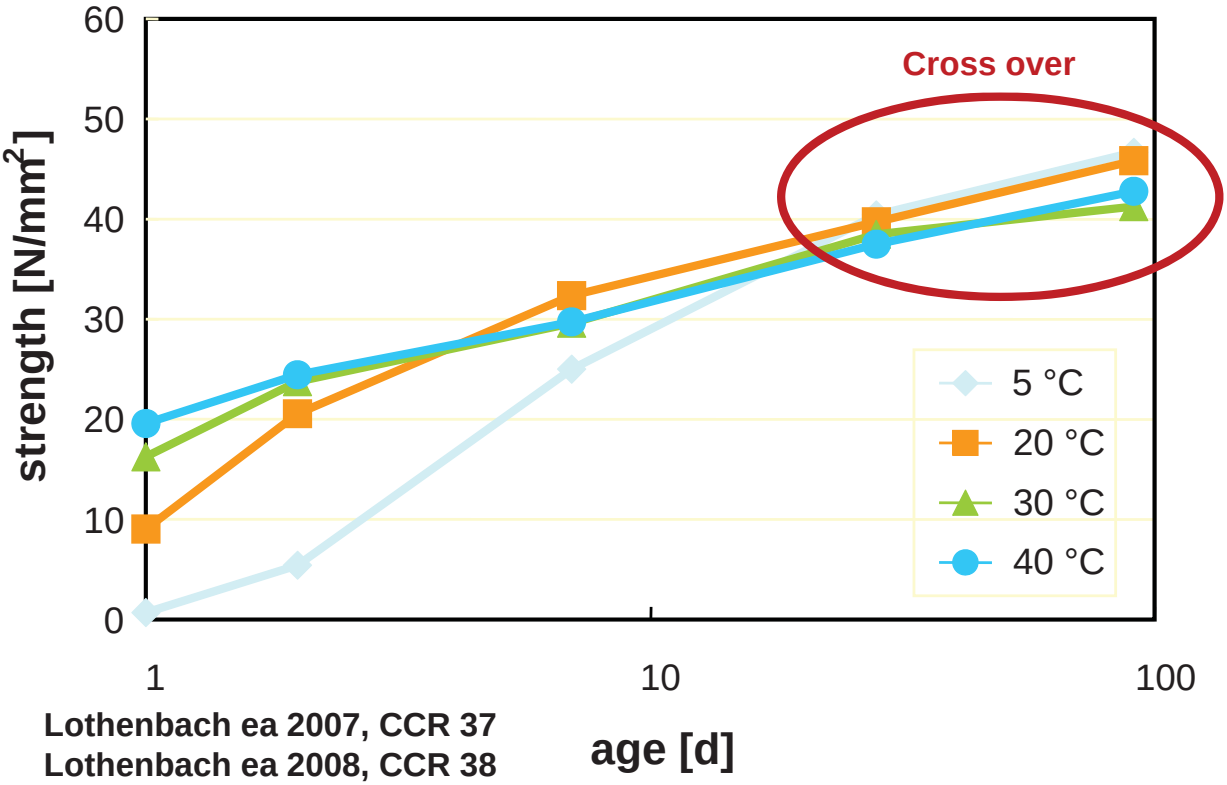
2) Influence of temperature

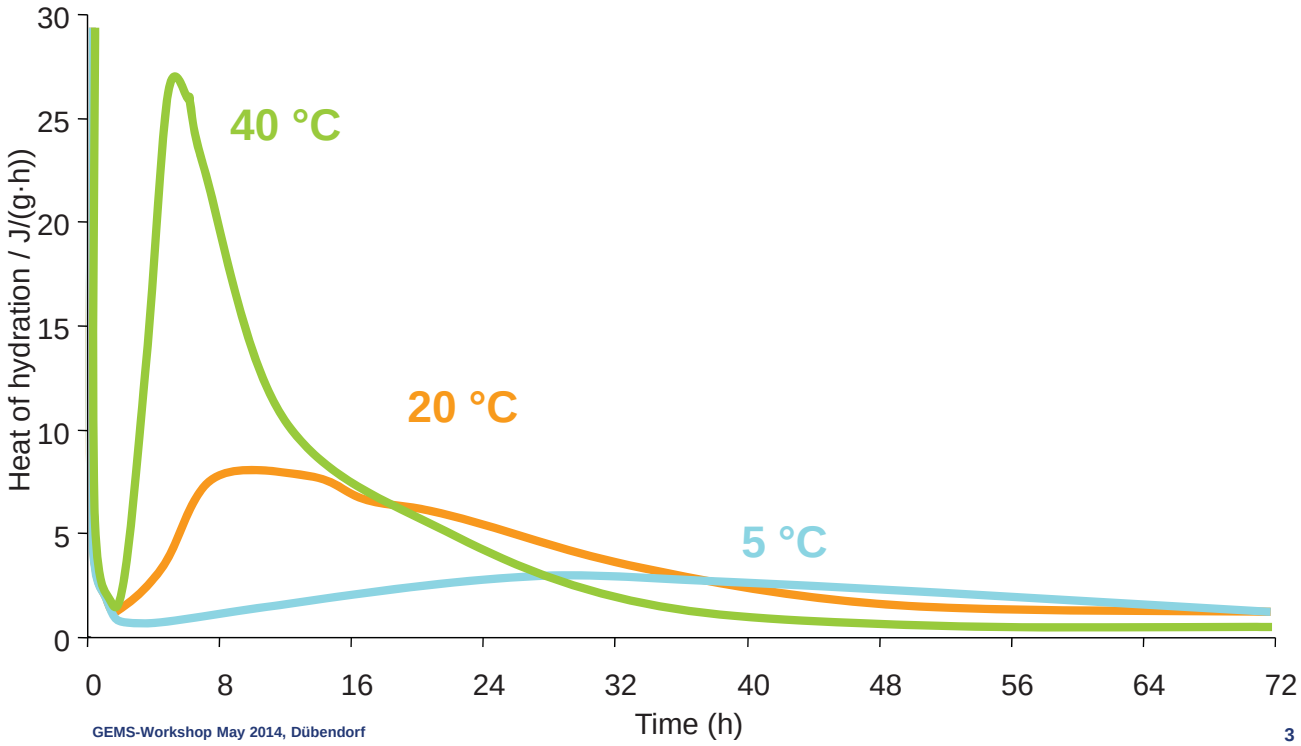
a. **Experimental evidence**
b. **Temperature extrapolation**
c. **Blended systems**

