Physico-chemical investigation of clayey rock/cement-based materials interaction in the context of geological waste disposal: experimental approach and preliminary results

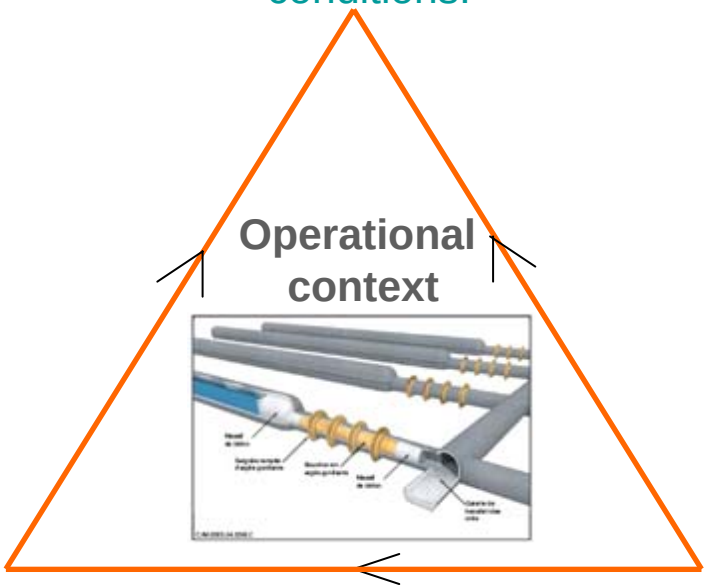
A.DAUZERES [1] [2], P.LE BESCOP [1], P. SARDINI [2]

[1] Laboratory of Concrete and Clay Behaviour Studies (LECBA)
CEA Saclay – Bât.158 – 91191 Gif sur Yvette-France

[2] Hydrogeology Clay Soil and Alteration (HYDRASA) – FRE 3114
University of Poitiers-Bât. sciences naturelles, 86000 Poitiers-France

Objectives

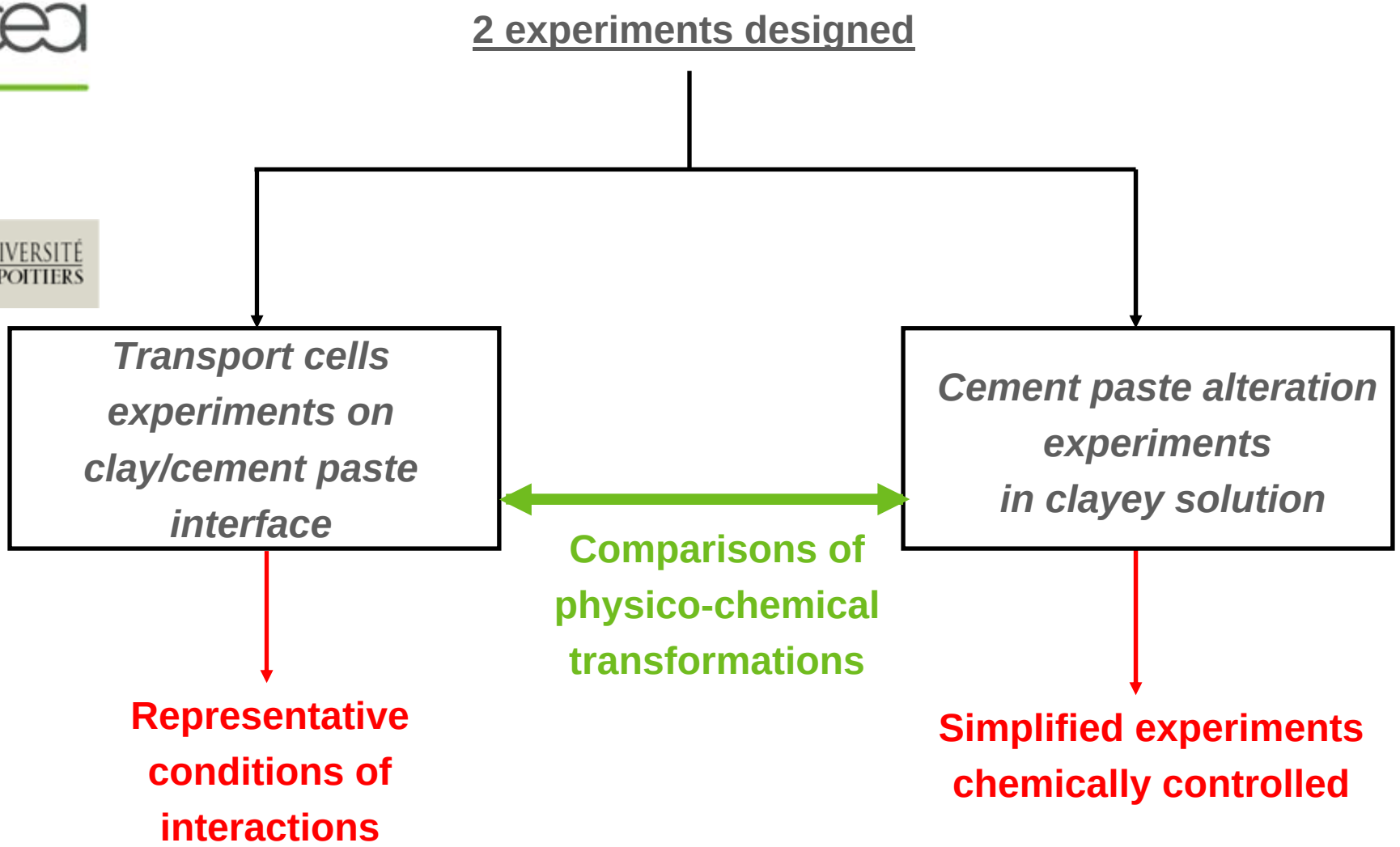
Knowledge of the physico-chemical behaviour of cement materials in geological disposal conditions.



Simulation of the chemical evolution of materials with reactive transport codes, and validation with experimental data

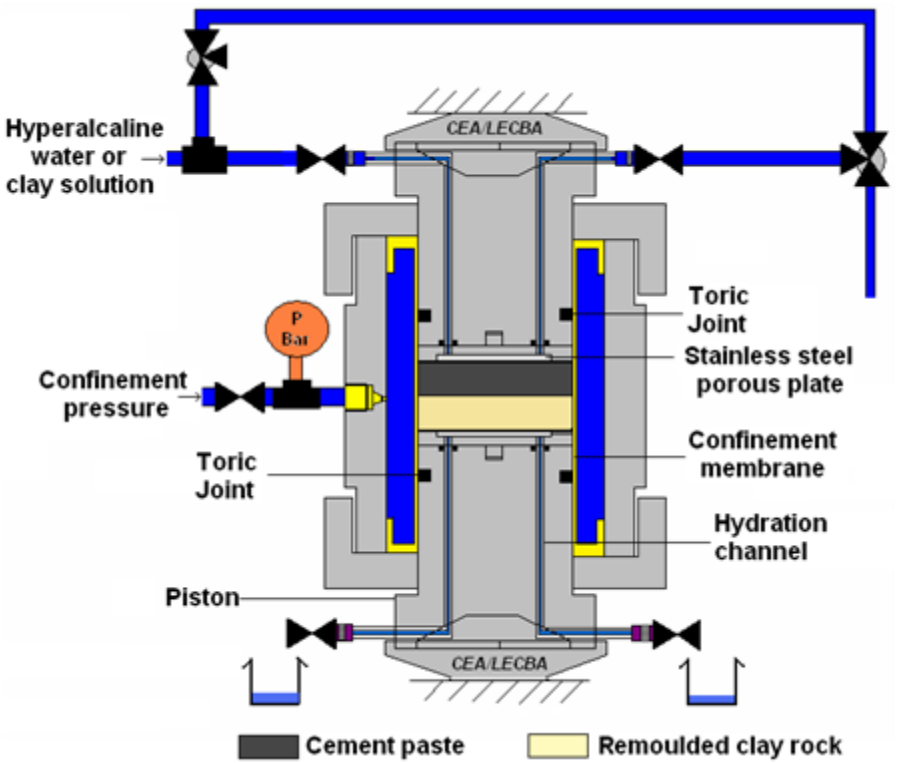
Characterization of clayey rock/cement-based materials interface related to chemical degradation

Experiments



Transport cell experimental device

The clayey rock hydration induce a swelling and a dislocation without confinement.



