Composition and Hydration of Roman (*Natural*) Cements

Christophe Gosselin

Laboratory of Construction Materials (*)

Ecole Polytechnique Fédérale de Lausanne

(*) now at Geotest, Lausanne

Natural cements in European cultural heritage
Les ciments naturels dans le patrimoine européen
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Introduction

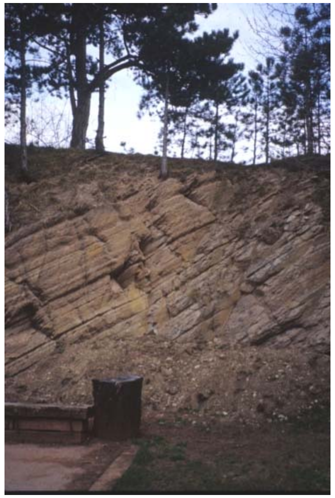
• Previous lecture on the different facilities of production of Roman cement

• What can be the composition of these cements?

• How do they hydrate?

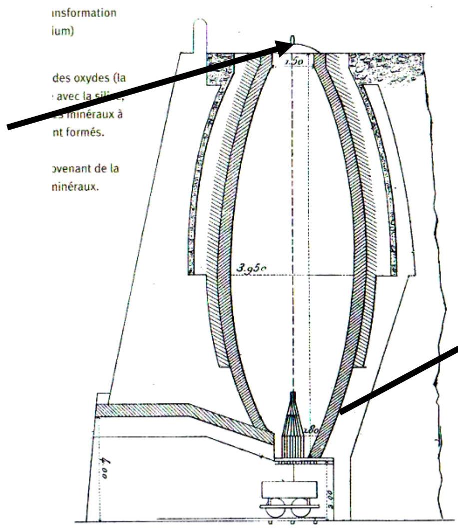
1/ Background

- Calcination of marlstone to produce cement is a complex process
- Involving the raw materials (minerals) and the kiln parameters (residence time, max. temp., quenching…)



Marlstone Quarry (Austria)

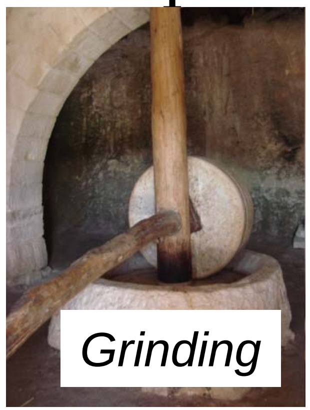
Crushed Marlstones



Shaft kiln

(~ 800-1000°C)

"Cement stones" (clinker)



Grinding

Images from C.Avenier (2007) D. Howe (2007) K Stingl (2009)

1/ Background

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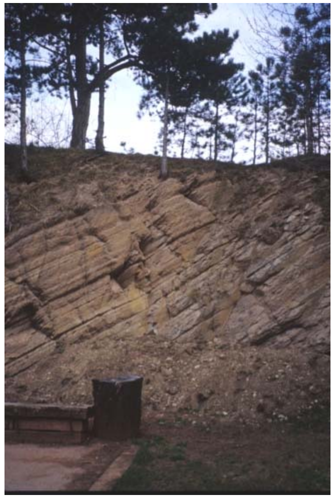

Marlstone Quarry (Austria)

Crushed Marlstones

<u>Limestone + 25-35%wt clay minerals</u>

- Calcite $CaCO_3$/ dolomite $CaMg(CO_3)_2$
- Quartz SiO_2
- Clay materials Al_2O_3, SiO_2, Fe_2O_3, Na_2O, K_2O
- If iron sulfur minerals (FeS_2, FeS…)→ SO_3

1/ Background

Calcination (1/3)

From 650°C, $CaCO_3$ will release CaO and CO_2

CaO

Al_2O_3 and Fe_2O_3 and if T >1000°C → **a bit of crystalline C_3A and C_4AF**

Al_2O_3 → **a lot of amorphous CaO - Al_2O_3**

React very quickly with water → flash setting (no workability)

1/ Background

Calcination (2/3)

From 650°C, $CaCO_3$ will release CaO and CO_2

CaO

+ SiO_2 ↓

$2CaO.SiO_2$
(C_2S, under two crystal structures
α' and β, so-called belite)

$+CO_2$
+High p_{CO2} ↓ **(possible reaction)**

carbonated C_2S

CaO

+ SiO_2
+ Al_2O_3
+ T >1000°C ↓

$2CaO.Al_2O_3.SiO_2$
(C_2AS, gehlenite)

Reactivity with water:

Carbonated C_2S < C_2AS <β-C_2S <**α'-C_2S**

1/ Background

Calcination (3/3)

Sometimes **under-burnt** materials ……

Remaining raw minerals

Cement phases

……… **burnt** and **over-burnt** part of the calcined stones are ground all together

Image K Stingl (2009)

1/ Background

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In the real life

Shut up !