Influence of temperature: Compressive strength

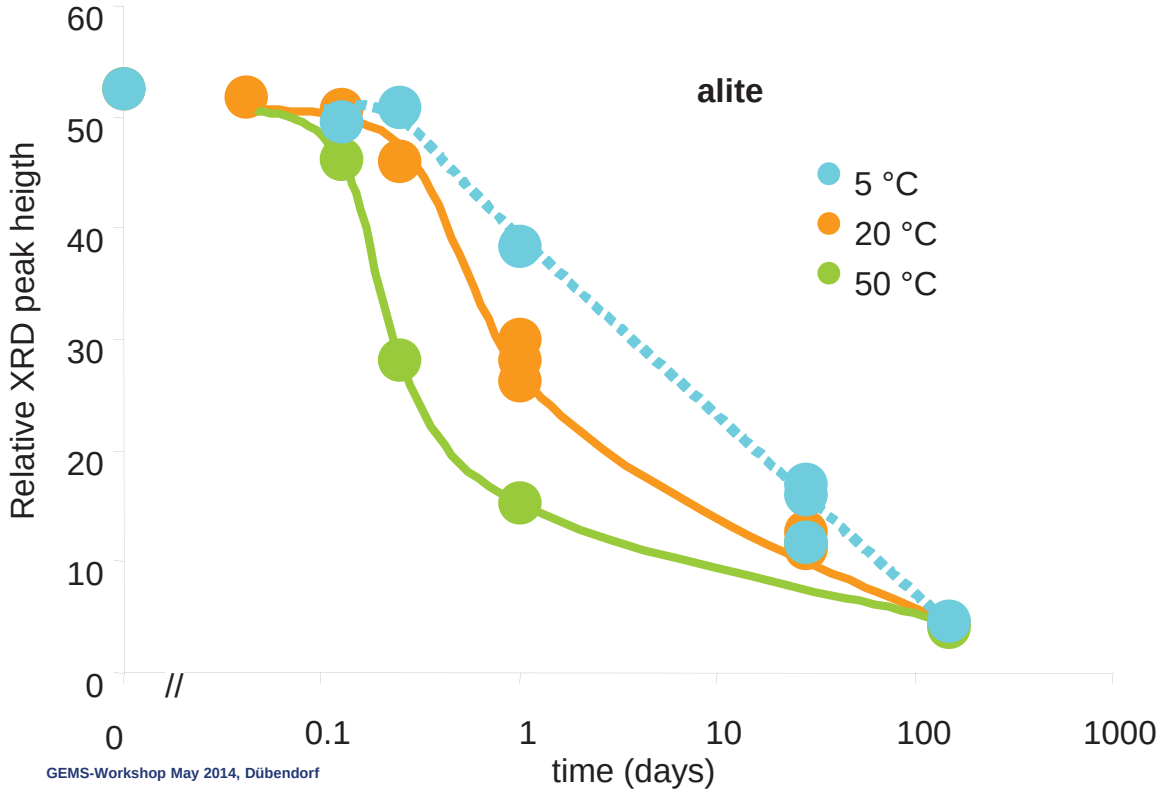


Lothenbach ea 2007, CCR 37
Lothenbach ea 2008, CCR 38

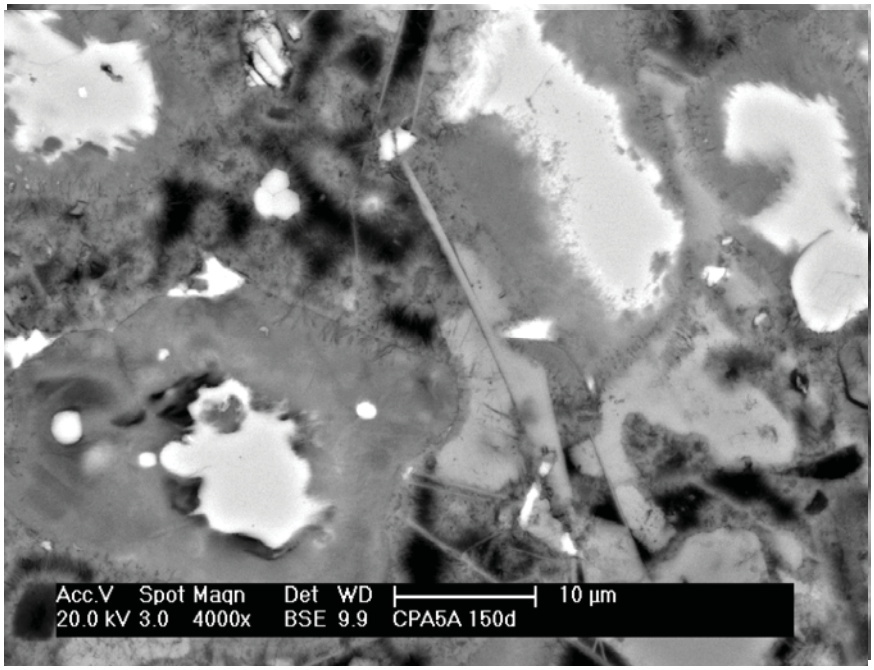