Composite embedding with a fluid resin to freeze the final microstructure.

Materials

CEM I Cement paste disc

Val d'Azergues (LAFARGE)

Diameter = 42 mm

w/c = 0.4

Remoulded clayey rock disc

Callovo-Oxfordian formation from Meuse/Haute-Marne

Depth : – 490m

Characterizations [1]	Unit	CEM I	Remoulded clayey Rock
Disc diameter	mm	**42**	**42**
Thickness	mm	**5**	**5**
Mercury porosity	%	**23**	**18**
Total water porosity	%	**34**	**-**
Hydraulic Conductivity	$m.s^{-1}$	**$4.1.10^{-11}$**	**$3.5.10^{-12}$**
Saturation state	%	**92**	**60**

[1] *LECBA 2008*

Interstitial solutions

Solution compositions are determined by ionic chromatography.

Interstitial solutions of hardened cement paste are extracted with a press. Loading: 280 to 660 MPa.

Resaturation solutions are very different :

-Hyperalkaline solution for the cement paste (pH>13.5).
-Neutral mineralized aqueous solution for the clayey rock with a CO_2 partial pressure of 1.3%.

Chemical composition of clayey rock pore solution (25°C)

	Concentrations ($mmol.l^{-1}$)
Na^+	45.6
K^+	1
Ca^{2+}	7.3
Mg^{2+}	6.6
Sr^{2+}	0.2
Cl^-	31
SO_4^{2-}	15.6
HCO_3^-	3.3
SiO2(aq)	0.2
pH	7.1
pCO_2 (atm)	$1.3.10^{-2}$

* BRGM Report RP-54416

Sulphate attack

Hydrolysis

Carbonation

Chemical composition of CEM I pore solution (28 and 90 days, w/c = 0.4)

		Concentrations ($mmol.l^{-1}$)				
Time	pH	$[Na^+]$	$[K^+]$	$[Ca^{2+}]$	$[Cl^-]$	$[SO_4^{2-}]$
28 days	13.6	47.3	452.3	0.8	1.3	5.6
90 days	13.64	50.3	474.1	1.6	0.6	6.6

Alkaline plume

Experimental protocol

Cell 1
CLAYEY ROCK

Cell 2
CEMENT PASTE

Confinement 30 Bars

Confinement 30 Bars

Resaturation with clayey solution

Resaturation with alkaline solution

SATURATION

Deconfinement

Deconfinement

Cell 1

Cement paste placed in contact with clayey rock disc

Confinement 30 Bars

System evolution in diffusive transport

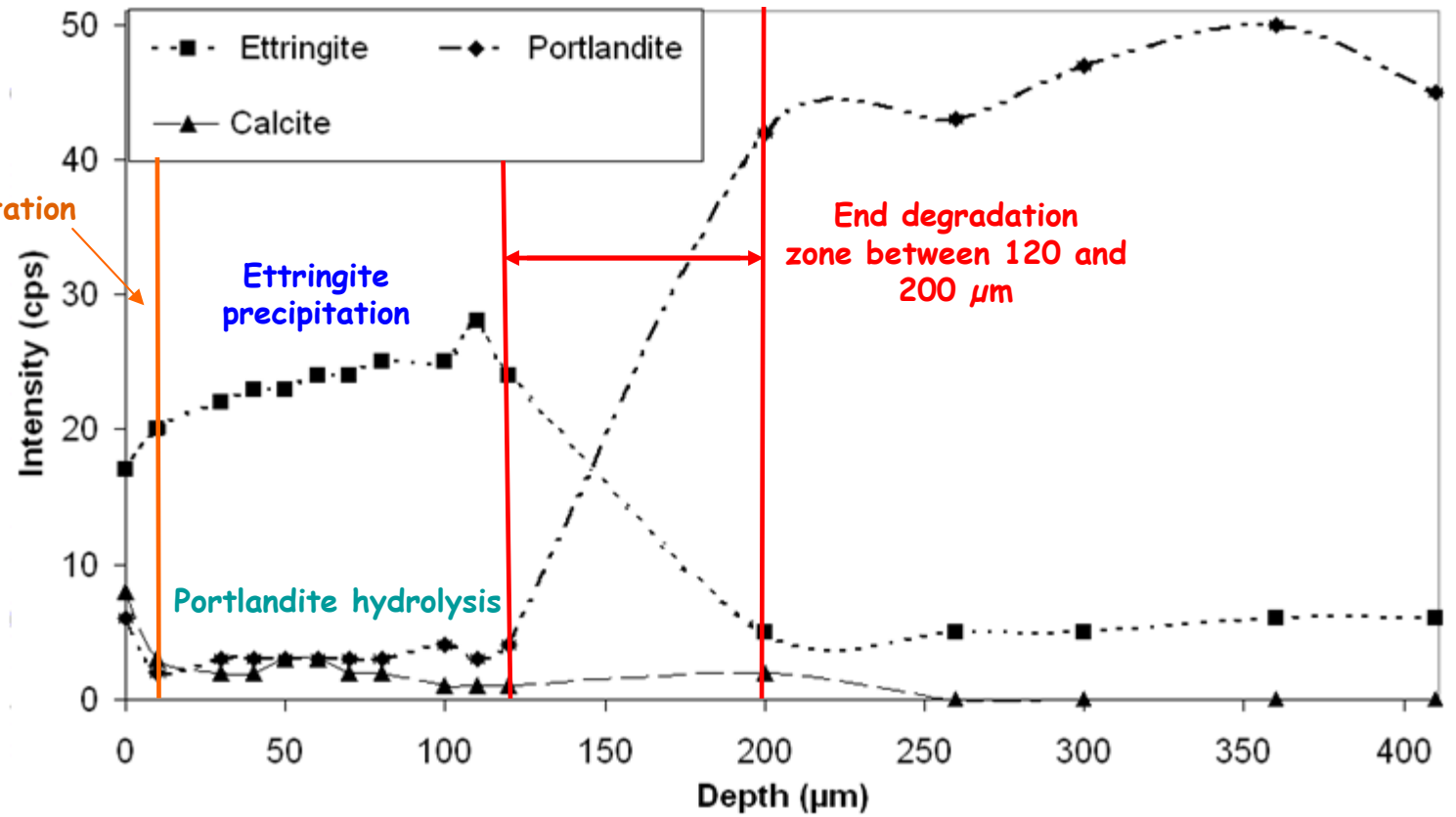
System evolution in convective transport