α' or β – C_2S ?!

Image: Demonstration Site, Chateau Valère, Sion, CH

2/ Composition of Roman cements

4 cements

- Cement from a historic Austrian marl Lilienfeld – reference cement fired under laboratory conditions

- Semi-Industrial MBM-Gartenau, Poland – pilot rotary kiln

- Industrial Vicat Prompt, France – shaft kilns

- Industrial Wittersdorfer & Peggauer, Austria - a rotary kiln

2/ Composition of Roman cements

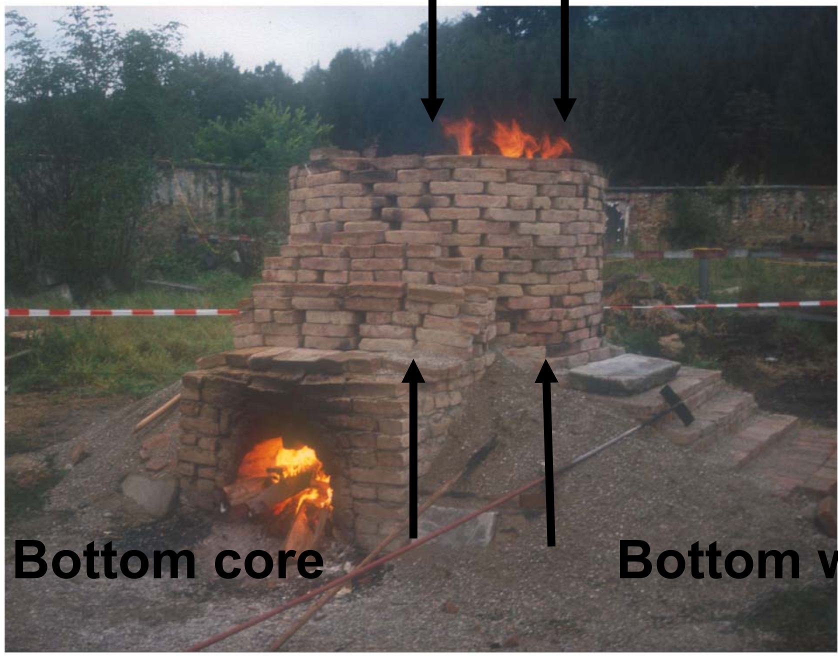
XRD crystalline composition

	Lilienfeld ~860°C	MBM-Gartenau 870 → 970°C	Vicat Prompt 600→1200°C (*)	Wittersdofer & Peggauer 800→1000°C
Total belite $\alpha' + \beta$-C_2S	48	47	44 But C_3S (also)	23
Ratio α' / β C_2S	6	0.6	0.3	0.35
Carbonated C_2S	6.9	16.5	15.2	7.1
Remaining raw materials (calcite, quartz, clay)	34.6	18.9	17.6	35.1

(*) Vicat cement differs because contains C_3S and gypsum

2/ Composition of Roman cements

- Composition of cements produced in a traditional kiln
- Four samples from the same calcination batch



Shaft kiln in Mauerbach, (Austria)

Images from K Stingl (2009)

2/ Composition of Roman cements

	1 Bottom core (939°C)	2 Bottom wall (859°C)	3 top core (1133°C)	4 top wall (841°C)
Total belite $\alpha' + \beta$-C_2S	54	35	72	34
Ratio a' / β C_2S	0.6	2.0	0.6	1.6
Carbonated C_2S	6.1	17.7	5.7	10.3
Remaining raw materials (calcite quartz mica)	11.1	27.9	1.9	43.6

2/ Composition of Roman cements

Summary

- A wide range of crystalline composition is obtained

→ due to the raw materials, the calcination parameters…

- The α'-C_2S polymorphism dominates but the relative amount of α'-C_2S and β-C_2S is changing with the calcination conditions

→ Influence on the hydration and strength development

- The carbonation of calcium silicate can occur (depends on the type of kiln and local reduction conditions)

