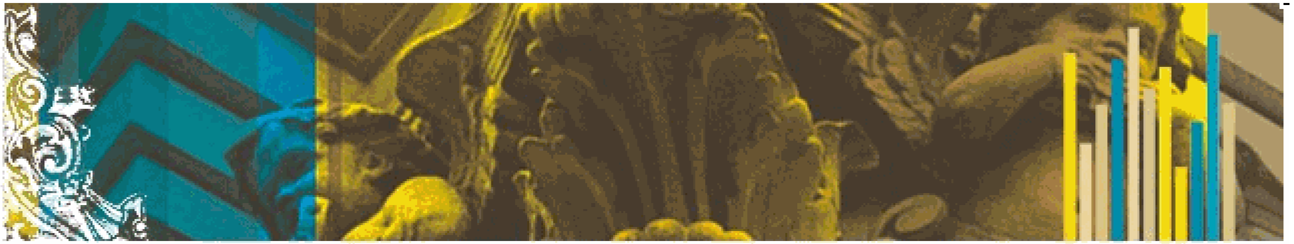
rocare ROMAN CEMENT



ROMAN CEMENTS FOR ARCHITECTURAL RESTORATION TO NEW HIGH STANDARDS

Composition and Hydration of Roman Cements

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Introduction

- **Previous talk on the different facilities of production**

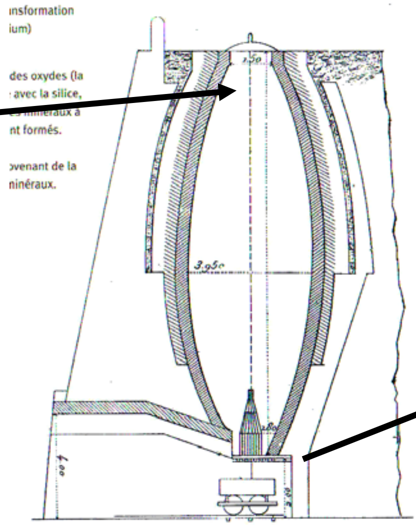
- **What is the composition of the cements?**

- **How do the cements hydrate ?**

Basic reactions

Quarry
(Austria)

Crushed
Marlstones



Shaft kiln

(~ 800-1100°C)

“Cement stones”
(clinker)

Grinding

Limestone + 25-35%wt clay minerals

Calcite $CaCO_3$/ dolomite $CaMg(CO_3)_2$

Quartz SiO_2

Clay materials (illite-muscovite-chlorite…) :
Al_2O_3, SiO_2, Fe_2O_3, Na_2O, K_2O

If iron sulfur minerals (FeS_2, FeS…)→ SO_3

Calcination (1/3)

CaO

Al_2O_3 and Fe_2O_3 → 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)

Calcination (2/3)

From 650°C, $CaCO_3$ and /or $CaMg(CO_3)_2$ 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

Spurrite $Ca_5Si_2O_8$ (CO_3)

Tilleyite $Ca_5Si_2O_7$ $(CO_3)_2$

CaO

+ SiO_2
+ Al_2O_3
+ T >1000°C ↓

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

Theoretical reactivity

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

Calcination (3/3)

Sometimes under-burn materials ……

Remaining
raw minerals

Cement phases

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

Image K Stingl (2009)

In the real world

Shut up !

α’ or $\beta - C_2S$?!

Image: Demonstration Site, Chateau Valère, Sion, CH

Reference cements:

Vicat Prompt (commercial)
Lilienfeld (Rocem)
Folwark (Rocem)

Rocare cements:

MBM-Gartenau cement (November 2010)

1 cement from pilot rotary kiln (870-920°C)

VFB cements (May 2010)

4 samples from the same in traditional shaft kiln (840-1130°C)

W&P cements (June and Dec. 2010)

4 samples from preliminary tests using the rotary kiln (~850°C)
1 sample (WP5) using optimized parameters (850-1000°C)

