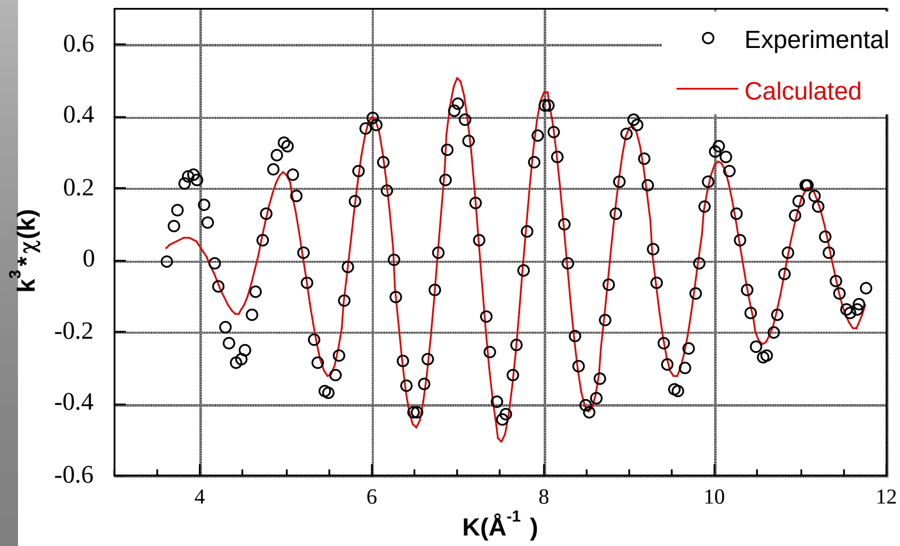
EXAFS at the Pb L edge

Pb radial distribution function

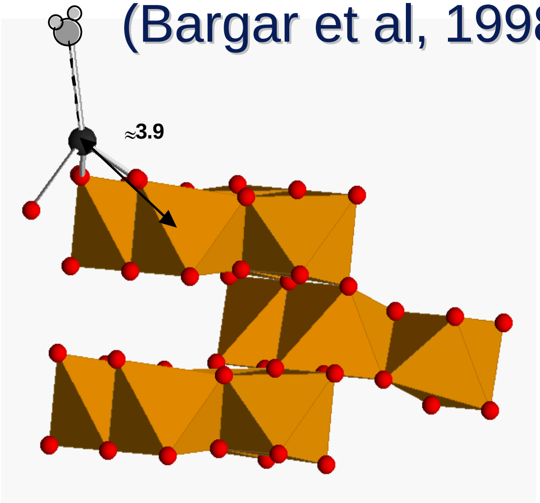
EXAFS at the Pb LIII edge (Pb+FeOOH)





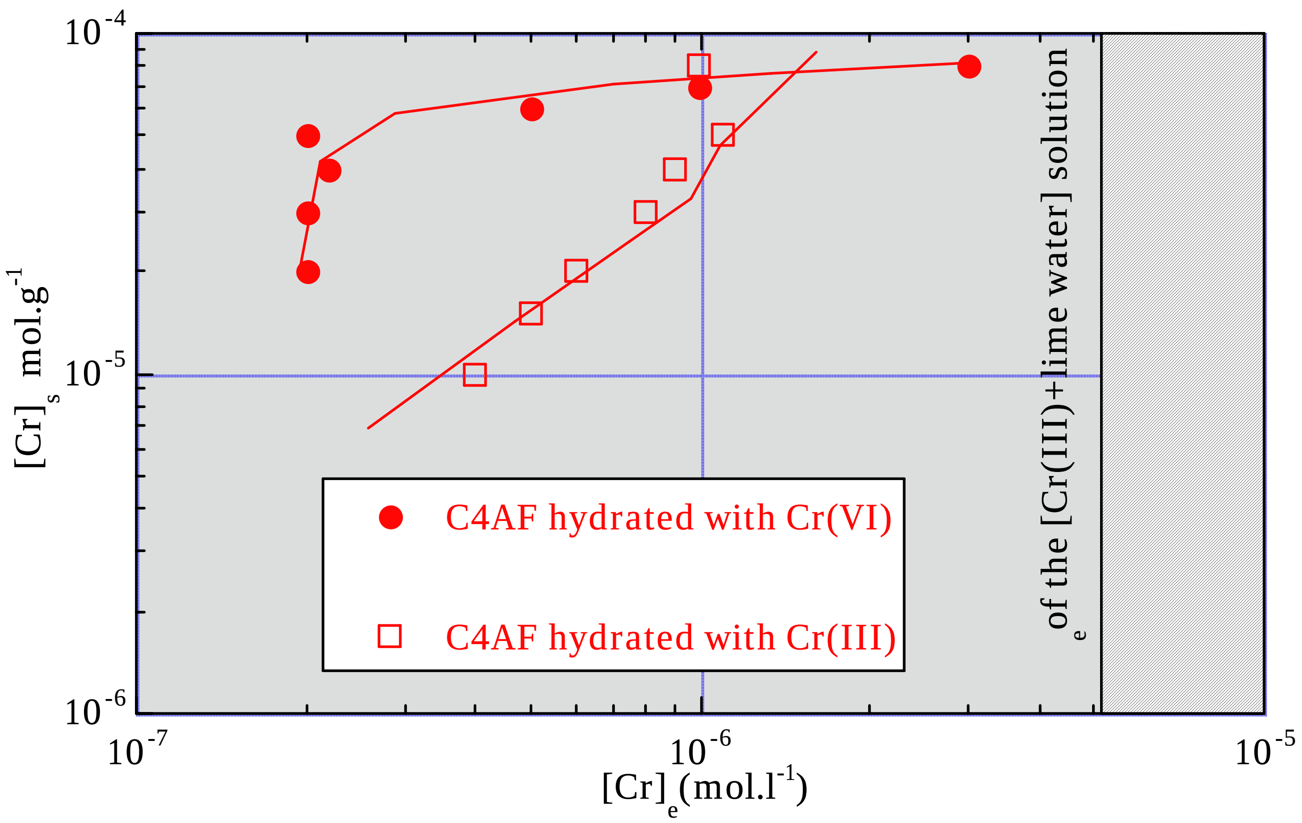


(Bargar et al, 1998)



C4AF hydrated in presence of metals

- Fe in presence of Cr

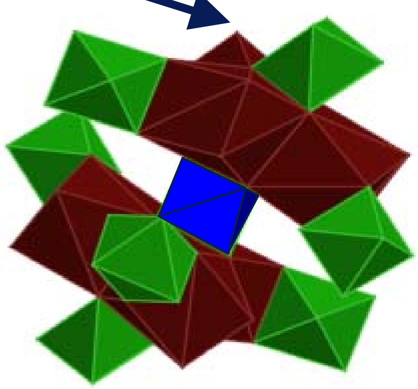


EXAFS at the Cr K edge

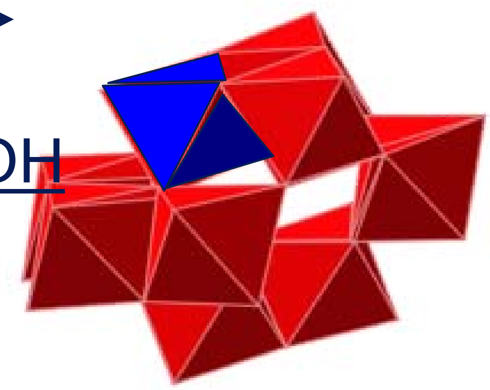
Atomic pair	R( )	σ( )	N	Residue
Cr--Cr/Fe	**3.29**	**0.080**	**2.0**	**0.0375**
Cr--Ca	**3.48**	**0.080**	**3.6**	
Cr--Cr/Fe	**3.55**	**0.102**	**3.5**	