Preliminary results

Diffusive transport experiment, 2 months, 25°C

XRD Analysis on the cement paste

XRD profile of calcite, ettringite and portlandite

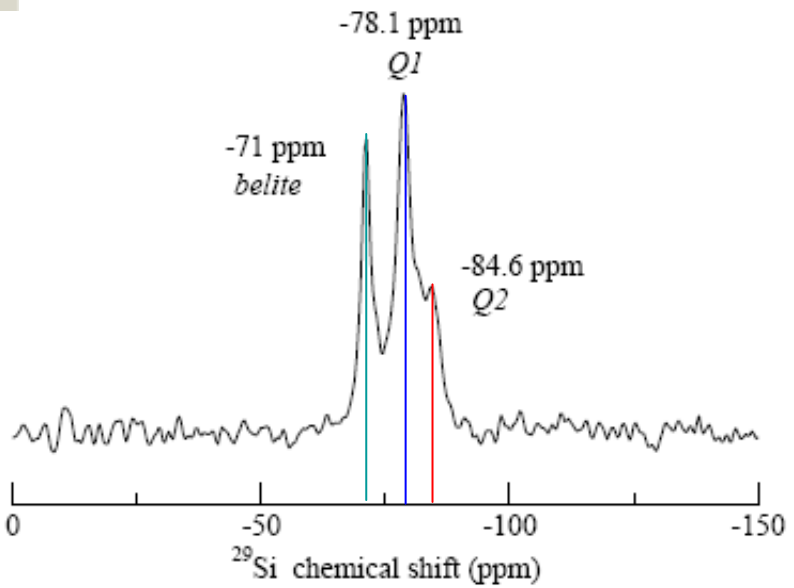


Preliminary results

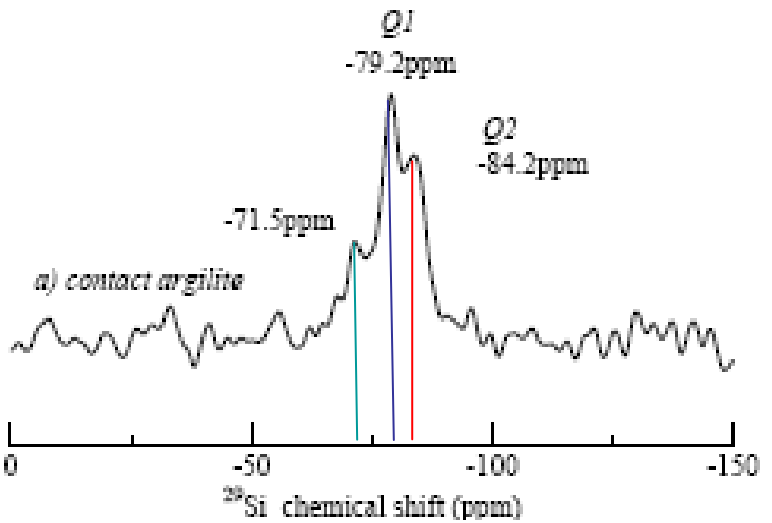
Diffusive transport experiment, 2 months, 25°C

Solid NMR ^{29}Si on the degraded cement paste zone

- Belite peak reduction.
- Q1/Q2 ratio reduction in CSH → C/S ratio decrease → Extension of Si tetrahedral chains



Initial cement paste CEM I

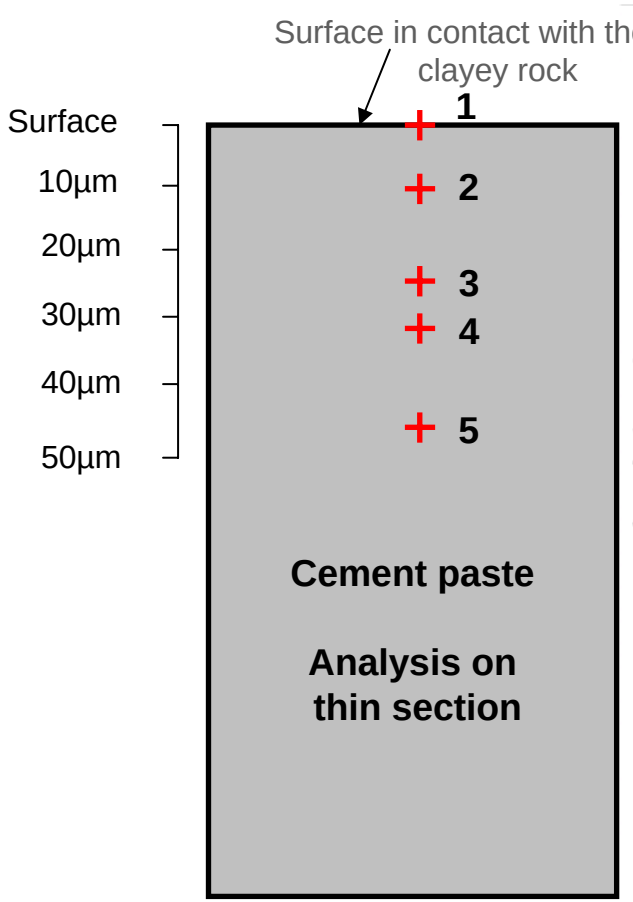


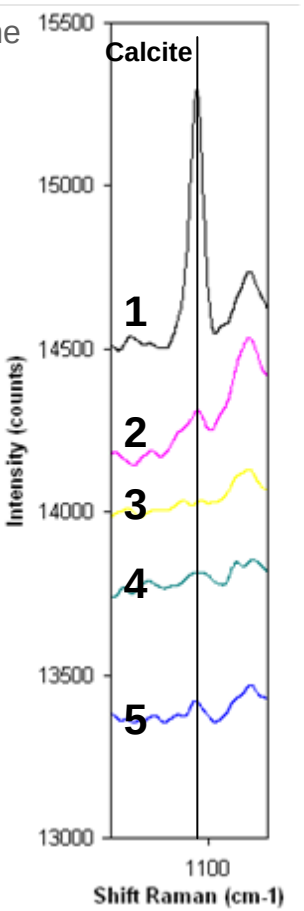
Cement paste in contact with clayey rock during 2 months

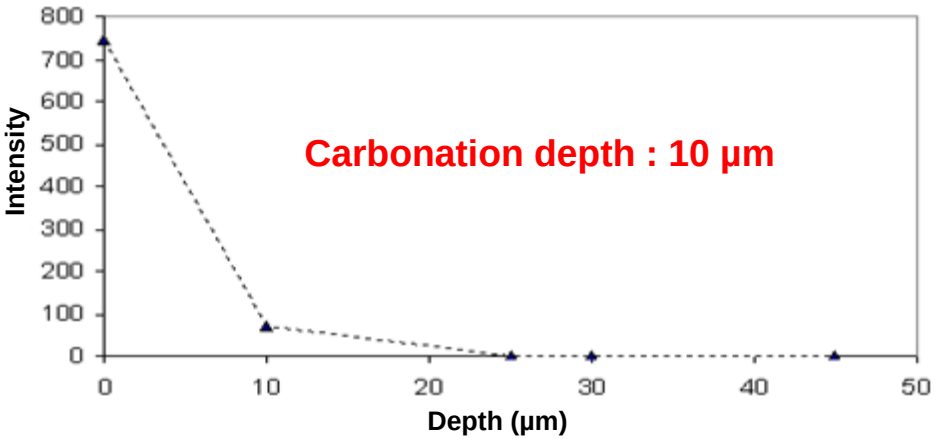
Preliminary results

Diffusive transport experiment, 2 months, 25°C

Micro-Raman Spectroscopy on the degraded cement paste zone







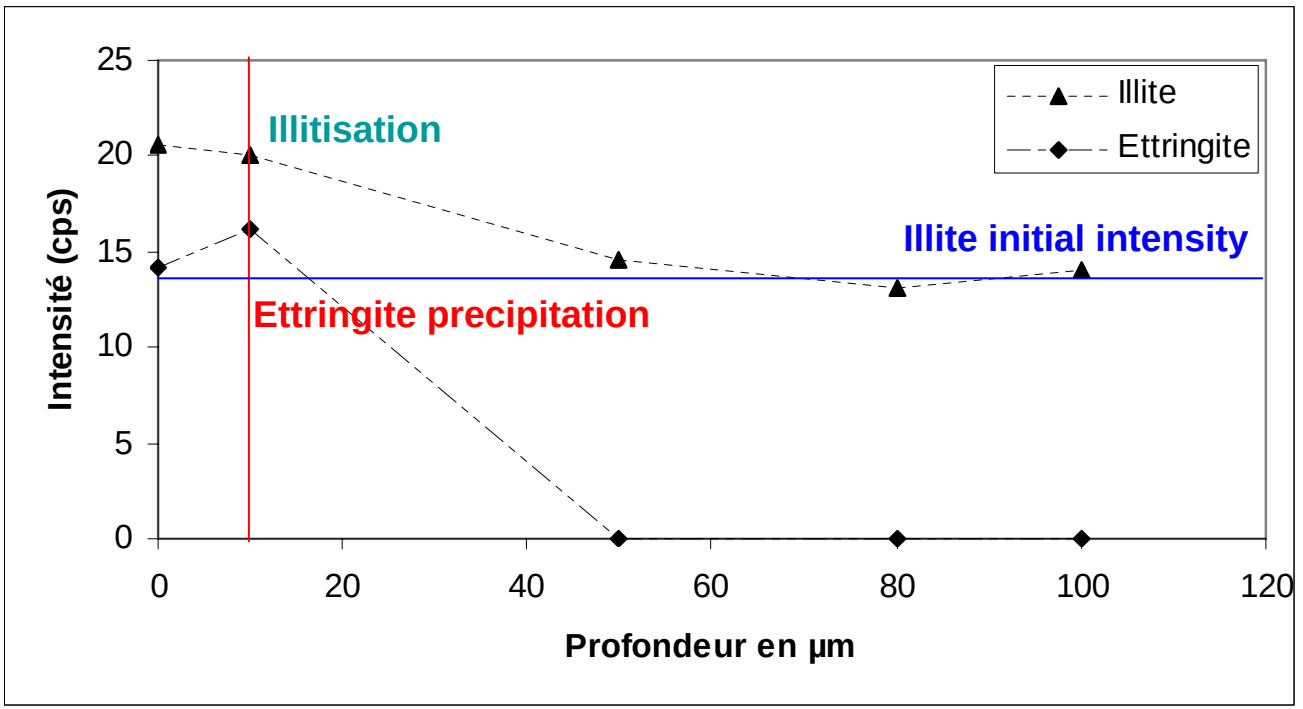
The carbonation depth is similar to the XRD analyses