XRD crystalline composition

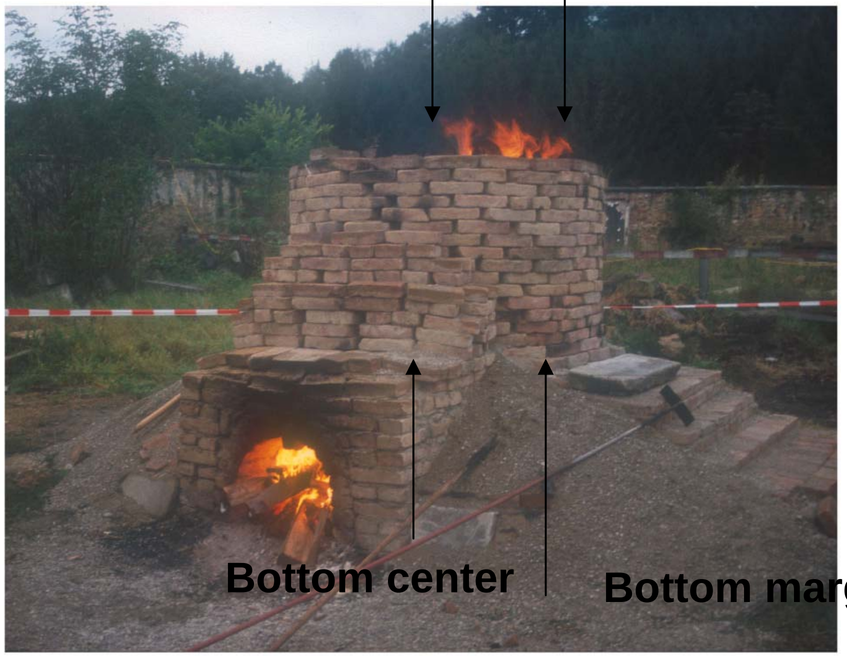
	Lilienfeld ~960°C	Folwark ~950°C	Vicat Prompt 600→1200°C	MBM 870→970°C	WP5 800→1000°C
Total belite $\alpha' + \beta\text{-}C_2S$	48	27	44	47	23 (Because C_2AS)
Ratio α' / β C_2S	6	2.8	0.3	0.6	0.35
Carbonated C_2S (Spurrite $Ca_5Si_2O_8(CO_3)$ + Tilleyite $Ca_5Si_2O_7(CO_3)_2$)	6.9	9.3	15.2	16.5	7.1
Remaining raw materials (calcite quartz muscovite albite…)	34.6	32.8	17.6	18.9	35.1

Here carbonation of C_2S favored when β dominates

low carbonation of C_2S in this kiln

Composition of VFB cements

Composition of four samples from the same batch



Shaft kiln in Mauerbach, (Au)

XRD crystalline composition of VFB cements

(May 2010) *From the same batch – different locations of cement in the kiln*	VFB bath 4 1 Bottom layer center (939°C)	VFB bath 4 2 Bottom layer margin (859°C)	VFB bath 4 3 top layer center (1133°C)	VFB bath 4 4 top layer margin (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 Spurrite $Ca_5Si_2O_8(CO_3)$ + Tilleyite $Ca_5Si_2O_7(CO_3)_2$	6.1	17.7	5.7	10.3
Remaining raw materials (calcite quartz mica)	11.1	27.9	1.9	43.6

Here carbonation of C_2S favored when α' dominates

Summary	Calcium silicate dominated by	« relative » Carbonation of C_2S	« relative » amounts of C_3A C_4AF and C_2AS
Lilienfeld	α' -C_2S	Low	Low
Folwark	α' -C_2S	Low	High
Vicat Prompt	β -C_2S	High	High
MBM	β-C_2S	High	High
VFB-1	β -C_2S	Low	High
VFB-2	α' -C_2S	High	High
VFB-3	β -C_2S	Low	High
VFB-4	α' -C_2S	High	High
W&P-1	α' -C_2S	High	Low
W&P-2	α' -C_2S	Low	Low
W&P-4	α' -C_2S	Low	Low
W&P-5 (main one)	β -C_2S	Very low	High C_2AS and other aluminate

Summary

A wide range of crystalline composition is obtained

→ due to the raw materials, the calcination parameters…

The amount and polymorphism of α'-C_2S and β-C_2S is changing according to the calcination conditions

→ What is the influence on the hydration and strength development?