Cr

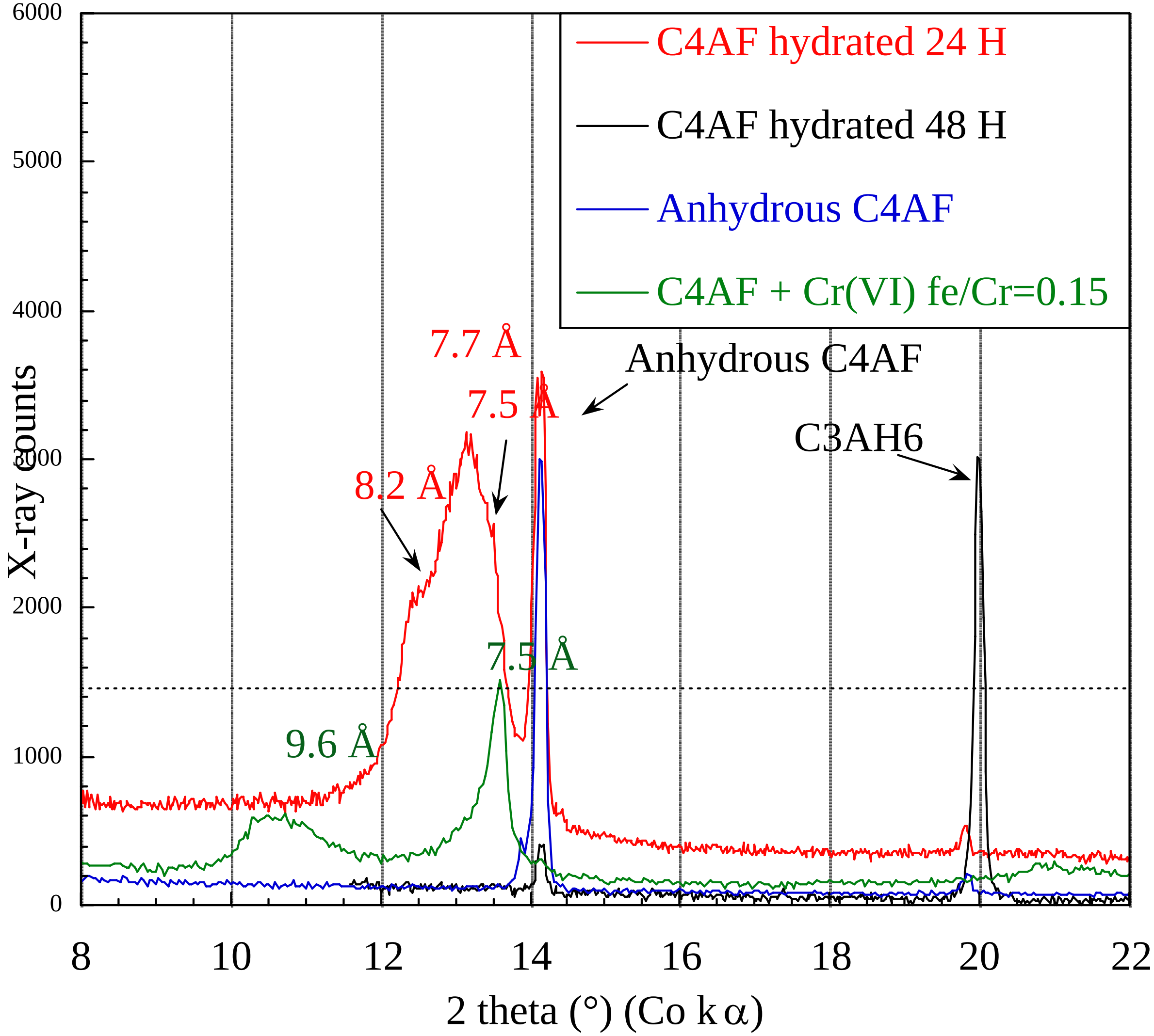
C3A(Cr)H6



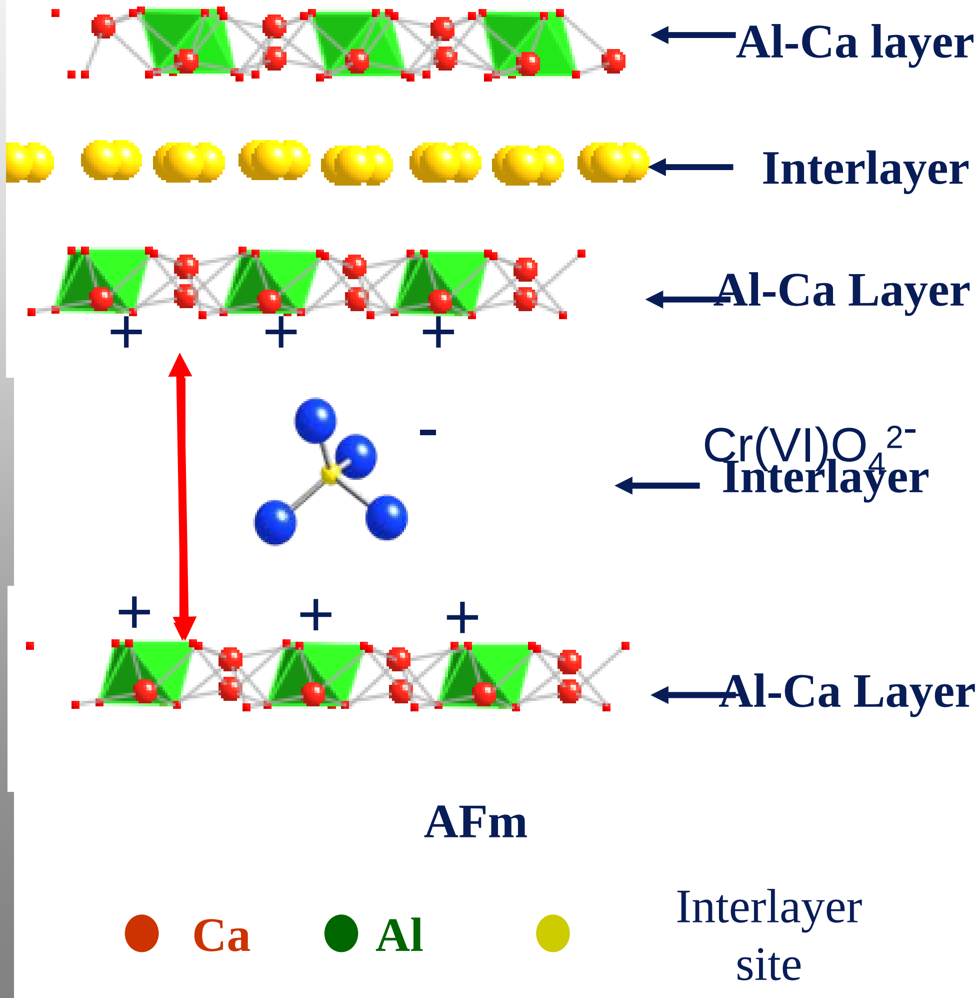
(Cr)FeOH

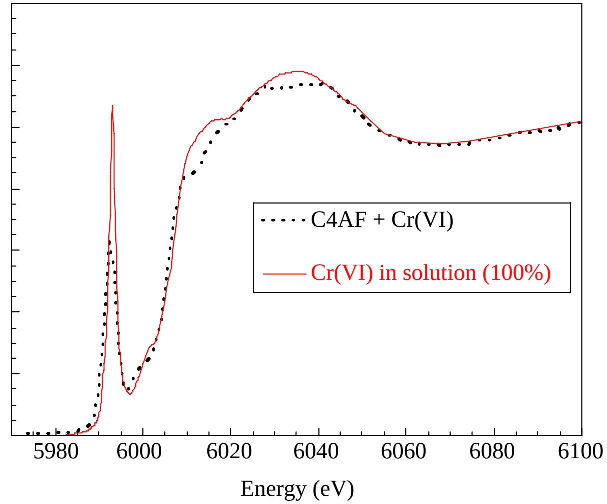


C4AF in presence of Cr(VI)

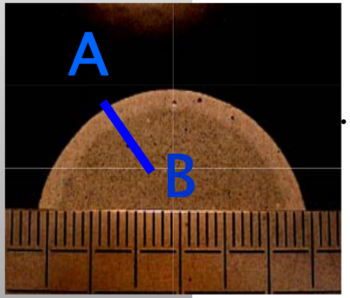


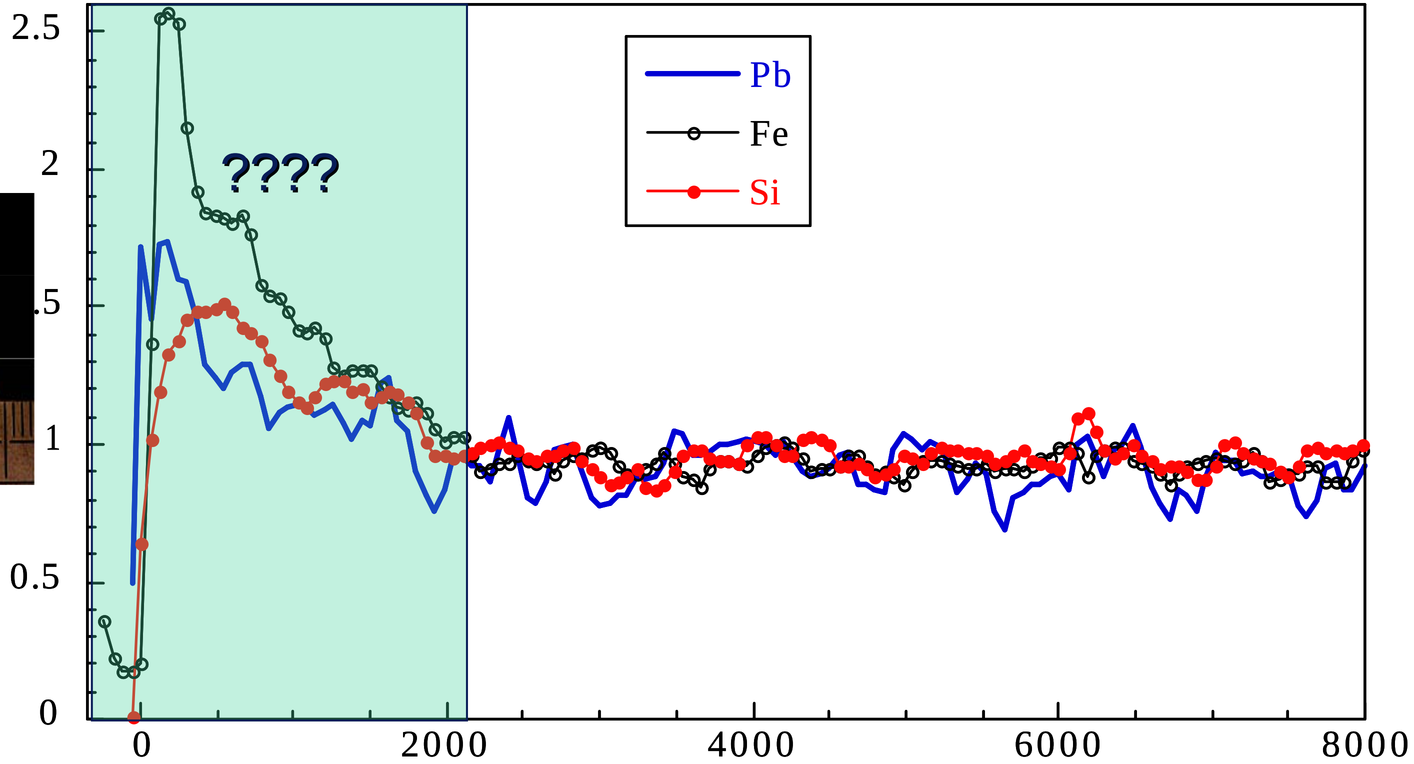
C4AF in presence of Cr(VI)





And in leached Portland cement?