Preliminary results

Diffusive transport experiment, 2 months, 25°C

XRD Analysis on the clayey rock

XRD profile of ettringite and illite in the clayey rock

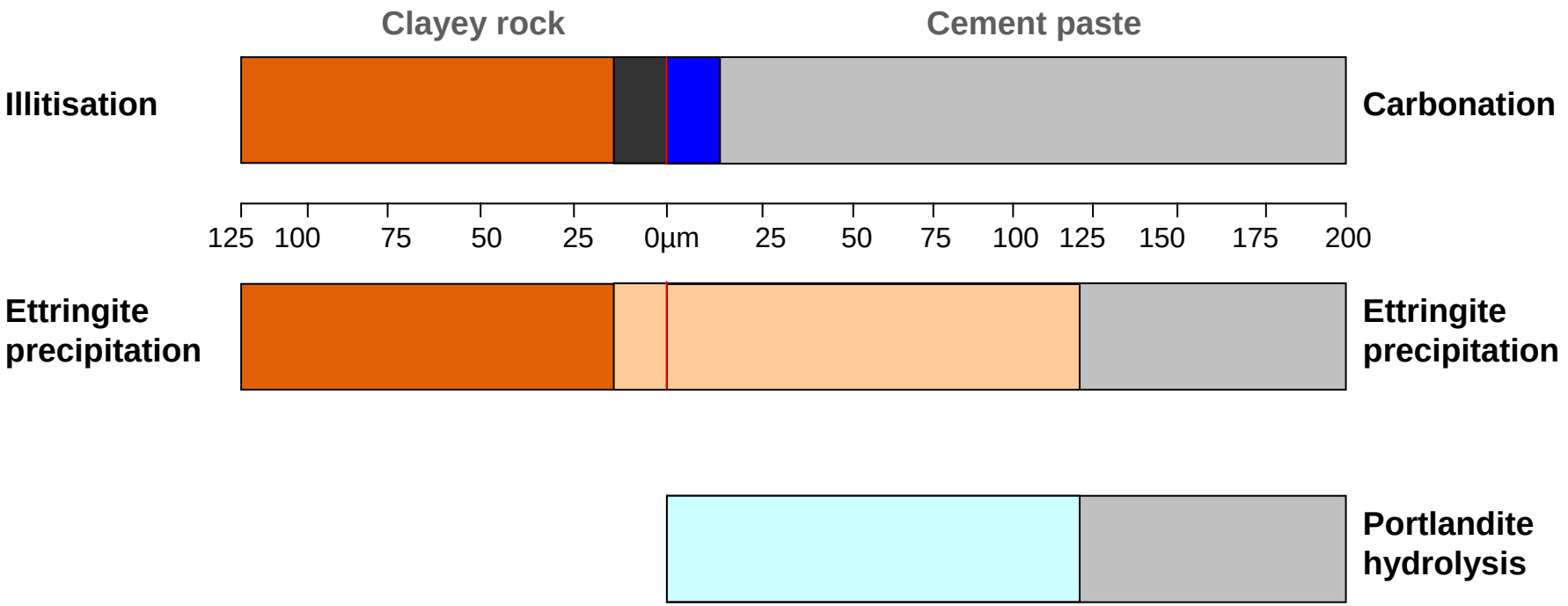


The two main evolutions observed on the clay material are the ettringite precipitation and the illitisation over 10µm.