→ Less C_2S is available for hydration

3/ Hydration of Roman cements

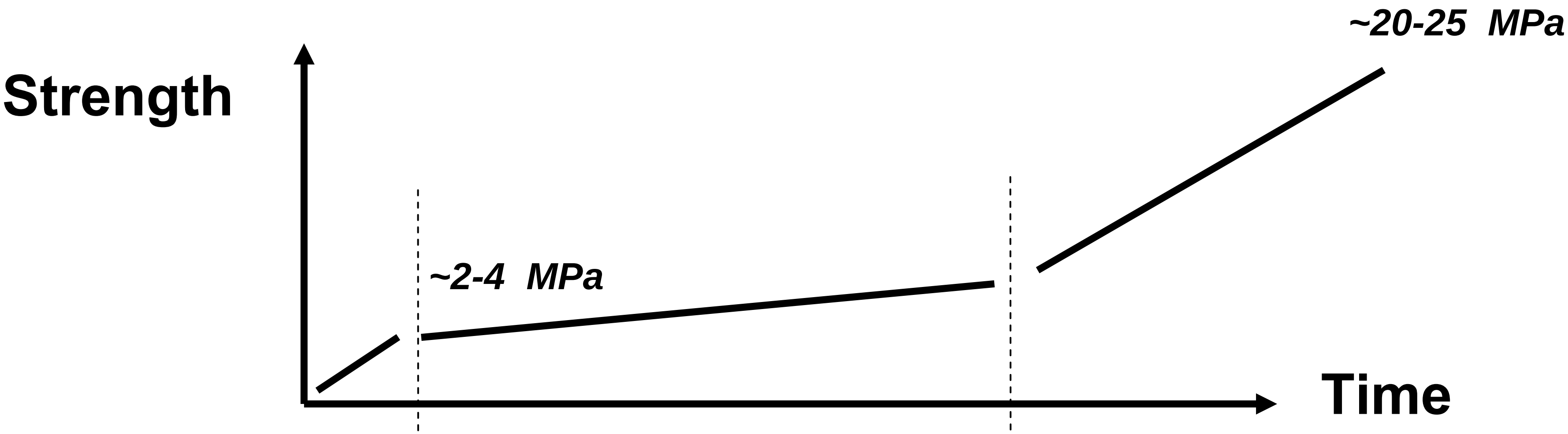
How do …

… Roman cements …

… hydrate ?

3/ Hydration of Roman cements

Three main stages



Minutes

- Early age
- Very rapid reaction
- Enough strength (i.e. for precast, or render)