The carbonation of calcium silicate can occur (reducing the availbilty of C_2S for hydration)

Mostly depends on the type of kiln and reduction conditions (low carbonation in the big rotary kiln W&P), rather than the dominating C_2S polymorph

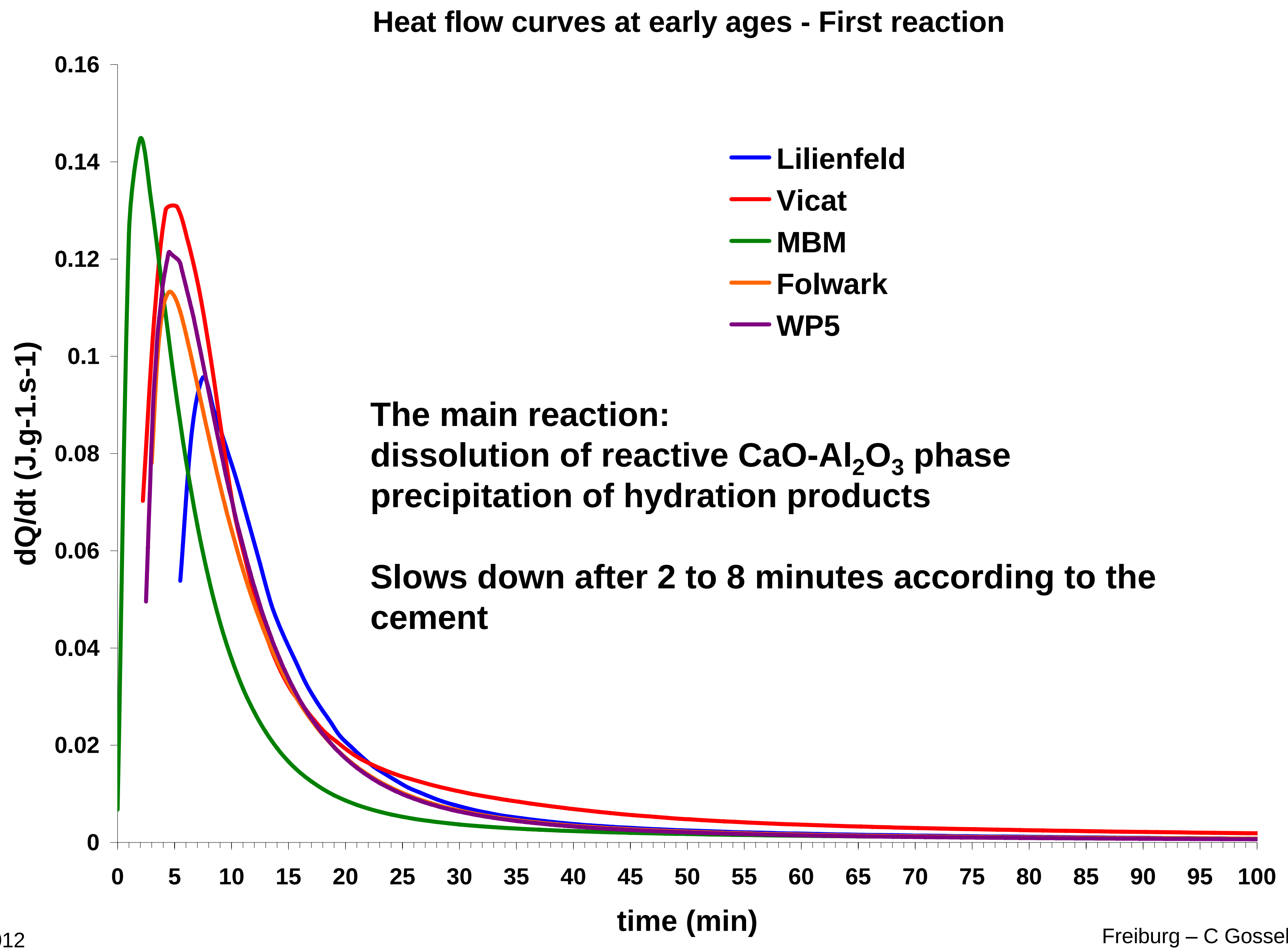
2/ Hydration