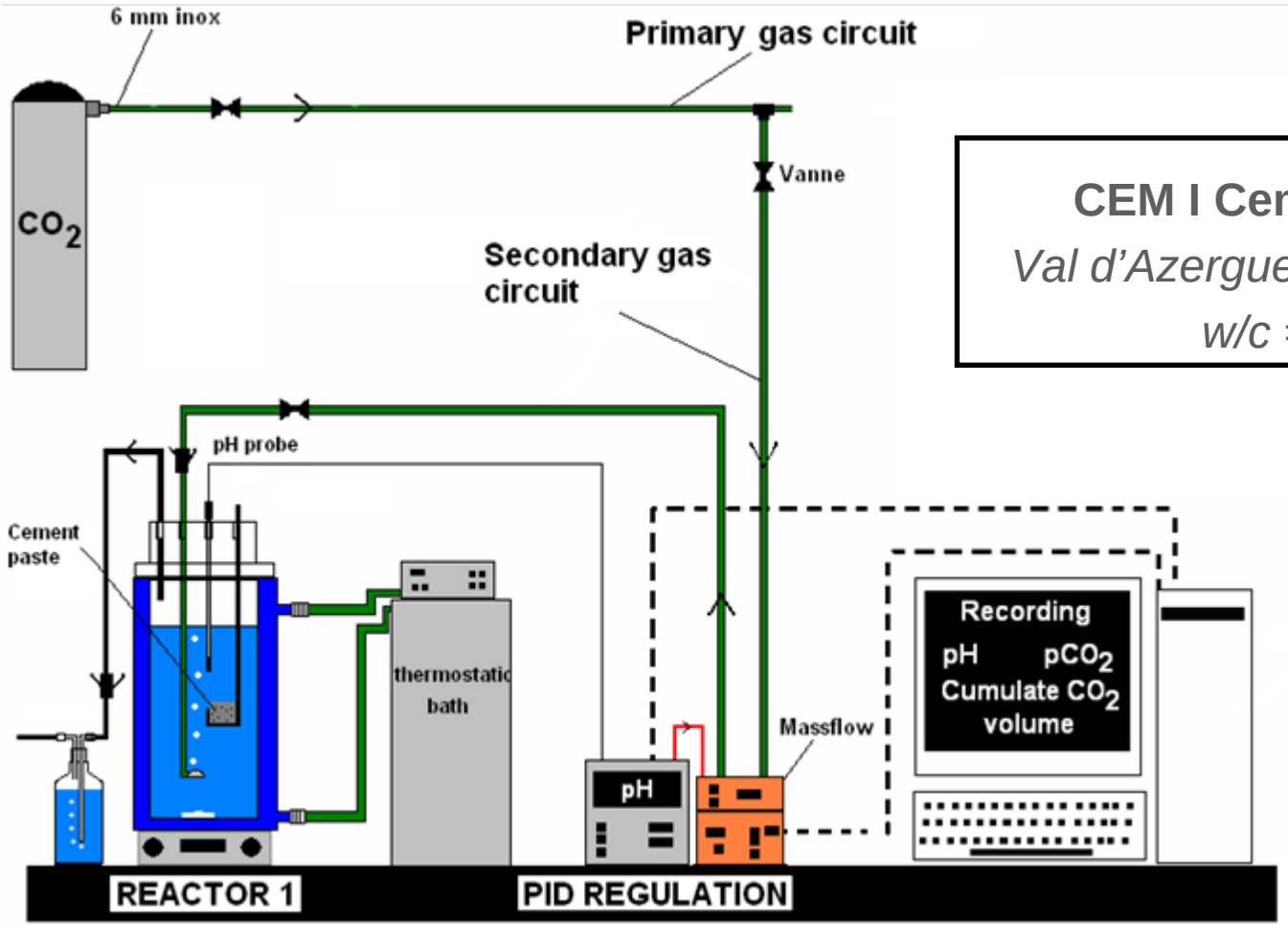
Preliminary results

Diffusive transport experiment, 2 months, 25°C

First conclusions : 4 main phenomena



Principle



CEM I Cement paste

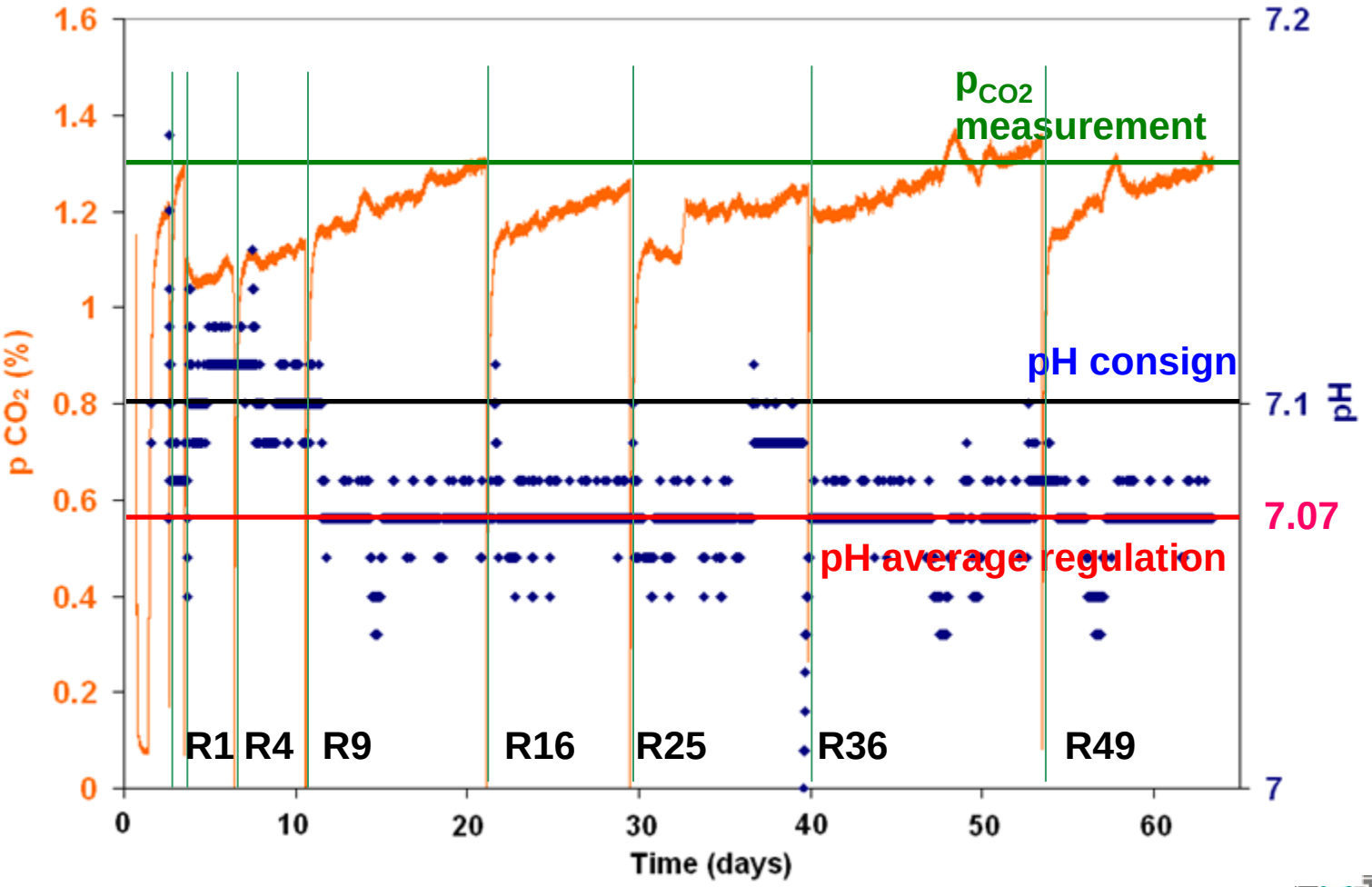
Val d'Azergues (LAFARGE)

w/c = 0.4

Experimental device

Control and measurements of experimental conditions

The chemical conditions are constant with regular solution renewal.

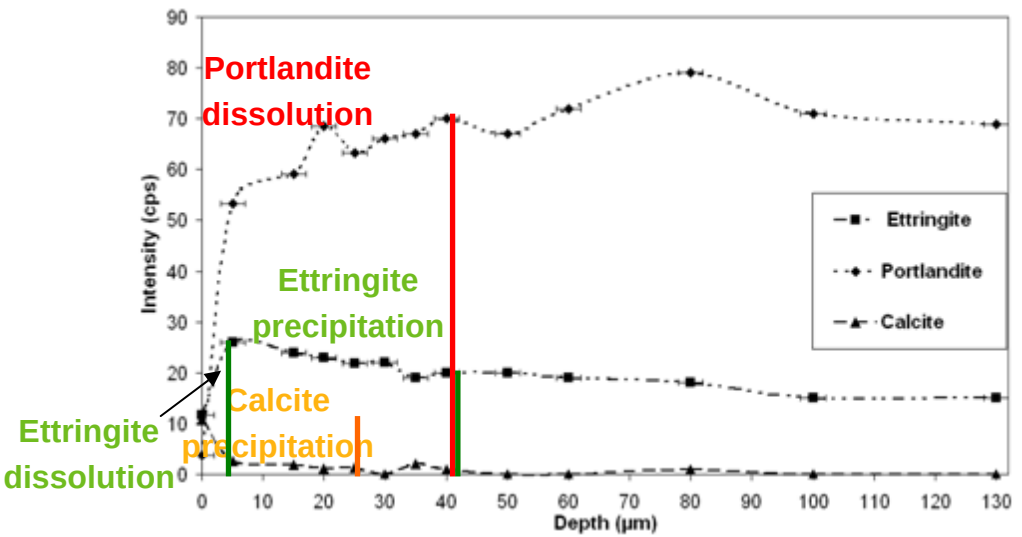


Preliminary results

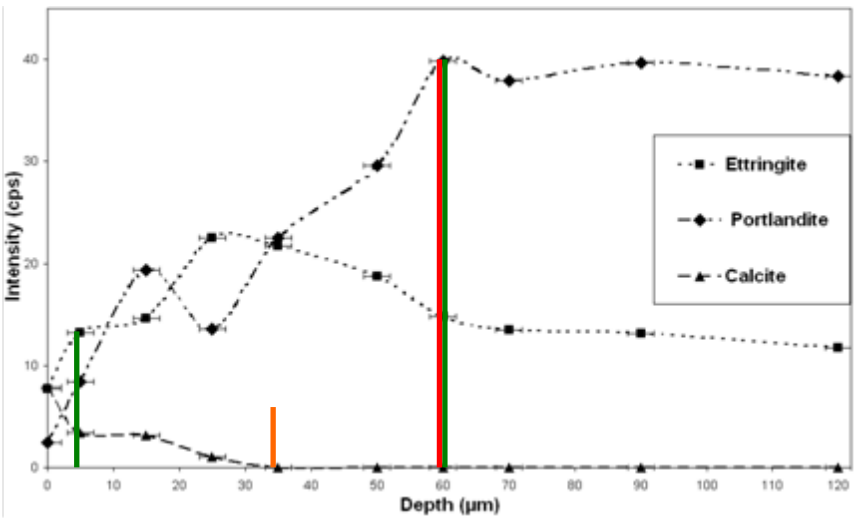
Alteration experiments during 1 and 2 months

XRD Analysis

XRD profile of calcite, portlandite and ettringite after 1 month in degradation



XRD profile of calcite, portlandite and ettringite after 2 months in degradation

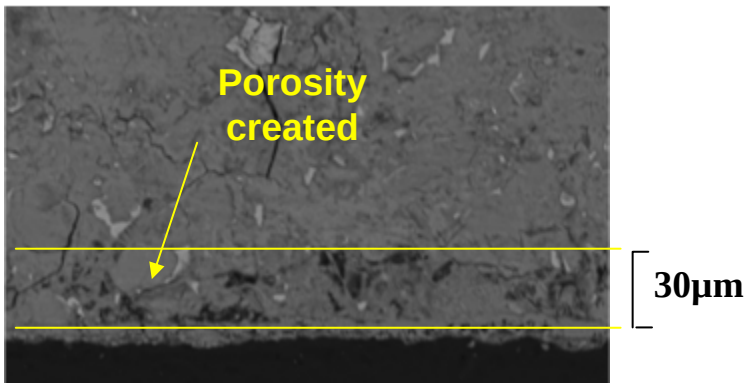


The altered zone increase with the time.