First day → …

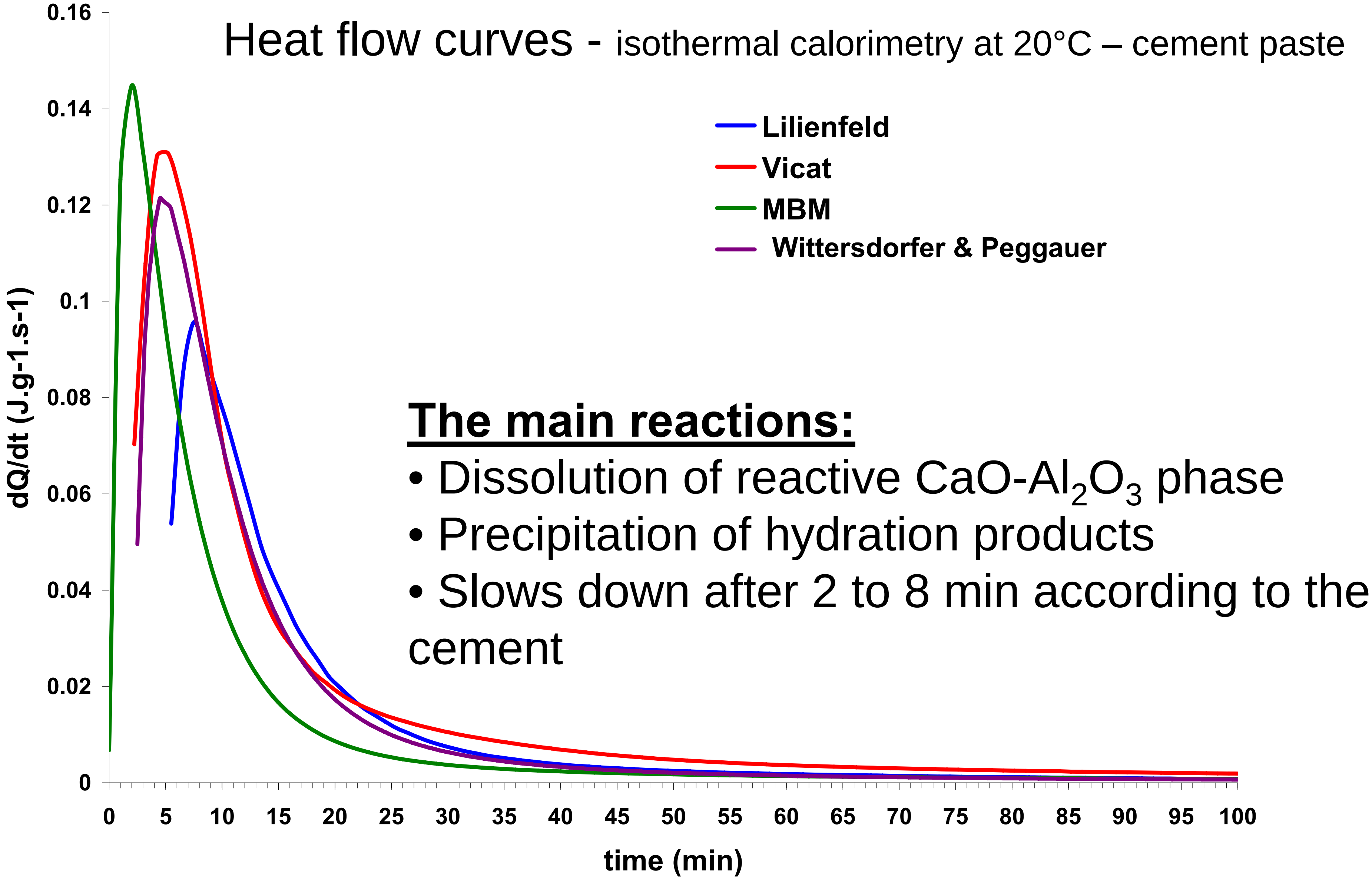
- Hydration reactions slow down

First month → years …

- Later age
- Hydration of C_2S (controlled by the type of polymorph, moisture conditions…)

3/ Hydration of Roman cements

Early age hydration



The main reactions:

- Dissolution of reactive $CaO\text{-}Al_2O_3$ phase
- Precipitation of hydration products
- Slows down after 2 to 8 min according to the cement

3/ Hydration of Roman cements

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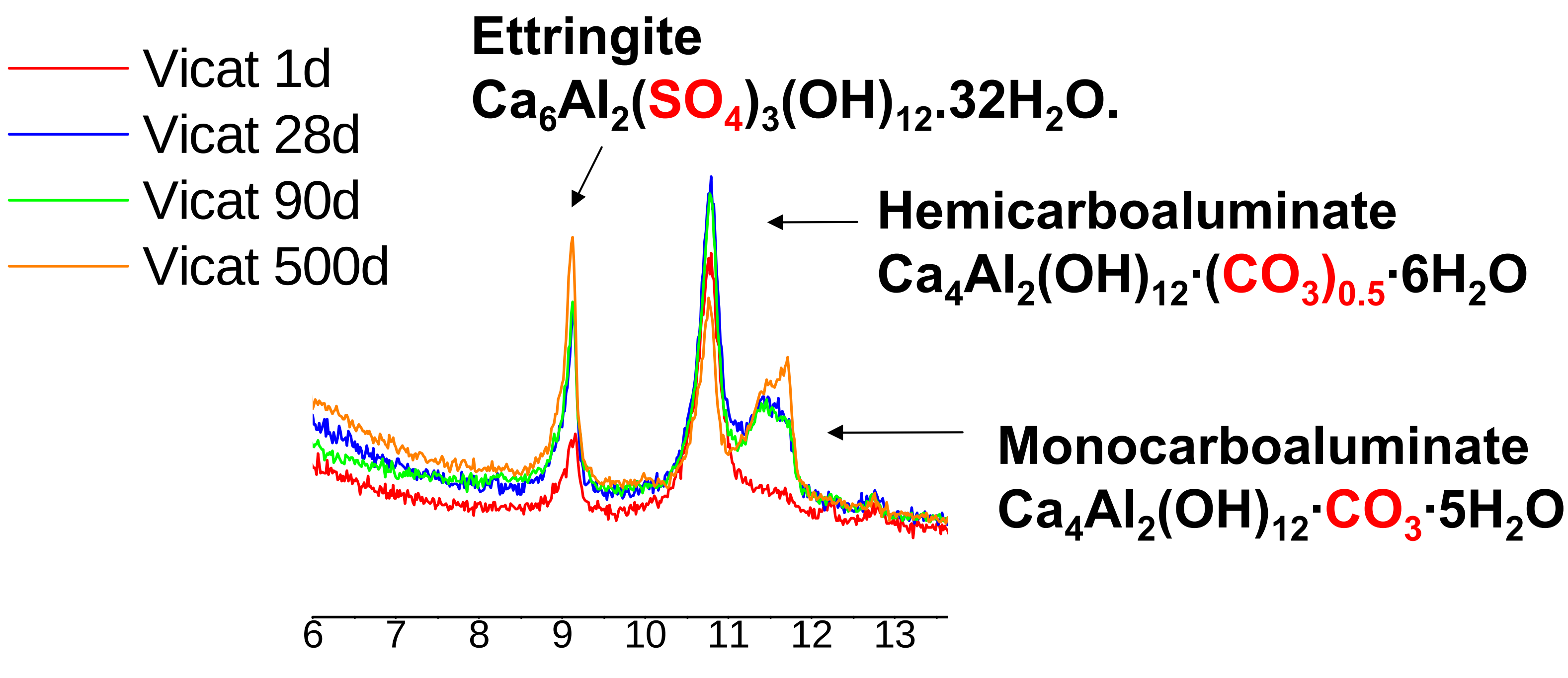
Early age hydration products