How do …

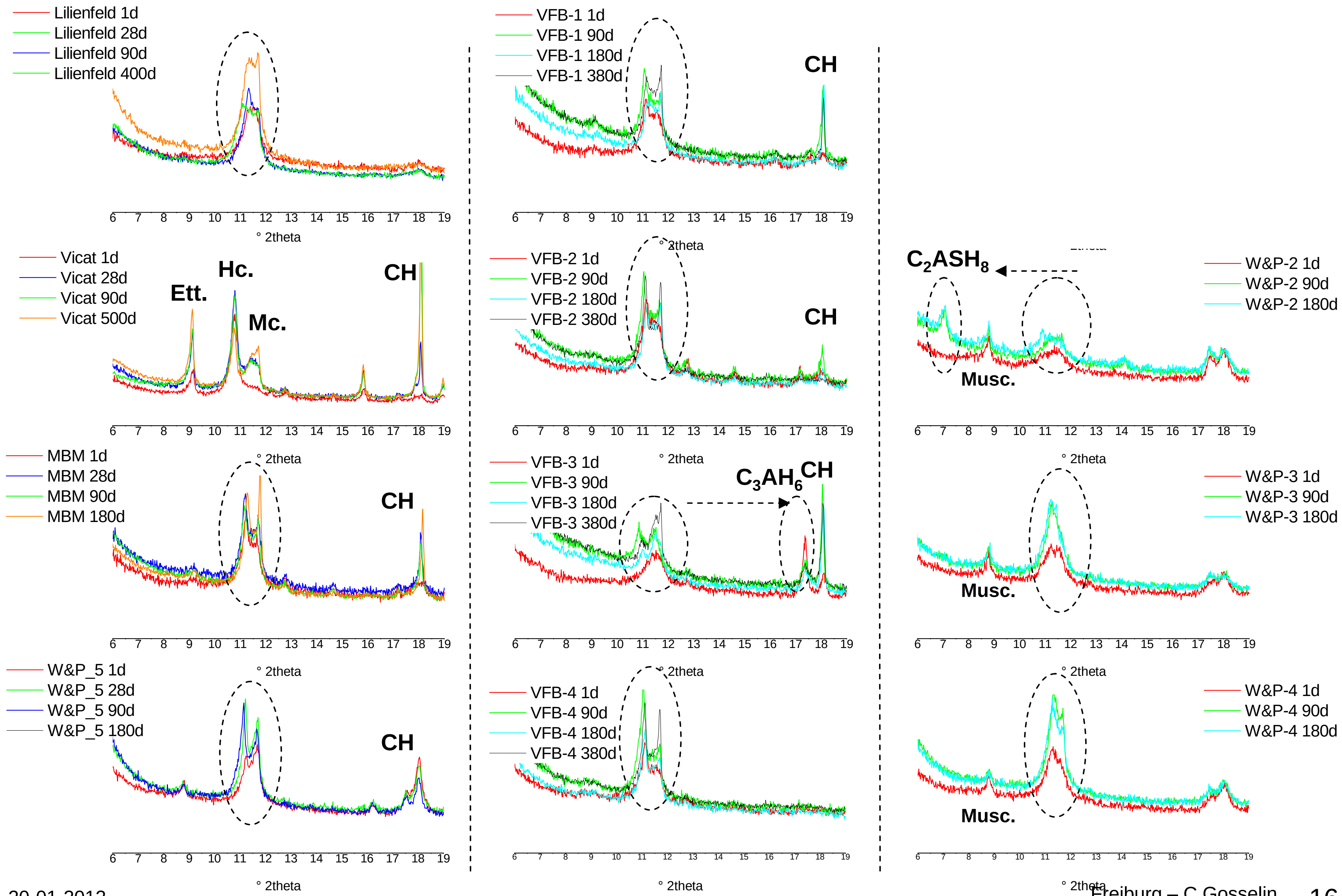
… Roman cements …

… hydrate ?

Early age hydration – isothermal calorimetry at 20°C (W/C 0.65)



Hydration products – X-Ray Diffraction



Hydration products

• **In most cases, monocarboaluminate and carbonated AFm are formed in (almost) all systems**