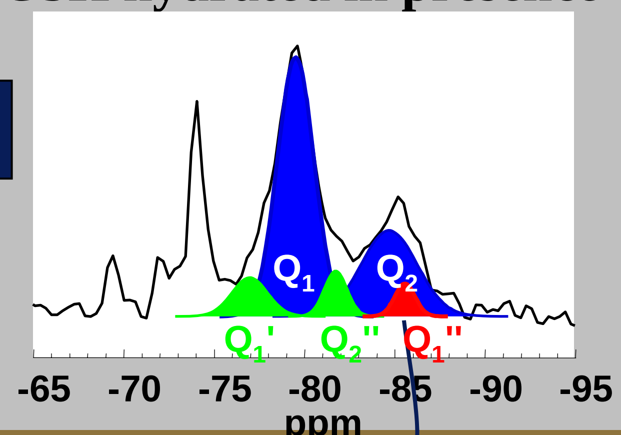




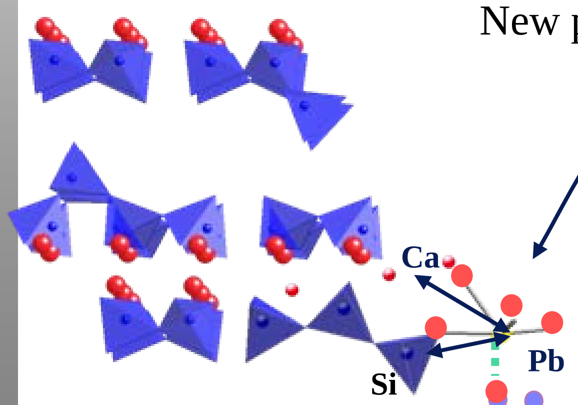
Lead and C-S-H

CSH hydrated in presence of Pb

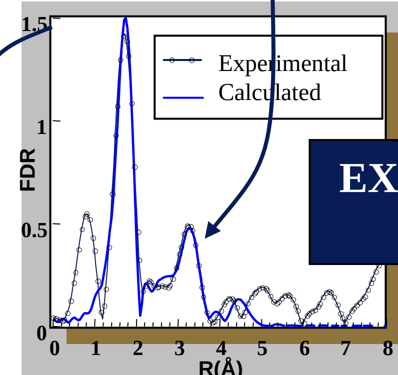
^{29}Si NMR



New peak at +85.6 ppm



CSH structure



EXAFS at the Pb LIII edge

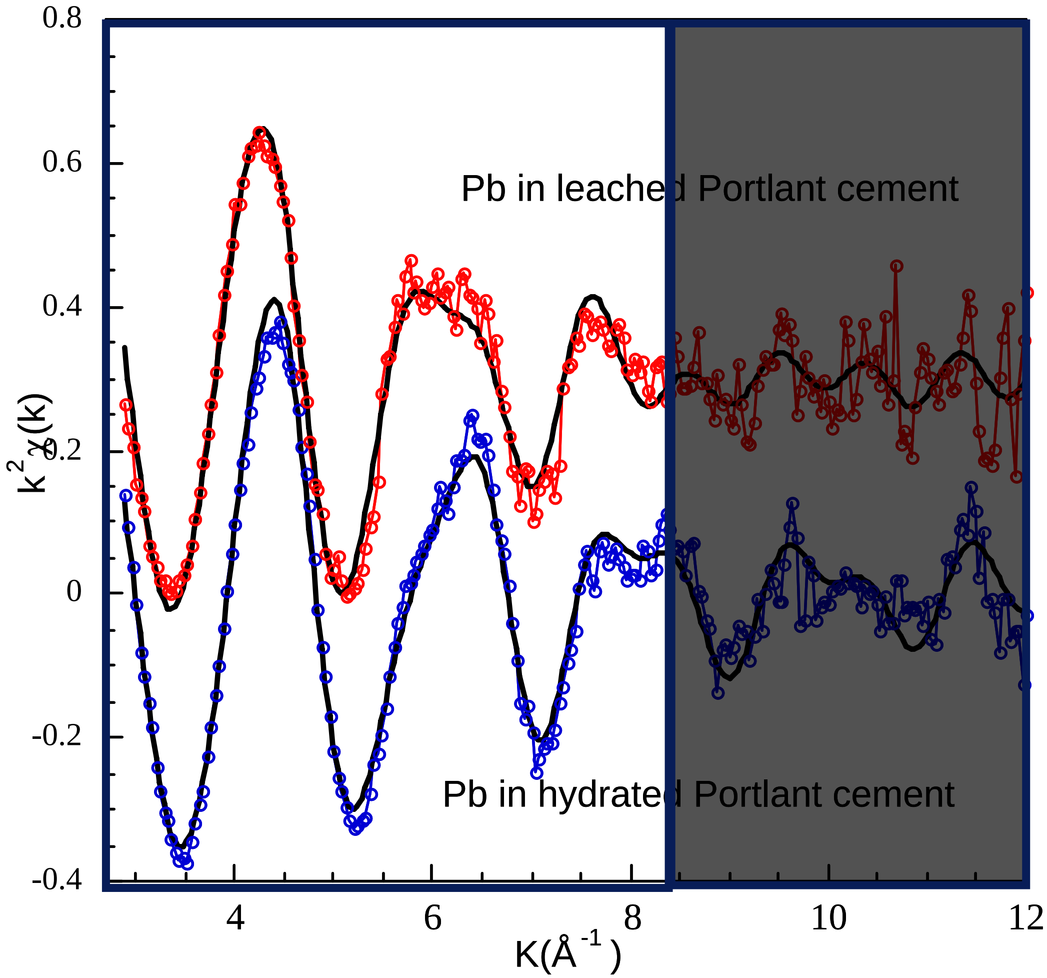
~1 Si at 3,75Å de Pb

~0,8 Ca at 3,58Å de Pb

Rose et al, *langmuir*, 2002

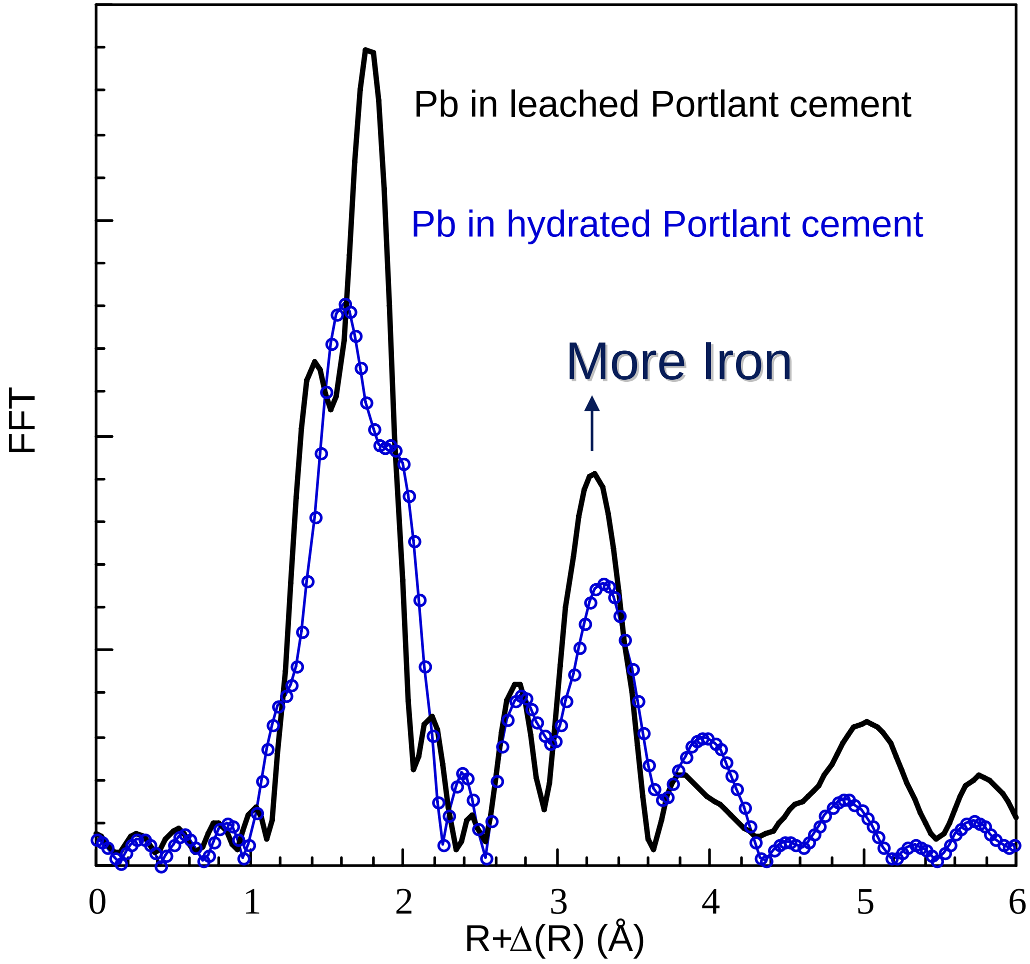
First EXAFS results (noisy)