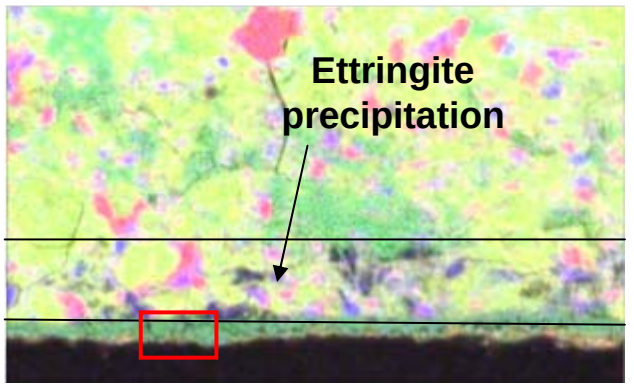
Preliminary results

Alteration experiments during 1 and 2 months

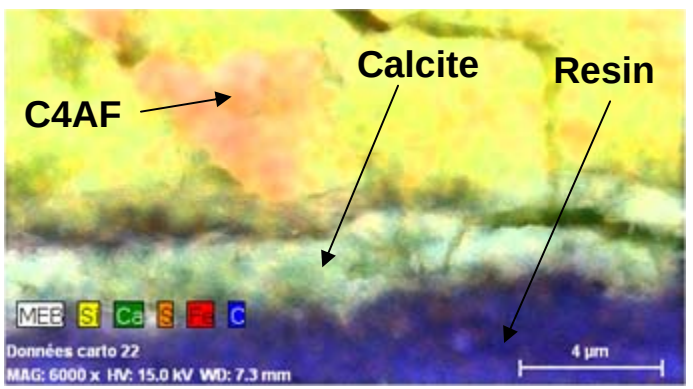
SEM Analysis after 1 month



SEM Image BSE (x750)



Elementary cartography (x750)
(S=blue, Ca=green, Si=yellow, Fe=red)



Elementary cartography FEG SEM (x6000)

Preliminary results

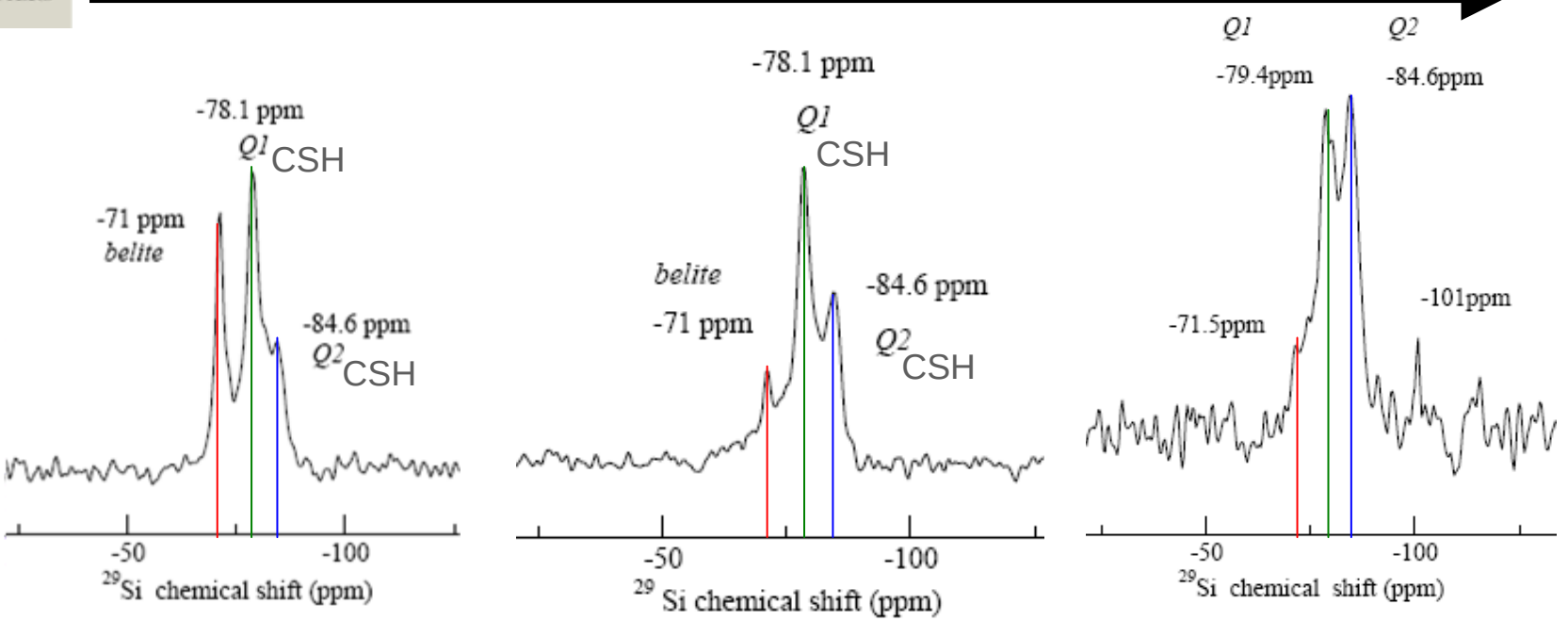
Alteration experiments during 1 and 2 months

Solid NMR ^{29}Si

Q1/Q2 ratio reduction → **CaO/SiO2 reduction in the degraded zone**

Extension of Si tetrahedral chains

Belite dissolution



Initial cement paste *Cement paste degraded 1 month* *Cement paste degraded 2 months*

Experiments

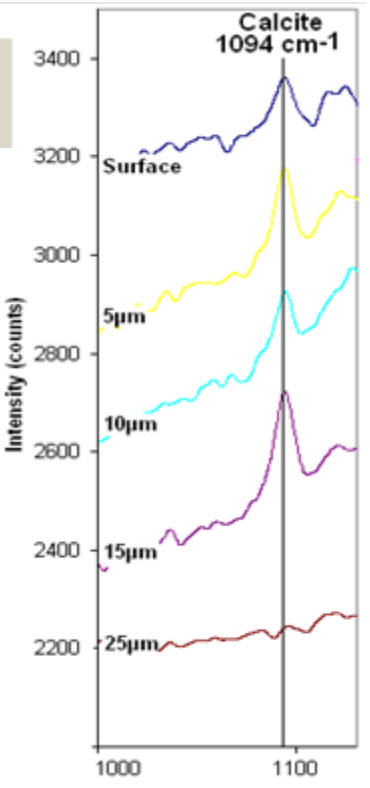
Cement paste alteration in clayey solution

Preliminary results

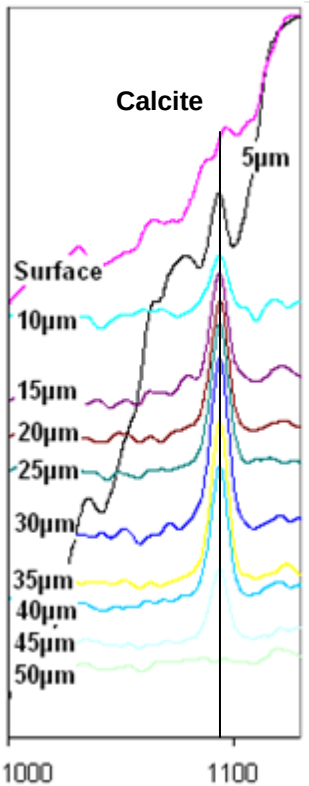
Alteration experiments during 1 and 2 months