Calorimetry



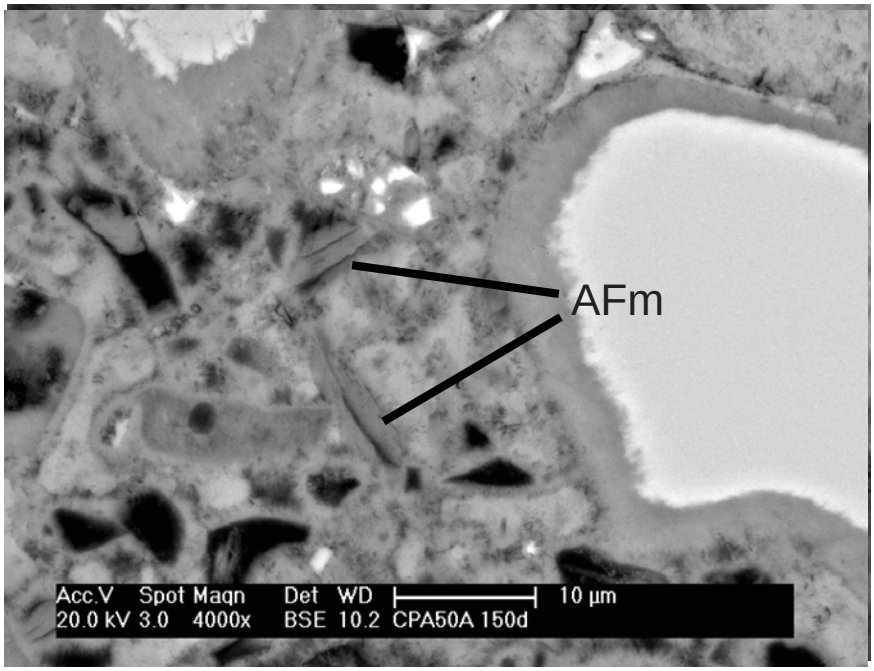
Progress of hydration



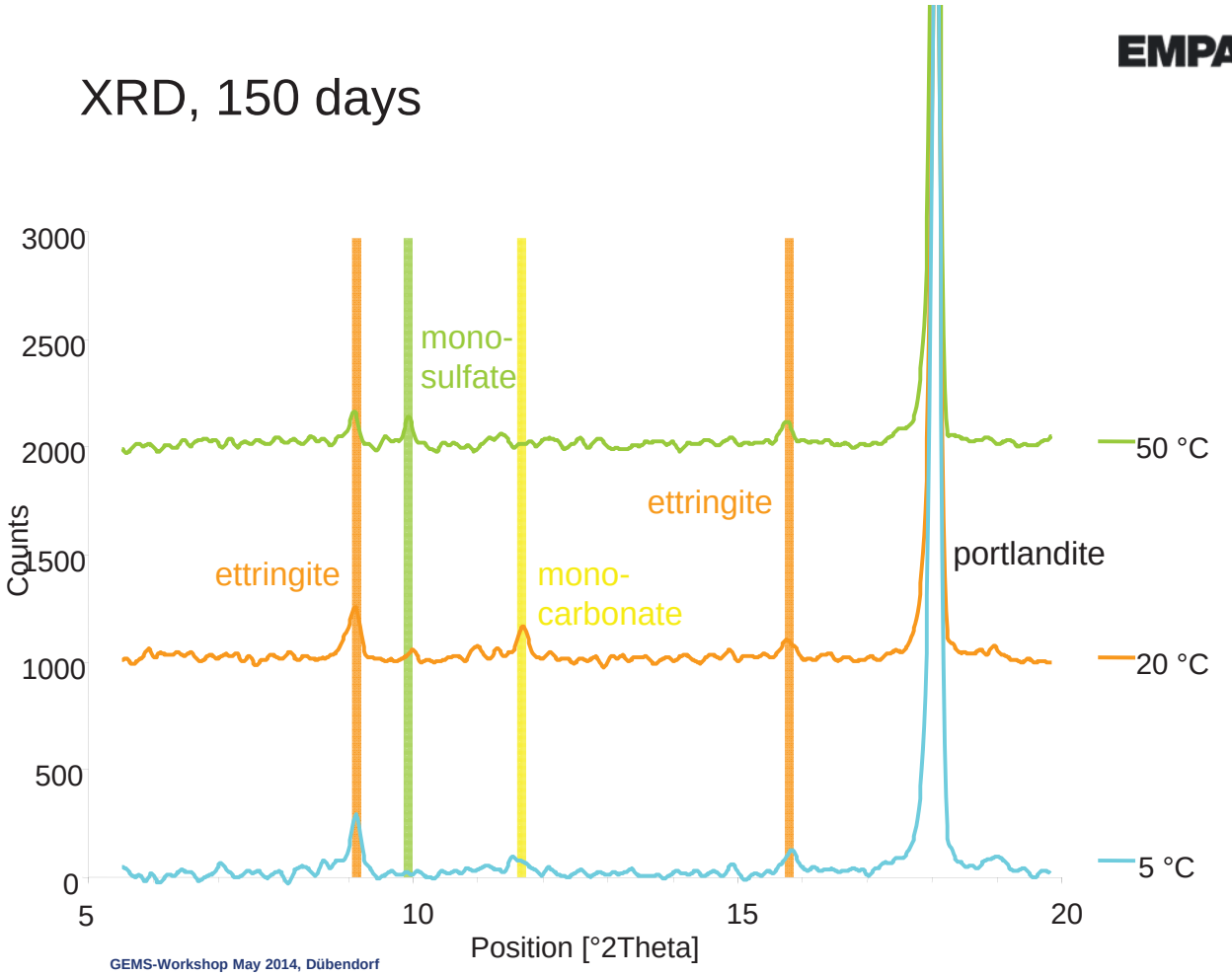
5 °C, 150 days



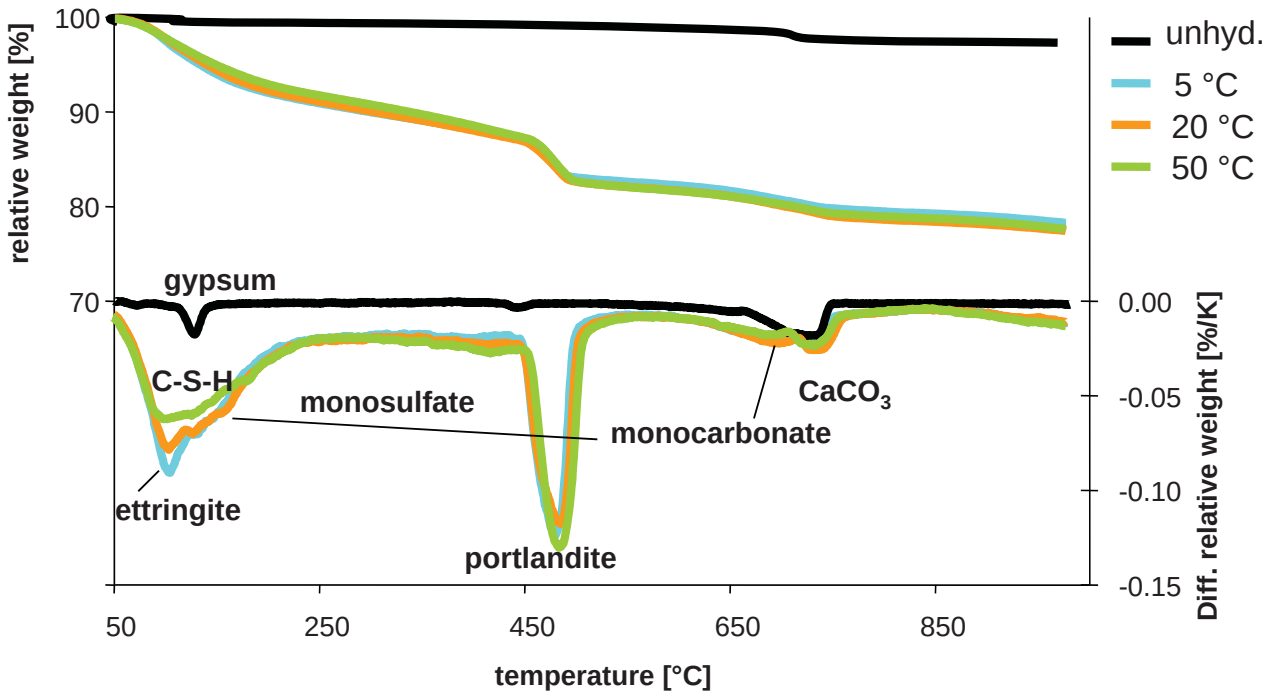