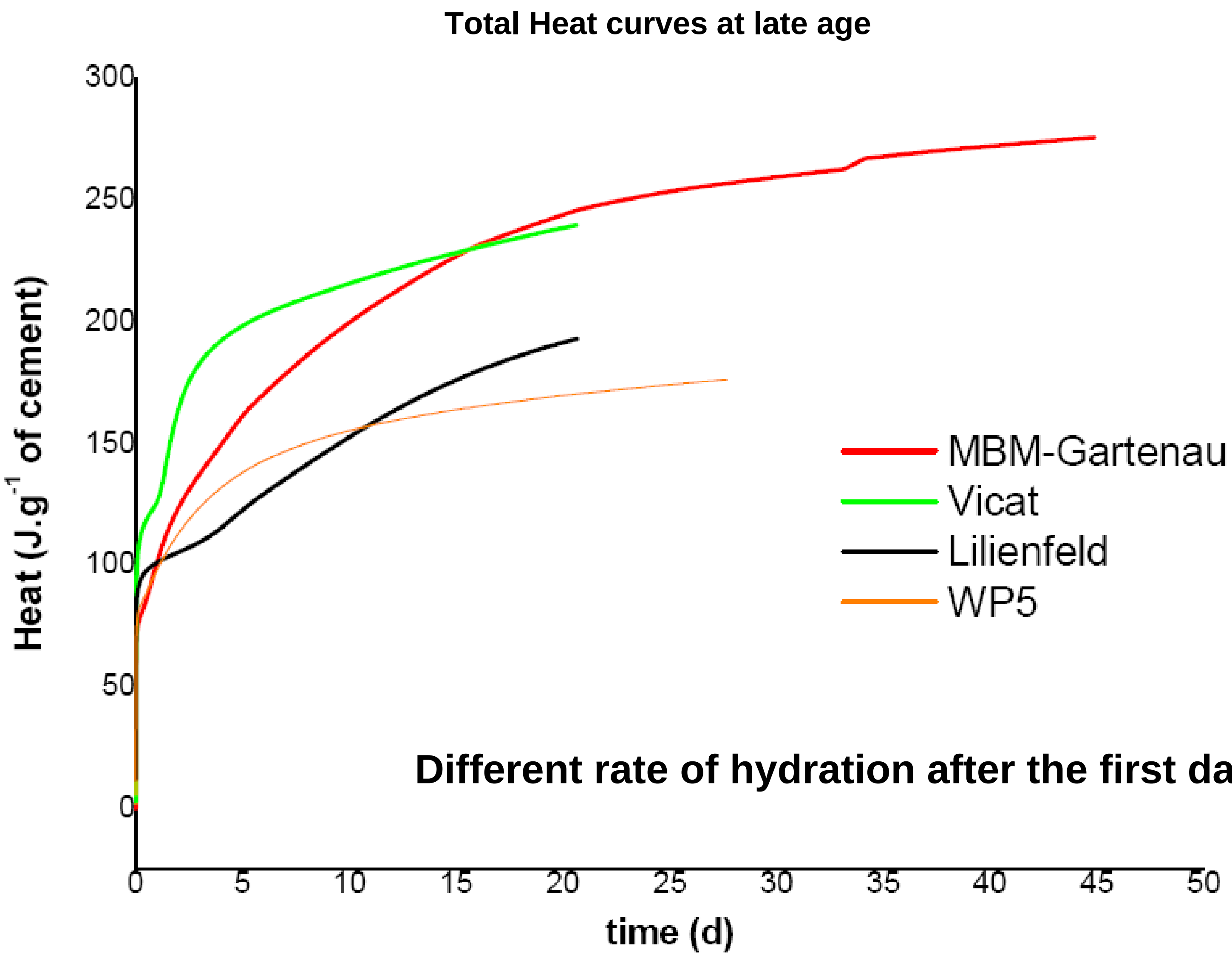
• **The relative amounts of these products is stable after the first days of curing**

• **For the systems with no calcite :**

- **VFB-3 : C_3AH_6 is rapidly stable (1 day)**
- **W&P-2, C_2ASH_8 is rapidly stable (from 7 days)**

→ role of the fine calcite grains rapidly soluble
→ release CO_3 ions to stabilize CaO, Al_2O_3 , H_2O into CO_3-AFm and monocarboaluminate