Micro-Raman Spectroscopy on the alterated cement paste zone

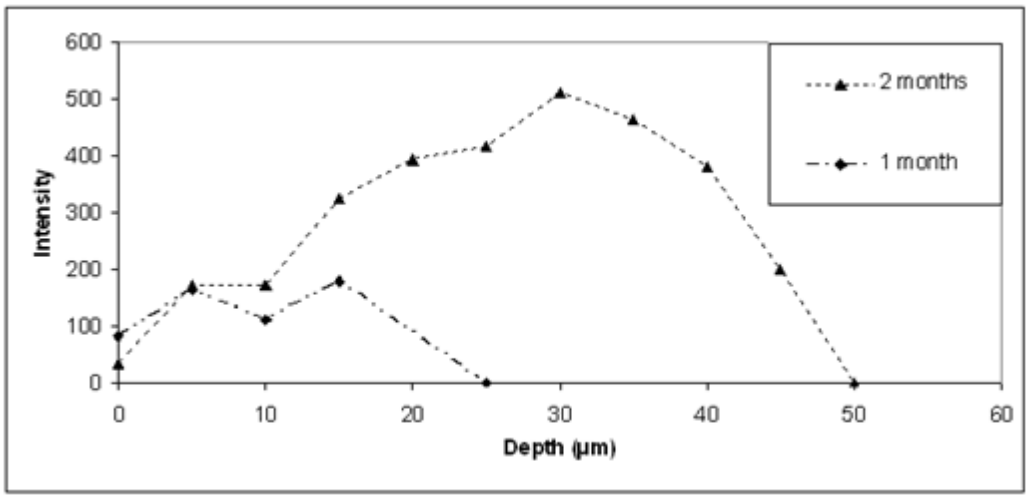
1 month



2 months



Carbonation profiles



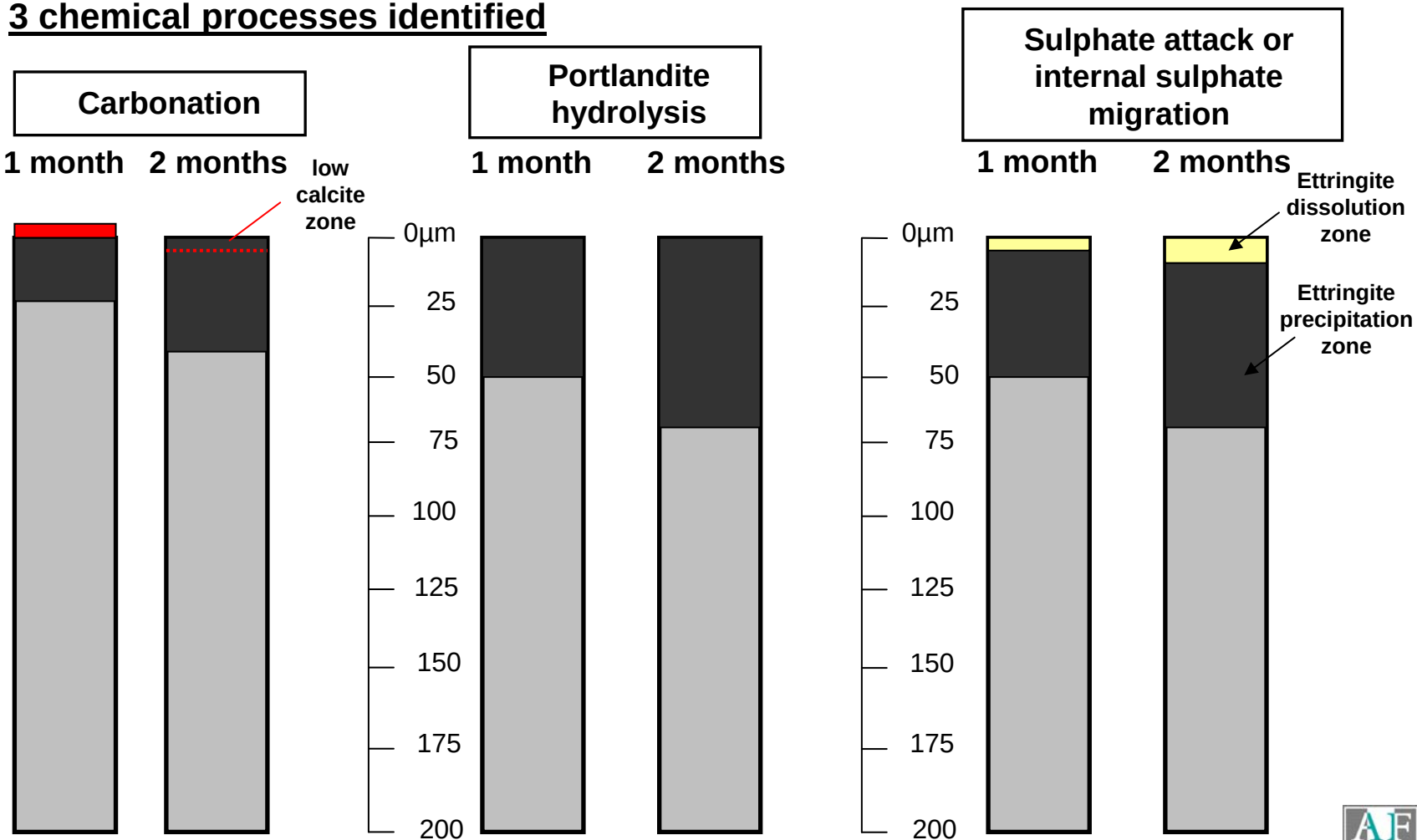
The carbonation zone increases with the time. These results are complementary to XRD analyses.

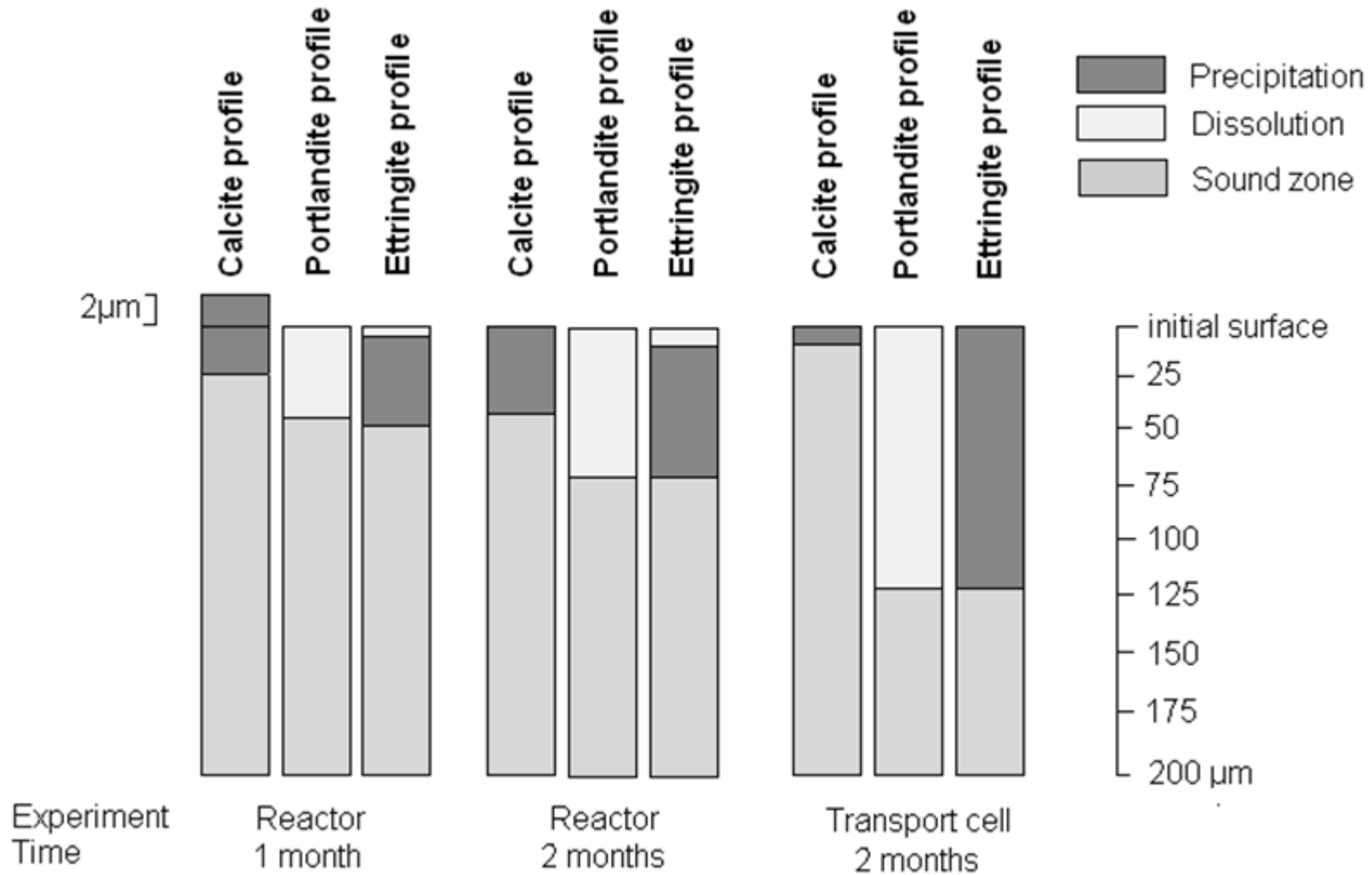
Micro Raman shows that the carbonation maximum is in the depth.