50 °C, 150 days



XRD, 150 days



150 days

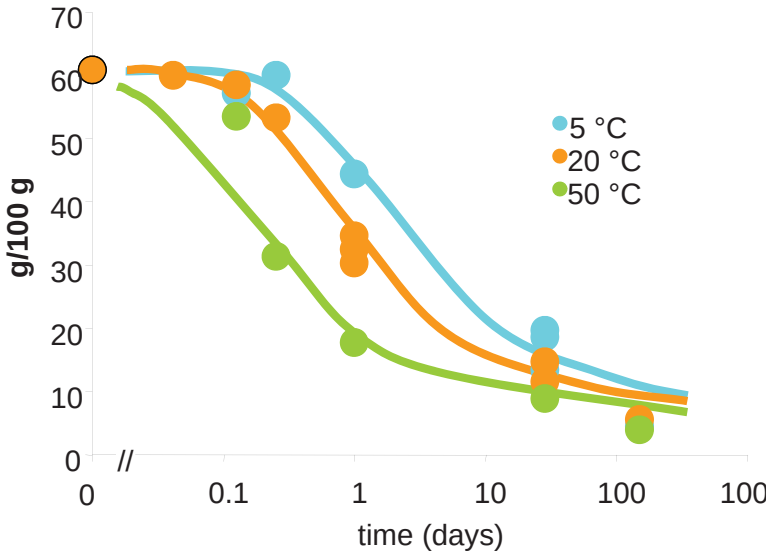


Modeling: Temperature

Arrhenius equation

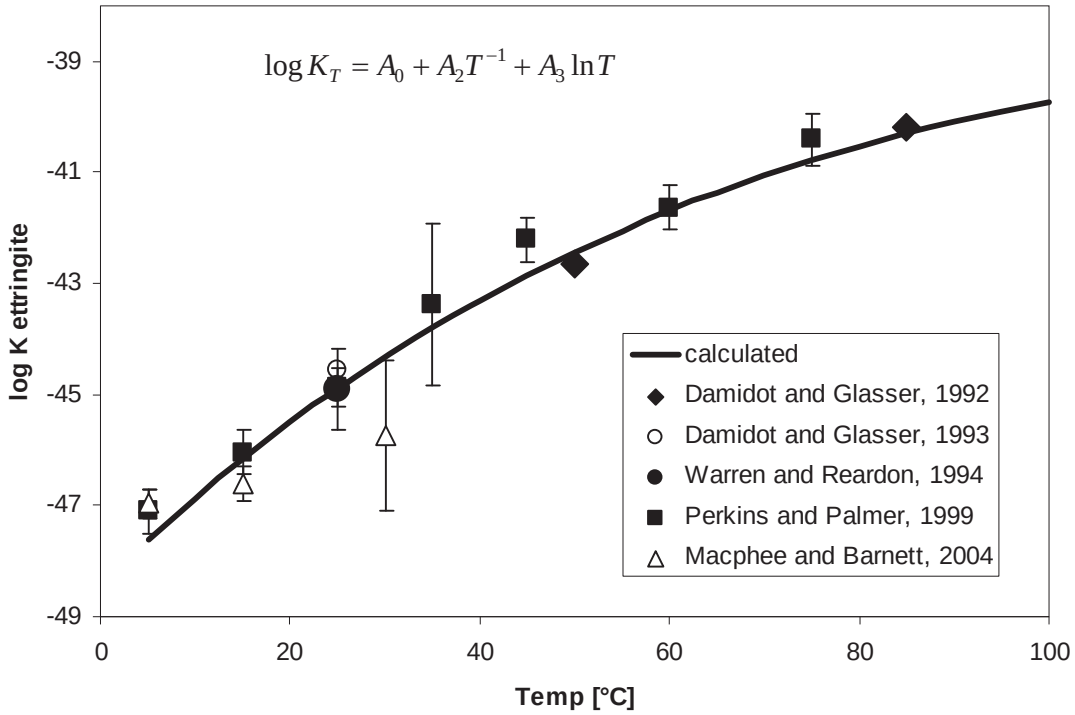