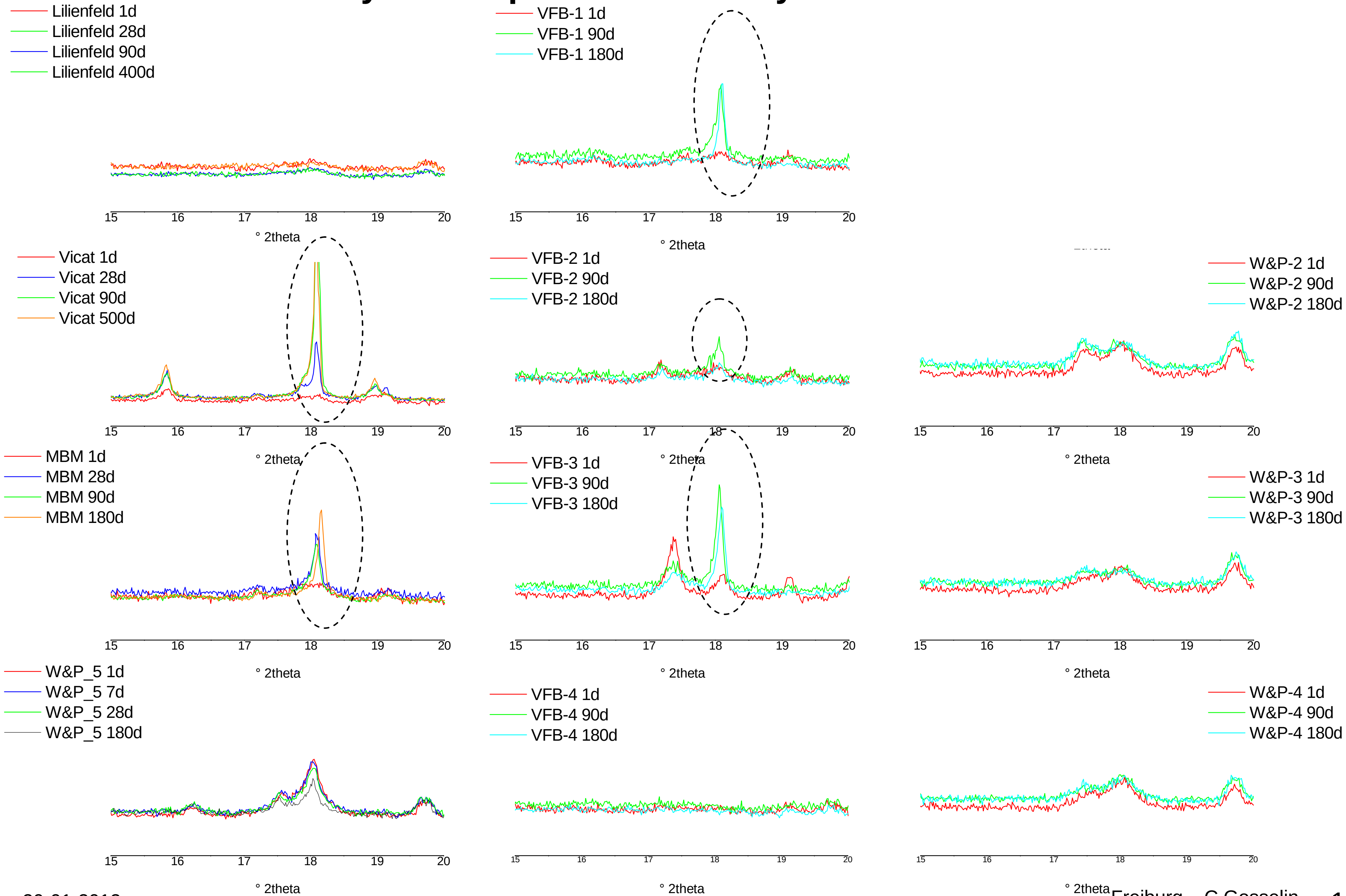
Late age hydration – isothermal calorimetry at 20°C (W/C 0.65)



Different rate of hydration after the first days

2/ Main patterns of hydration

Hydration products – X-Ray Diffraction



Conclusion (1/2)

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

- **Their mechanical and transport properties result from the rapid development of a complex microstructure**

- **Rapid formation of $CaO\text{-}Al_2O_3\text{-}CO_3\text{-}H_2O$ hydrates (AFm) at the very start of hydration → poorly packed microstructure leading to minimal strength**

- **Later, C_2S hydrate:**
  - **Filling up of the microstructure after few days/weeks with other products (C-S-H, CH…)**

Conclusion (2/2)

• **In terms of production, shall be a RC target composition based only on the C_2S type we want to produce?**

- **The relative reactivity of α' and β C_2S was discussed**
- **The carbonation of C_2S in the kiln also reduce the C_2S availability**
- **The formation of CH is not well detected by X-Ray diff. although the development of the microstructure and the strength occurs**