In cements containing sulfate and carbonate
(Vicat)



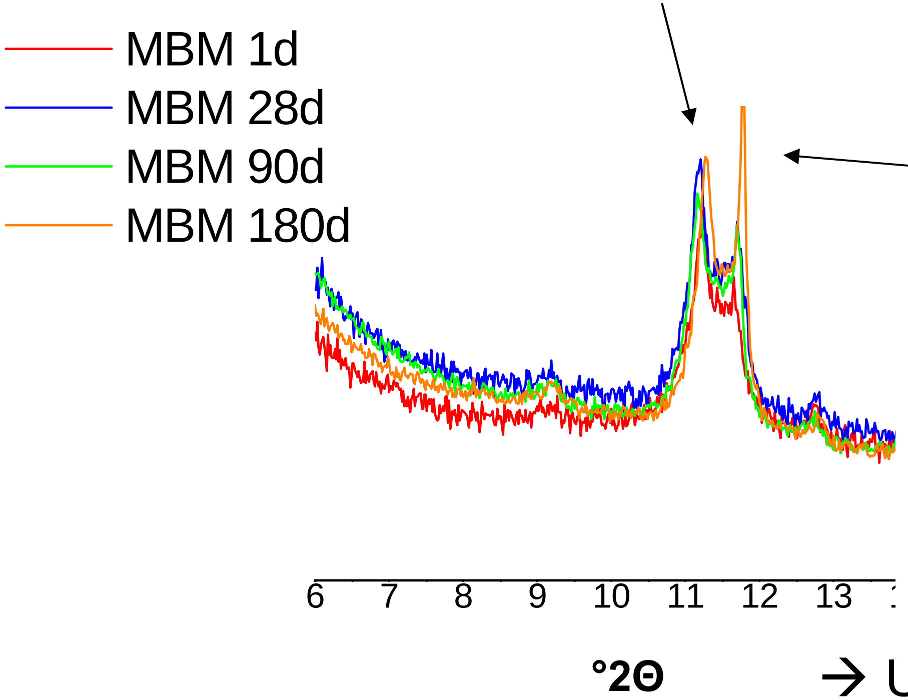
→ Assemblage typical to Vicat cement

3/ Hydration of Roman cements

Early age hydration products

In cements containing no sulfate but carbonate
(Lilienfeld, Wittersdorfer & Peggauer)

Phase containing CO_3 (solid solution)