$$R_T = A\, e^{-\frac{E_a}{RT}}$$

E_a: activation energy



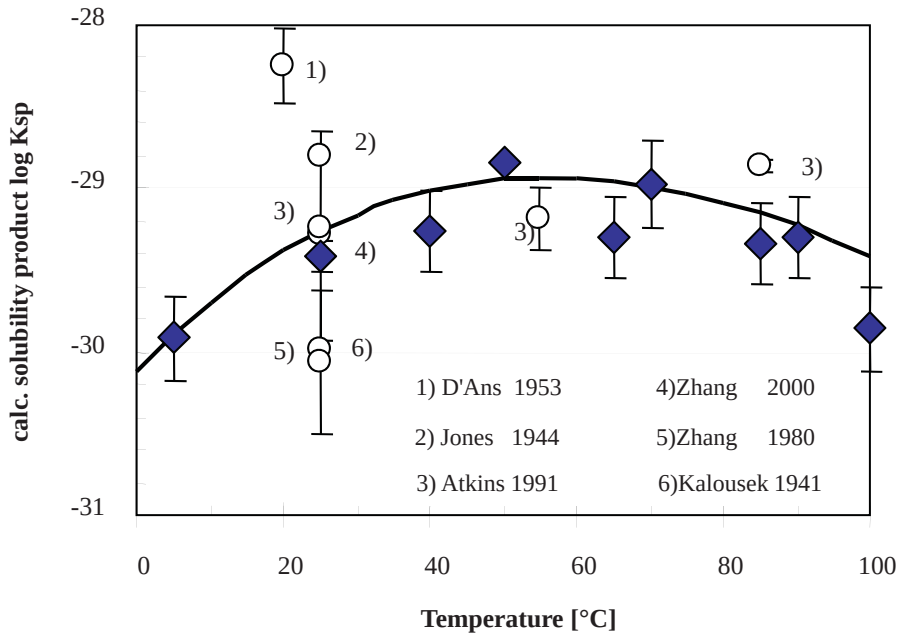
Chemical reactions accelerate with increasing temperature

Solubility of ettringite as f(T)