First fits with Fe in the second coordination sphere



Fe in second coordination sphere

EXAFS results



No enough…

Conclusion

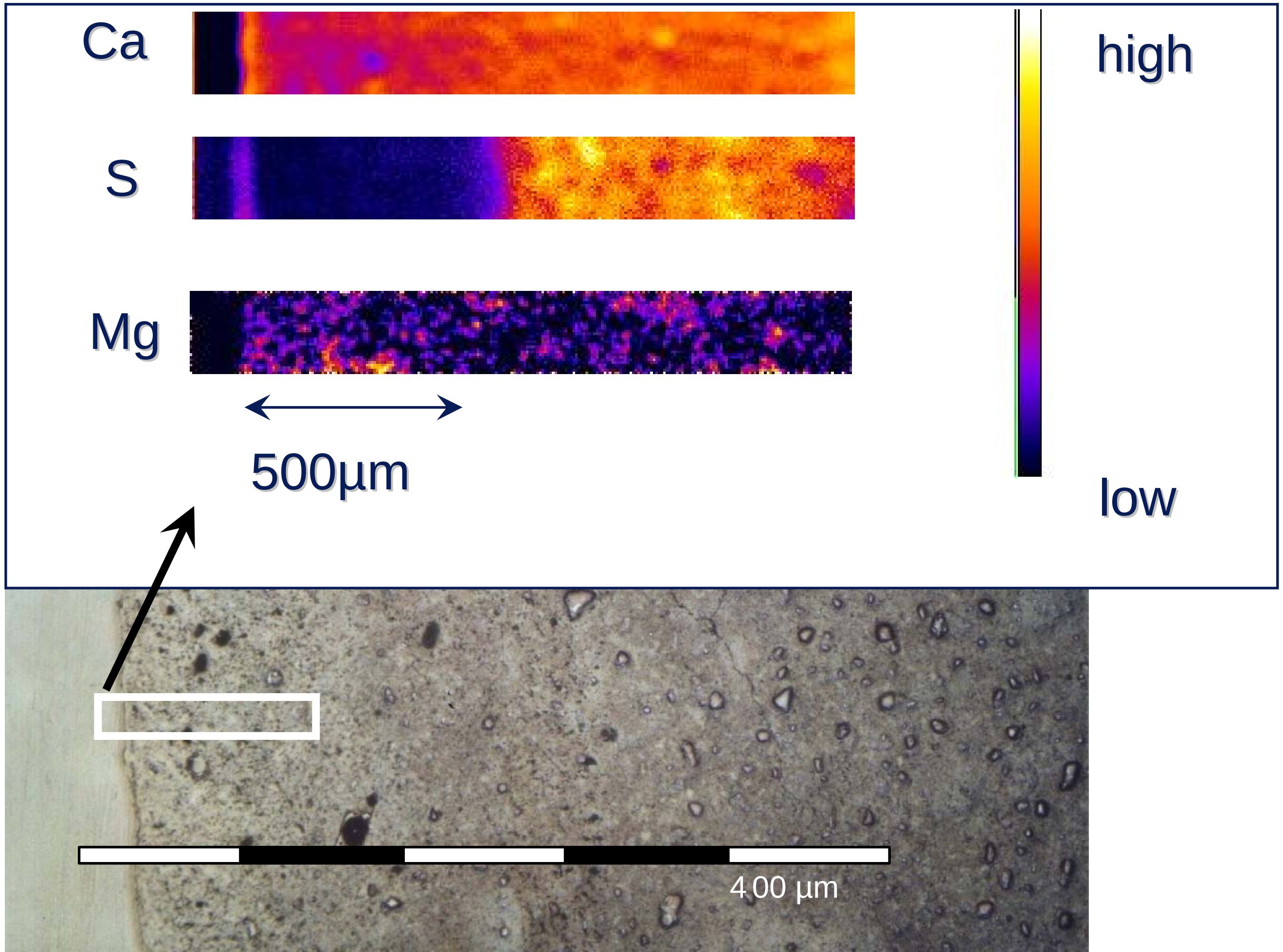
- Existence of FeOOH amorphous phase after cement hydration
- Iron phases formed after C4AF hydration strongly “incorporate” metals (Cr, Pb…)
- Metal and iron in cement: needs further investigation (µ-XRF at the micron scale in leached zones…)
- Implications: iron(III) phases may play a positive role for the long term fixation of metals and metalloids… but under oxic conditions (reductive dissolution of iron).

Acknowledgment

- J-L Hazemann and O. Proux (ESRF, FAME beamline)
- V. Briois (LURE, D44 beamline and SOLEIL Samba)
- A-M Flank (SLS-Soleil, Lucia beamline)

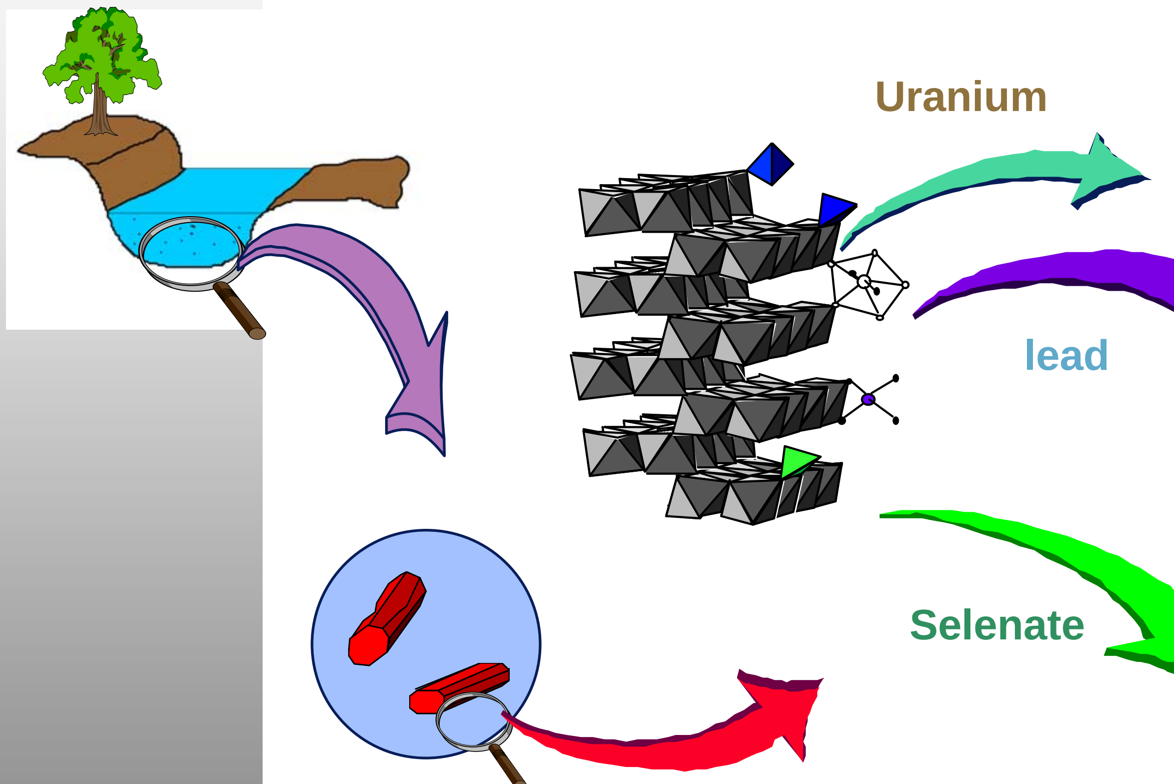
- Funding from the European Community through the INERWASTE Craft European program, and the YPREMA company.