Preliminary results

Alteration experiments during 1 and 2 months

3 chemical processes identified





Preliminary simulations on the cement paste degradation by clayey solution

Simulations were realised with the ALLIANCES numerical plat-form developed by ANDRA, CEA, EDF.

An exponential diffusion law, Richet-Tognazzi law is imposed :

$$D_{Togn} = D_{ini}.\exp(9.95(c_p - c_p^{ini}))$$

Reactive-transport code is used.

Chemical code = CHESS

Transport code = CAST3M

Clayey solution composition

Na^+ = 45.6 mmol/l

K^+ = 1 mmol/l

Ca^{2+} = 7.3 mmol/l

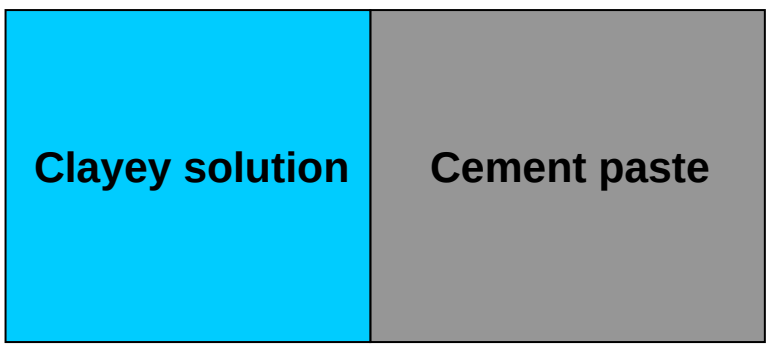
Mg^{2+} = 6.6 mmol/l

SO_4^{2-} = 15.6 mmol/l

HCO_3^- = 3.3 mmol/l

pH = 7.1

1D



Initial composition of the cement paste (for 1l of paste)

Jennite = 4.741 mol/l

Ettringite = 0.131 mol/l

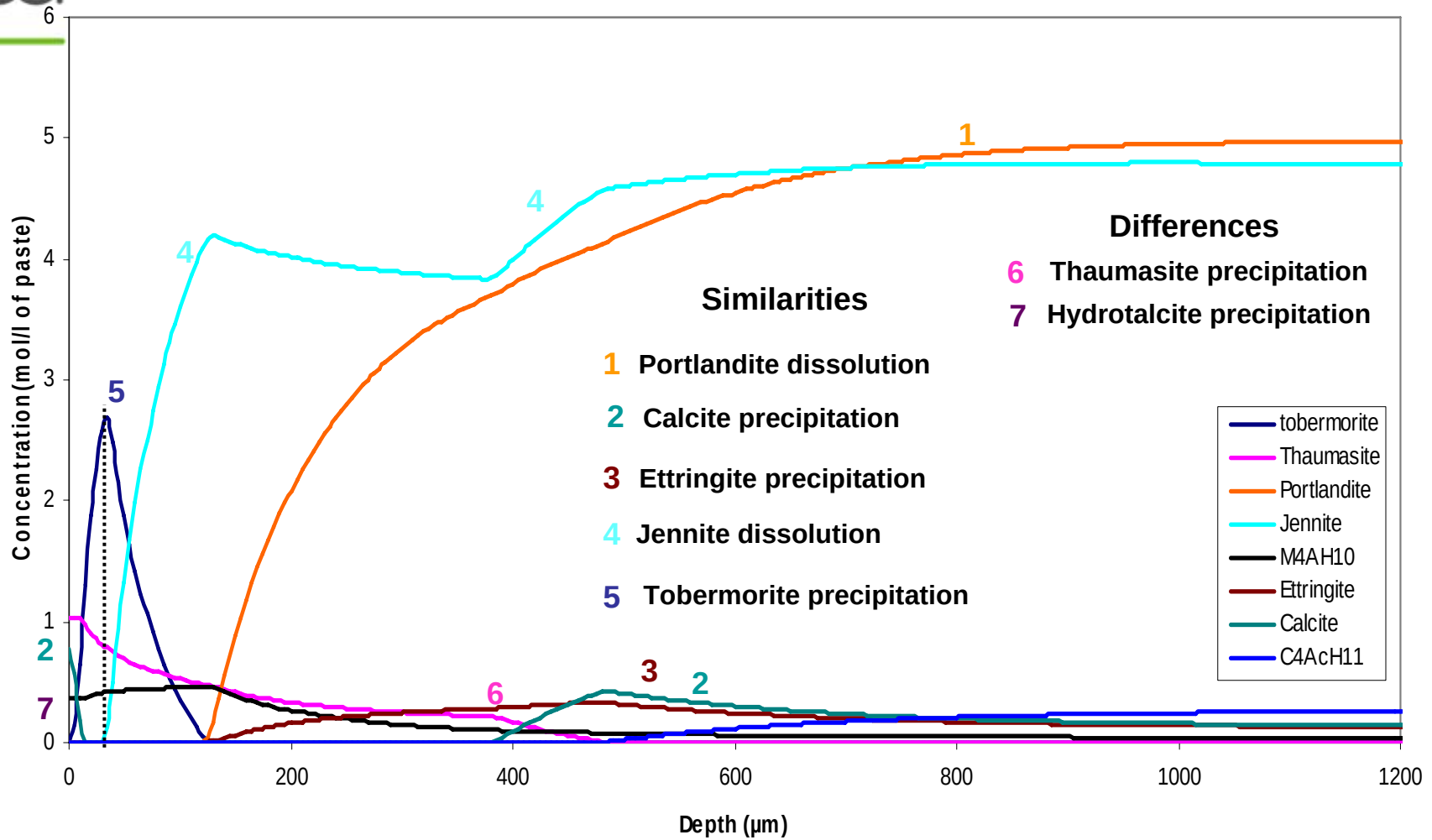
Calcite = 0.148 mol/l

Monocarbo = 0.254 mol/l

Hydrotalcite = 0.046 mol/l

Portlandite = 4.906 mol/l

Cement paste mineralogical evolution at 2 months



Preliminaries conclusions

→ The cement material alteration is more important with cell transport experiments.

→ The alterated depth is linked to the carbonation intensity.

→ Short-term (1, 2 months): no new phase as zeolites.

→ Long-term (5 months, 1 year): experiments are in progress.

→ Similar experiments will be performed with low-pH cement paste in 2009 (25 and 50°C).

→ Other experiments will be achieved to evaluate the impact of mineralogical transformations on transport properties (diffusion coefficients, porosity and permeability) in order to simulate interaction changes.

Acknowledgements

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