Monocarboaluminate
$Ca_4Al_2(OH)_{12}\cdot CO_3\cdot 5H_2O$

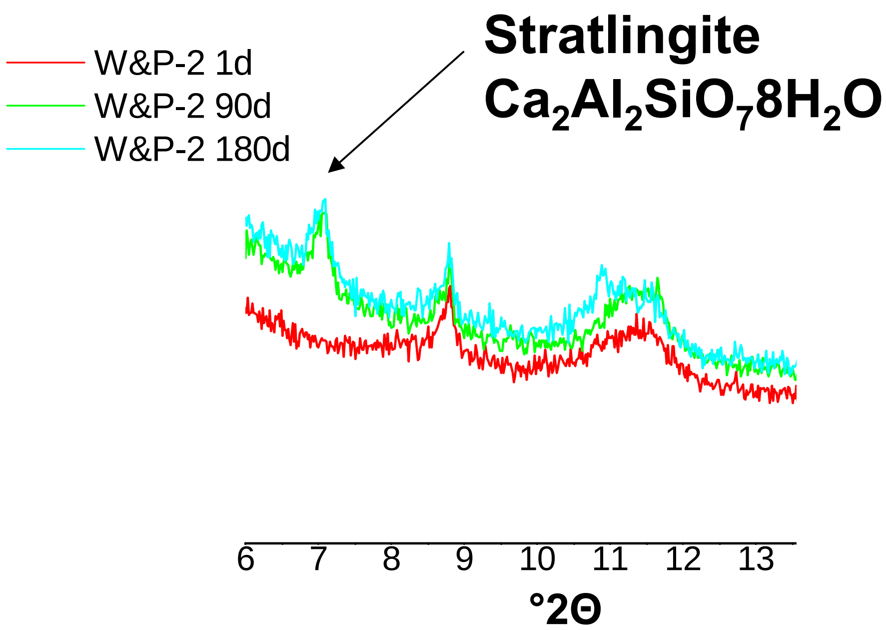
→ Usual phases in Roman Cements

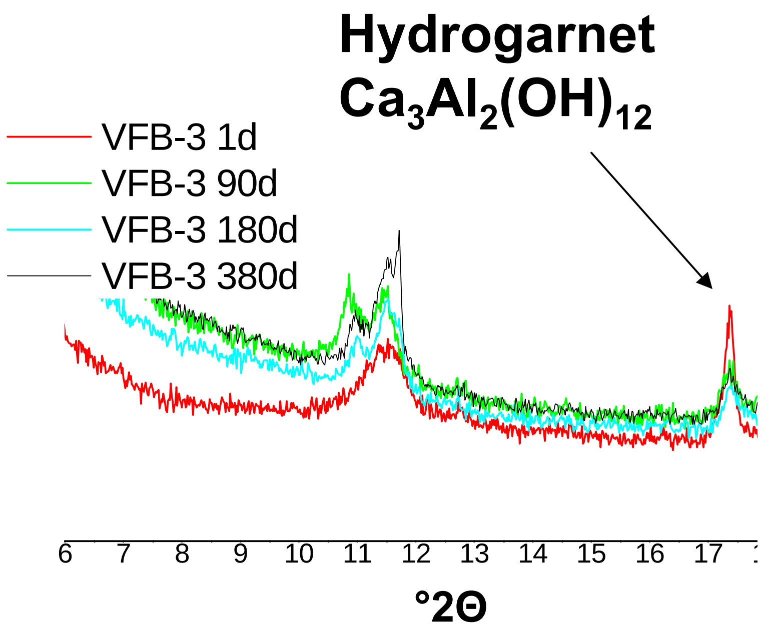
3/ Hydration of Roman cements

Early age hydration products

In cements containing no sulfate nor carbonate
(one VFB and one prototype W&P cement)

Other phases than Hemi– and Monocarboaluminate are formed





→ Usual phases in other cementitious systems, but rarely reported in Roman Cements

Concluding remarks (1/3)

- Roman cements are unique materials (cement chemistry and mortars properties)

- The mechanical and transport properties of mortars result from the rapid development of a complex microstructure

- Vicat remains a specific cement because contains C_3S and gypsum

Concluding remarks (2/3)

- The nature of the first hydration products depends on the presence of carbonate and/or sulfate in the cement

- The assemblage made of $CaO\text{-}Al_2O_3\text{-}CO_3\text{-}H_2O$ is identified in mostly all Rocare RCs

- Regardless of their nature, these first products are stable for several years

Concluding remarks (3/3)

- Later, C_2S hydrate to fill the microstructure up after few days/weeks with other products (C-S-H, CH…) → strength increase

- But the relative reactivity of C_2S strongly depends on the type (α' or β) and the possible carbonation in the kiln, reducing their availability

For additional information see
www.rocare.eu

If you have any questions contact me at
christ.gosselin@gmail.com