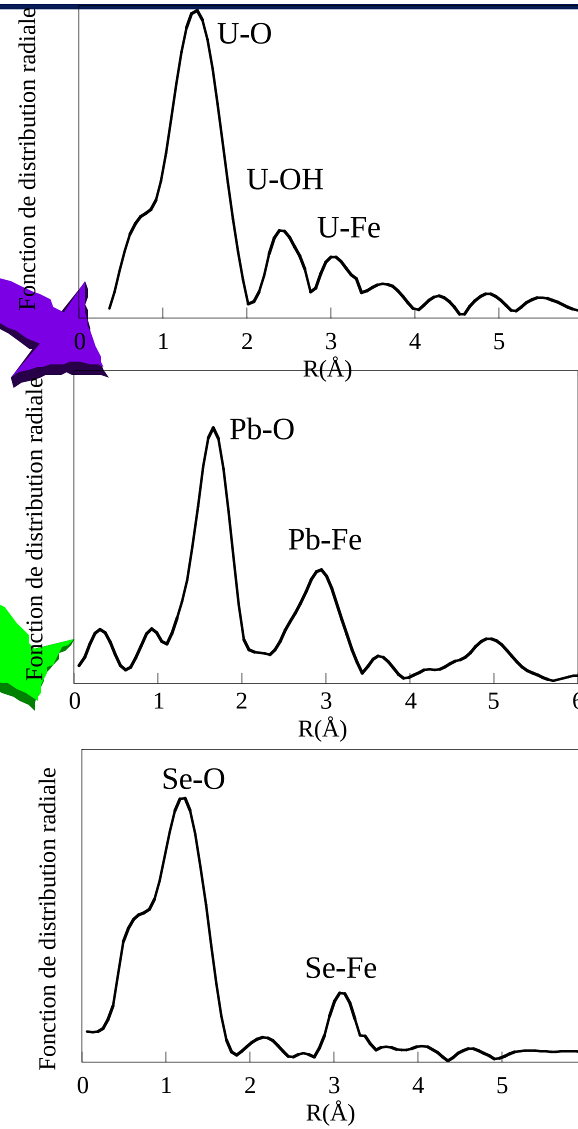
µ-XRF



XGT-5000 X-ray spectro-microscope (HORIBA).
(Rh X-ray source, 15 KV voltage, 10 µm spot