Lothenbach et al. (2008), CCR 38, 1-18

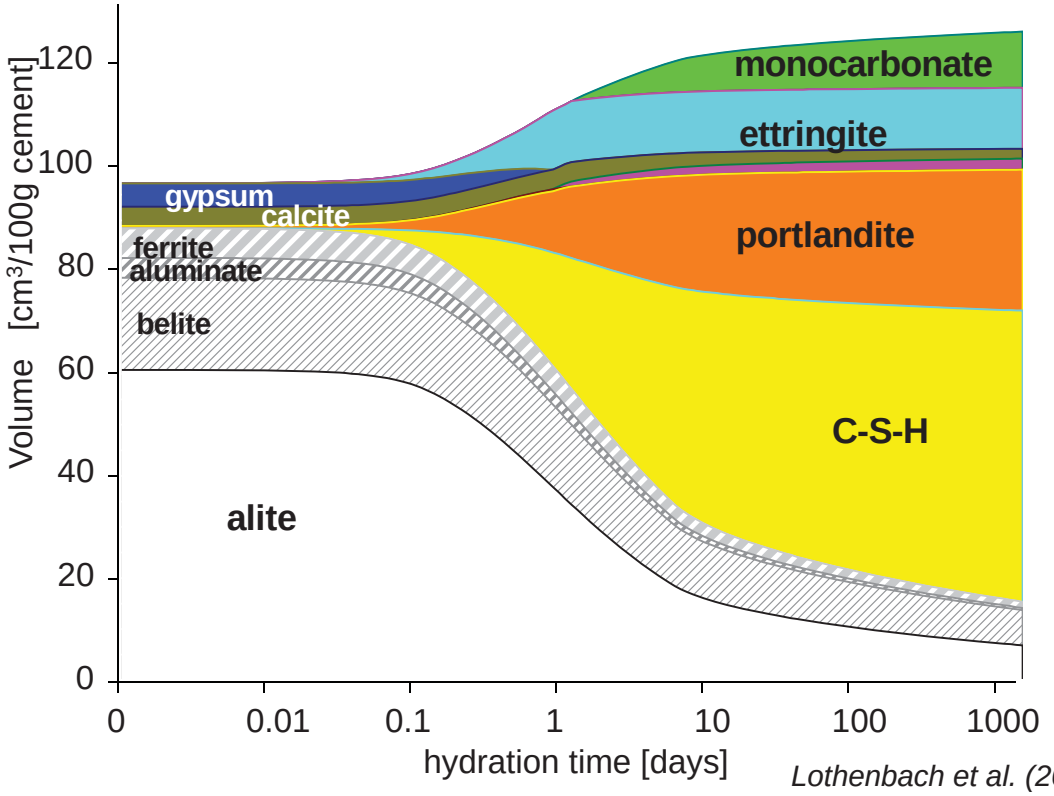
Solubility of monosulfate



Matschei et al. (2007), CCR 37, 1379-1410

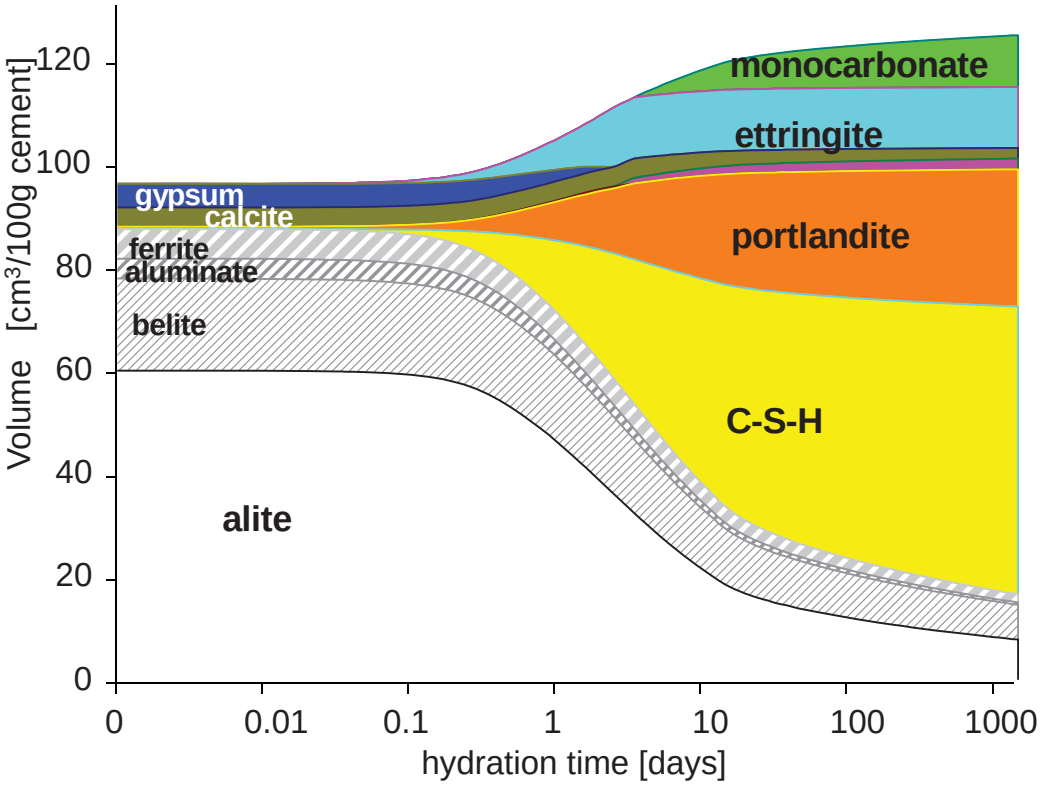
EMPA

Hydration: 20 °C

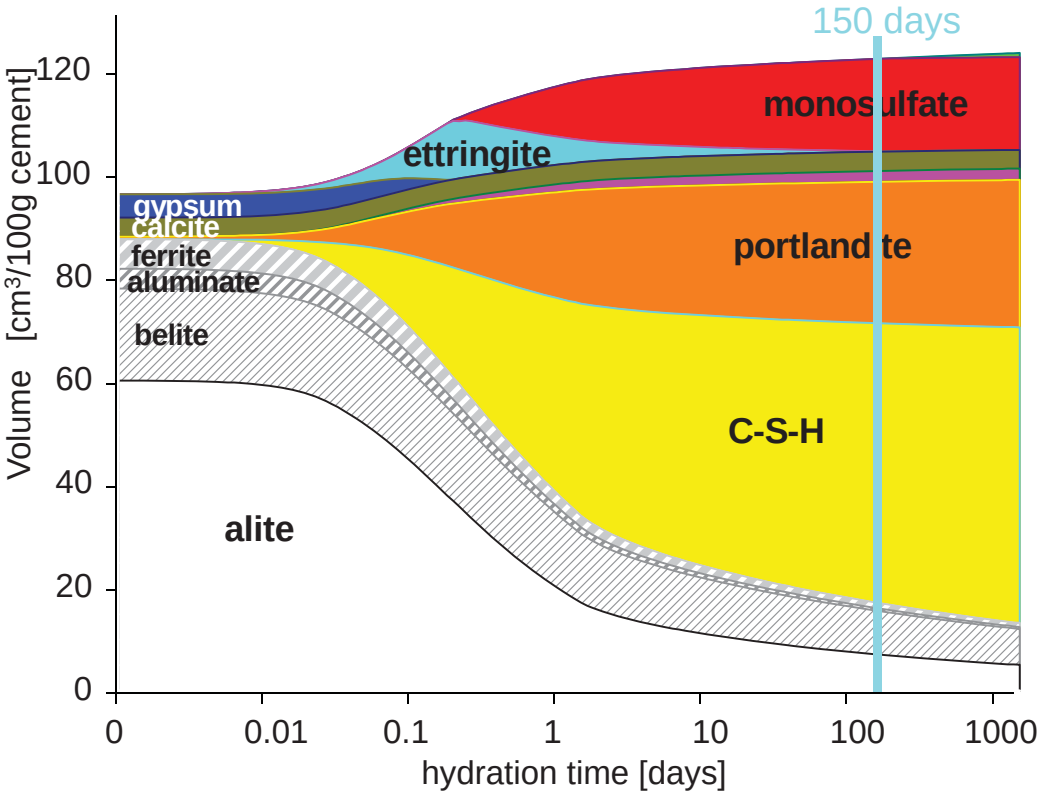


Lothenbach et al. (2008), CCR 38,

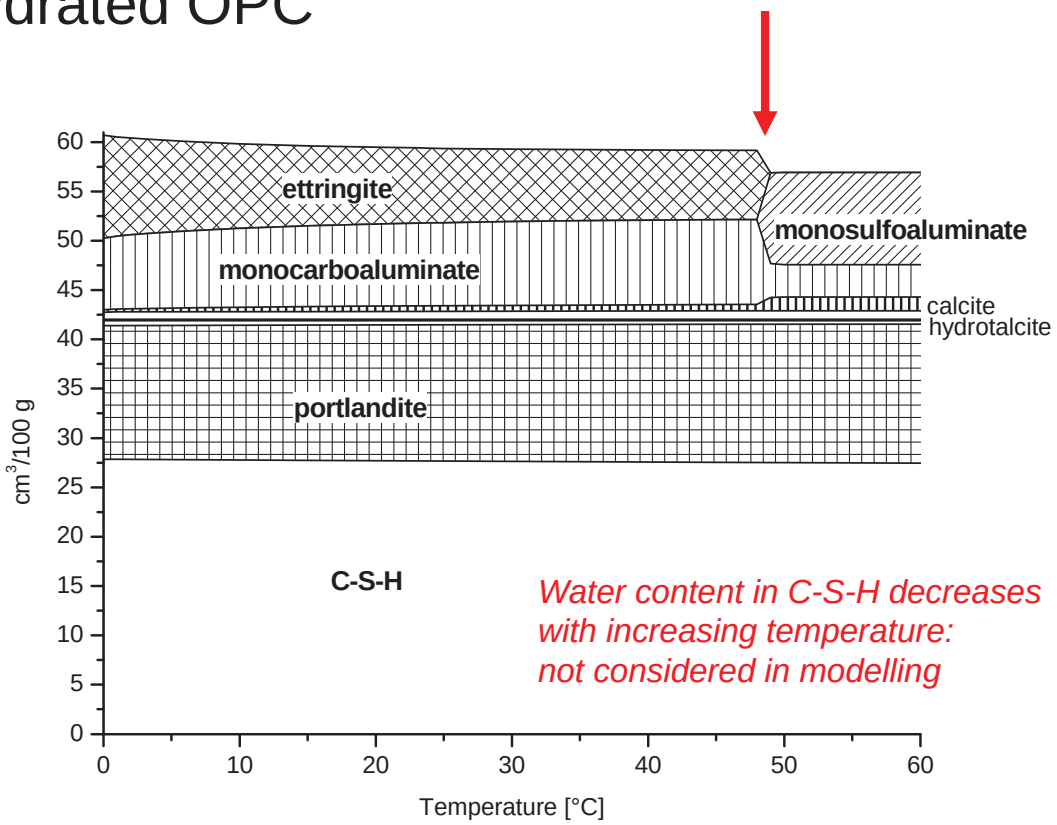
hydration: 5 °C