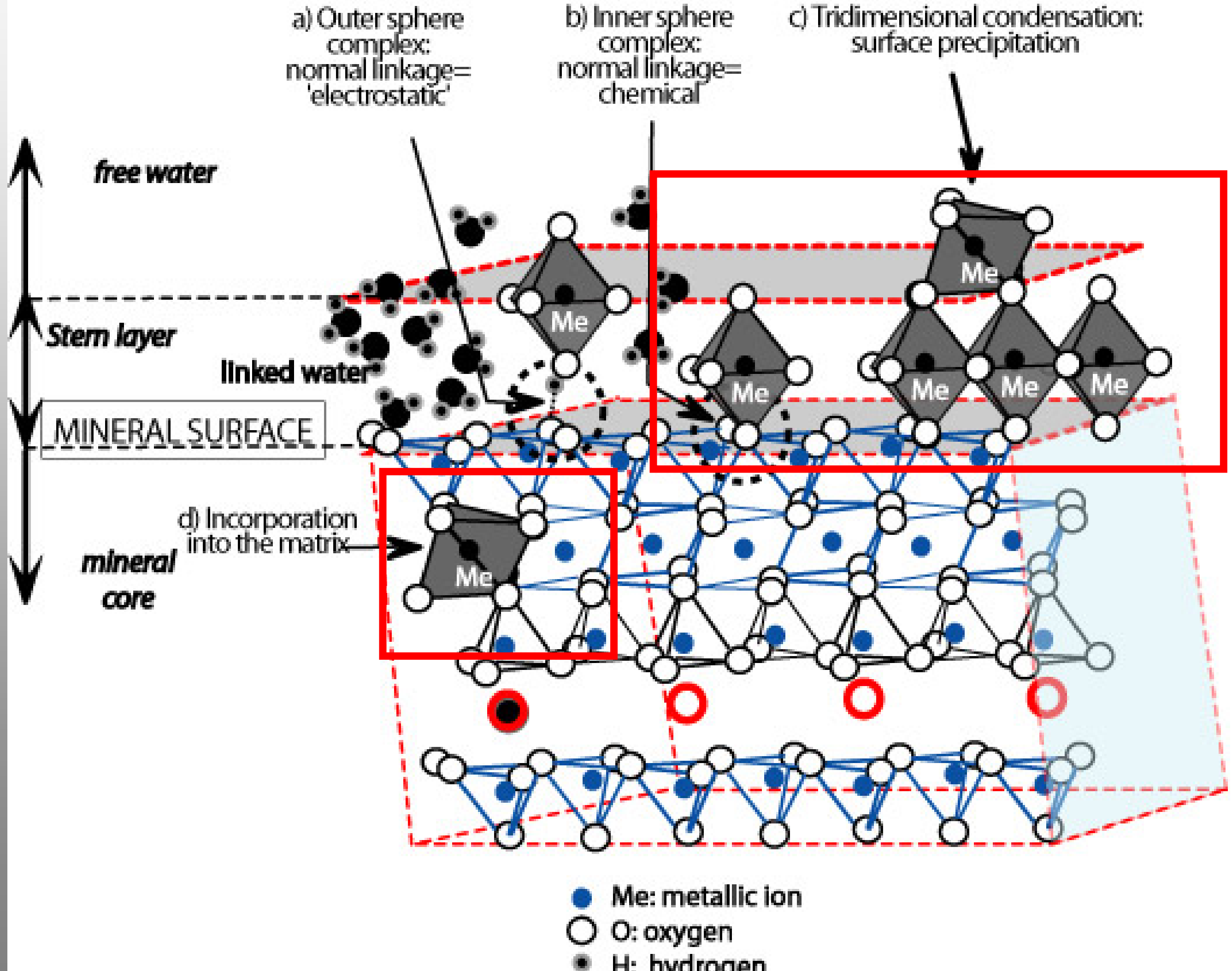
Reactivity of Iron oxide



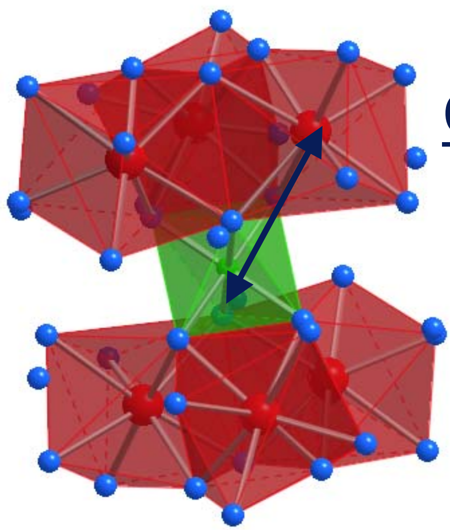


Highly reactive particles (U, Cr, Co, Ni, Mn, As, Se, Pb, U…)

Reactivity of iron oxide

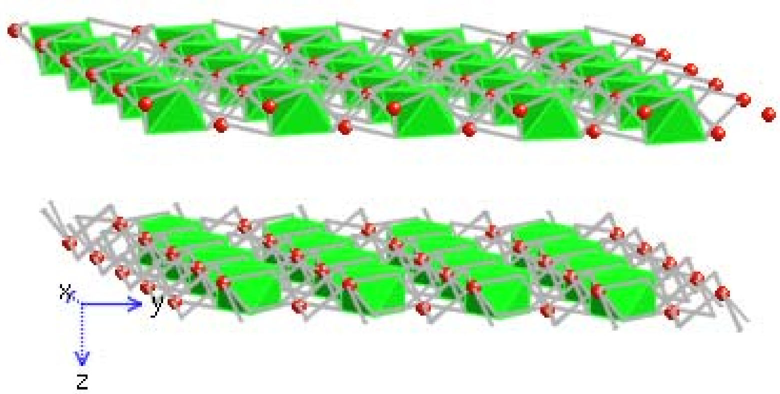


Structural approach

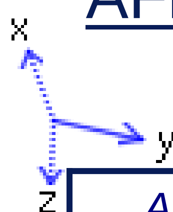


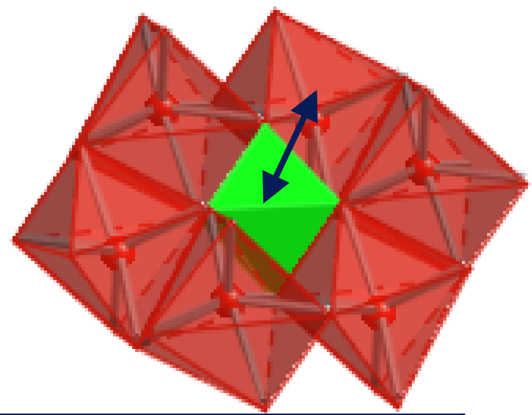
C3AH6

Atomic pair	Distance	Number
Al/Fe-O	*1.91Å*	*6*
Fe--Ca	*3.51Å*	*6*



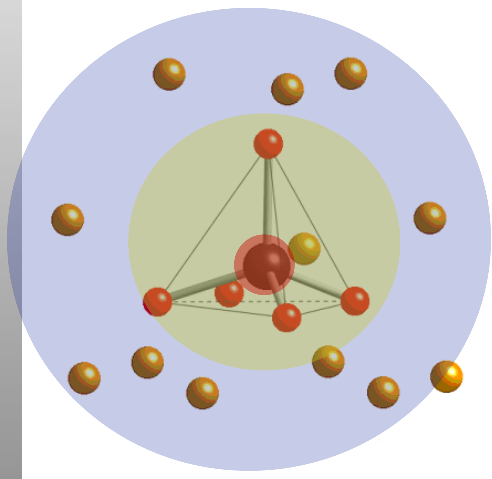
AFm

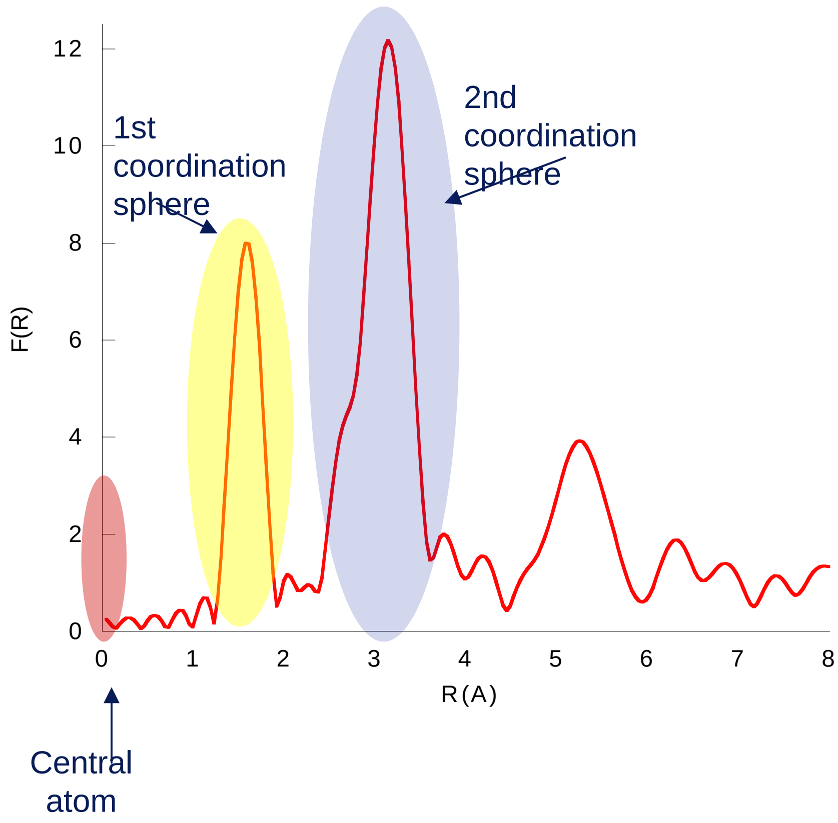




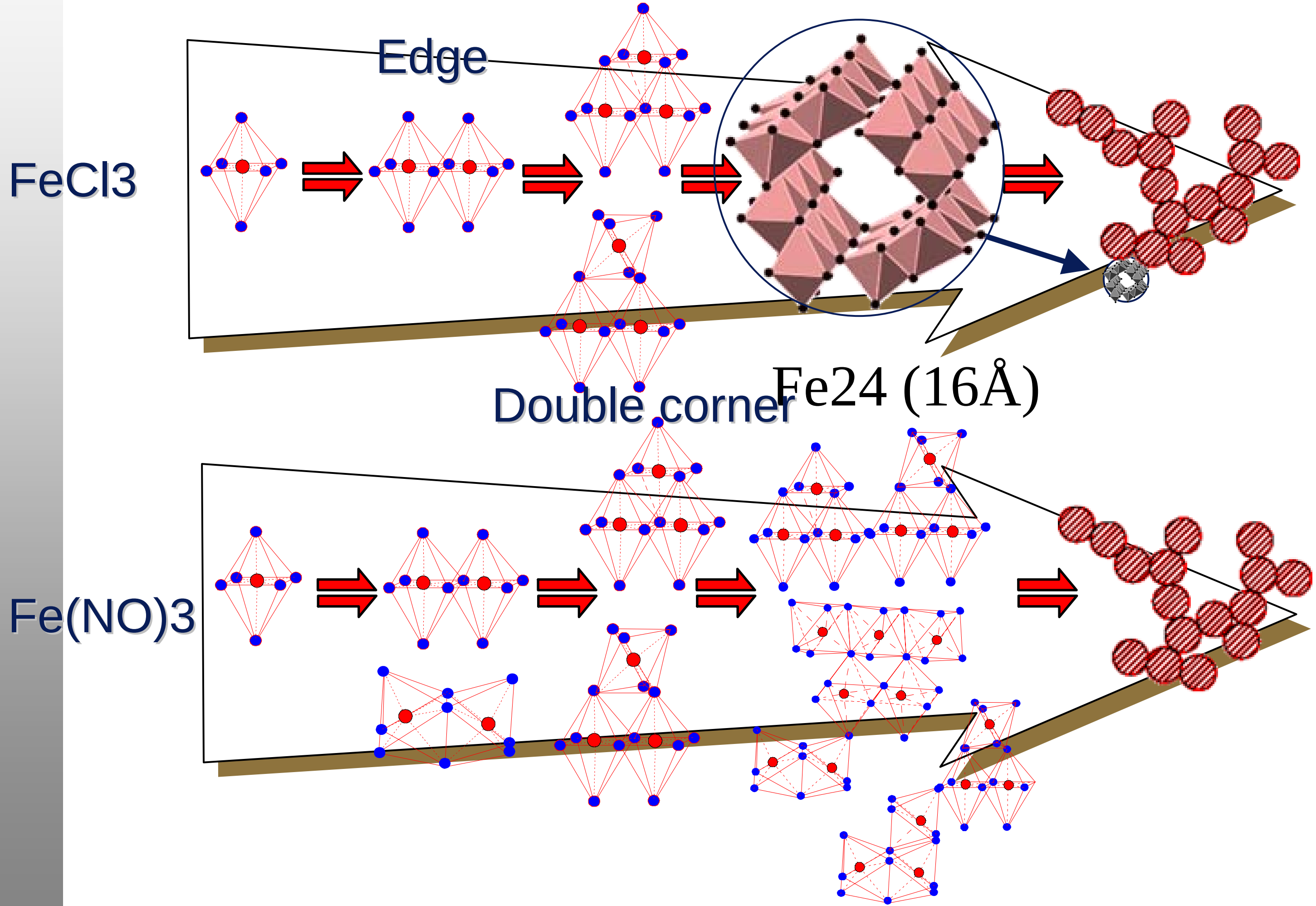
Al/Fe-O	*1.90Å*	*6*
Al/Fe--Ca	*3.35Å*	*6*

EXAFS




1st coordination sphere
2nd coordination sphere
Central atom
F(R)
R (A)
0
2
4
6
8
10
12
0
1
2
3
4
5
6
7
8

Nucleation and growth of FeOOH (in water) = Ferrihydrite??