hydration: 50 °C

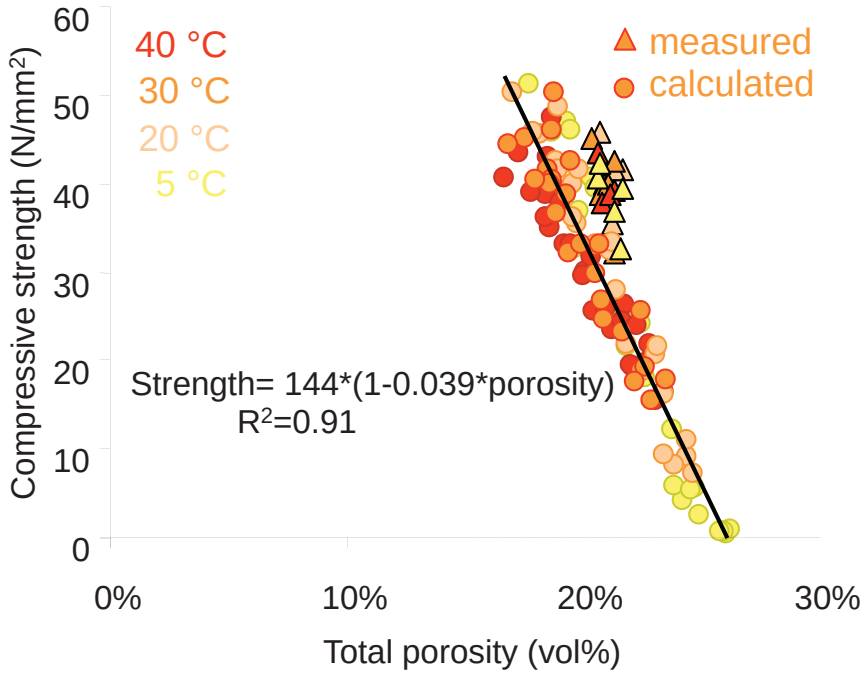


Hydrated OPC



Lothenbach et al. (2010), Advances Cem Res 22, 211-223

Strength-porosity



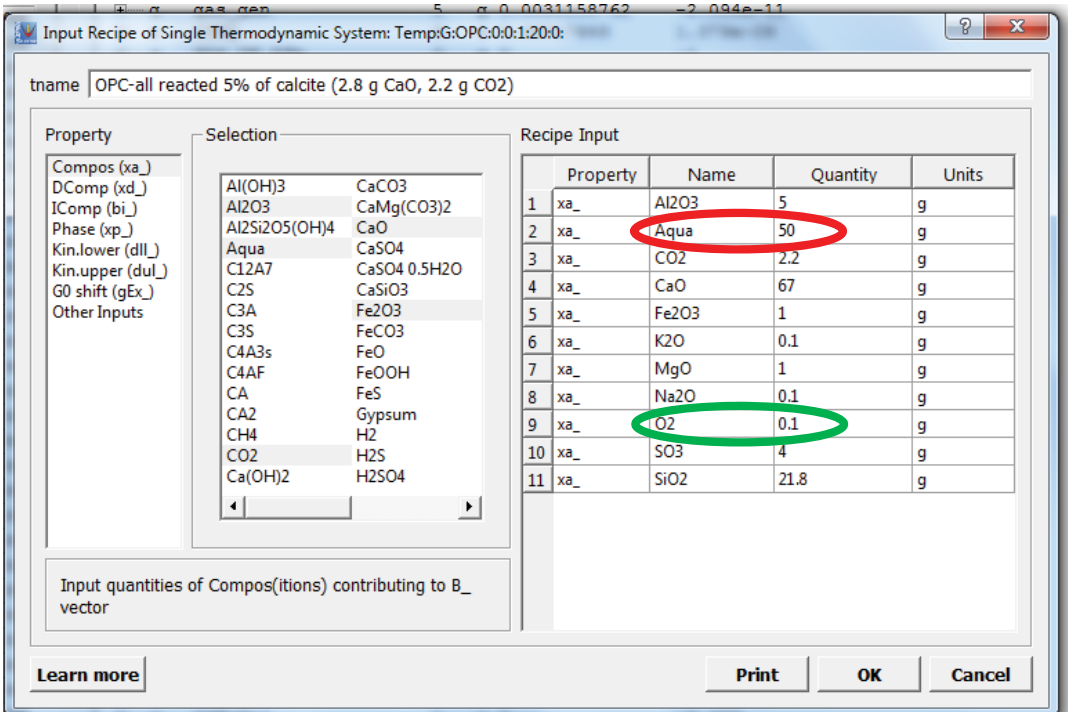
Influence of temperature

Higher temperature:
→ kinetic of hydration
→ morphology (inhomogenous), denser C-S-H
→ coarser porosity
→ pore solution (SO_4, Al)