(Bottero et al, 1994, Rose et al, 1997)

Modeling

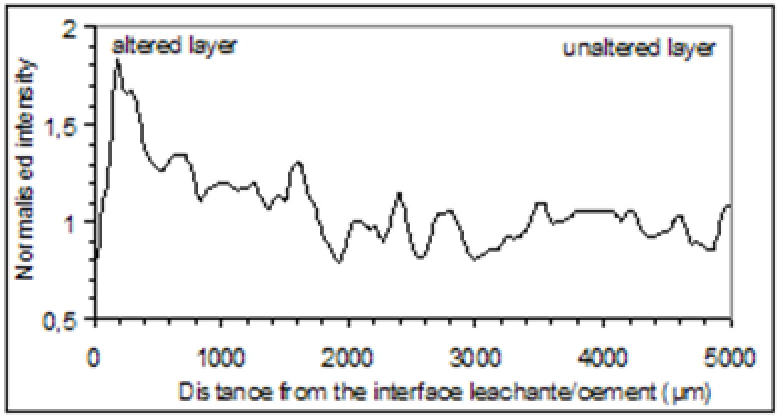
Calculation:
Translation into a chemical-transport model code (CHESS-HYTEC)

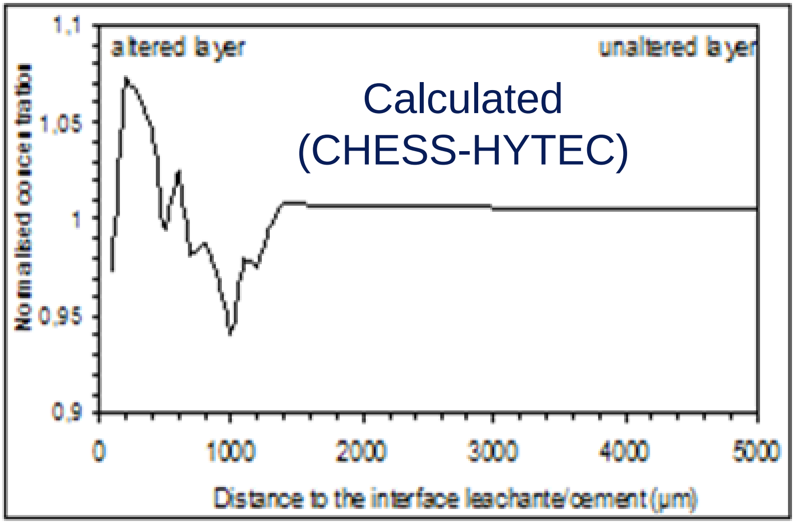
- <u>**Translation of experimental data into thermodynamic data**</u>

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

$SiOH + Ca^{2+} + Pb^{2+} + 3H_2O - 4H^+ \Longleftrightarrow SiOCaPb(OH)_3$ log K(25°C) = -33.4
$SiOH + SiOH + SiO_{2(aq)} + Ca^{2+} + Pb^{2+} - H_2O - 4H^+ \Longleftrightarrow SiOH\text{-}CaSiOPb\text{-}SiOH$ log K(25°C) = -23.3

Experimental (µ-XRF)





Benard, Rose et al., *in prep*