→ hydrates (ettringite, monocarb. → monosulfate)
→ volume decrease
→ decrease in strength

Solubility of ettringite increases with temperature
-> less stable

Influence of temperature: tutorial

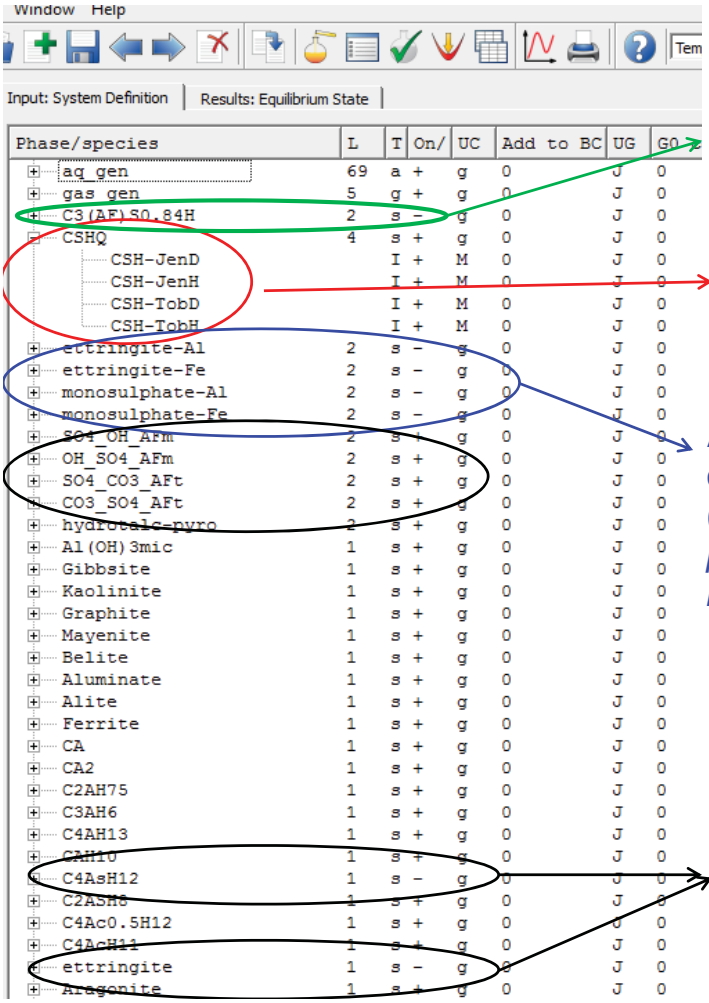
- Cement: «OPC» in project «Temp»



Cement composition in g/100 g: => All reacts!

w/b = 0.5

Some O_2 to ensure oxic conditions

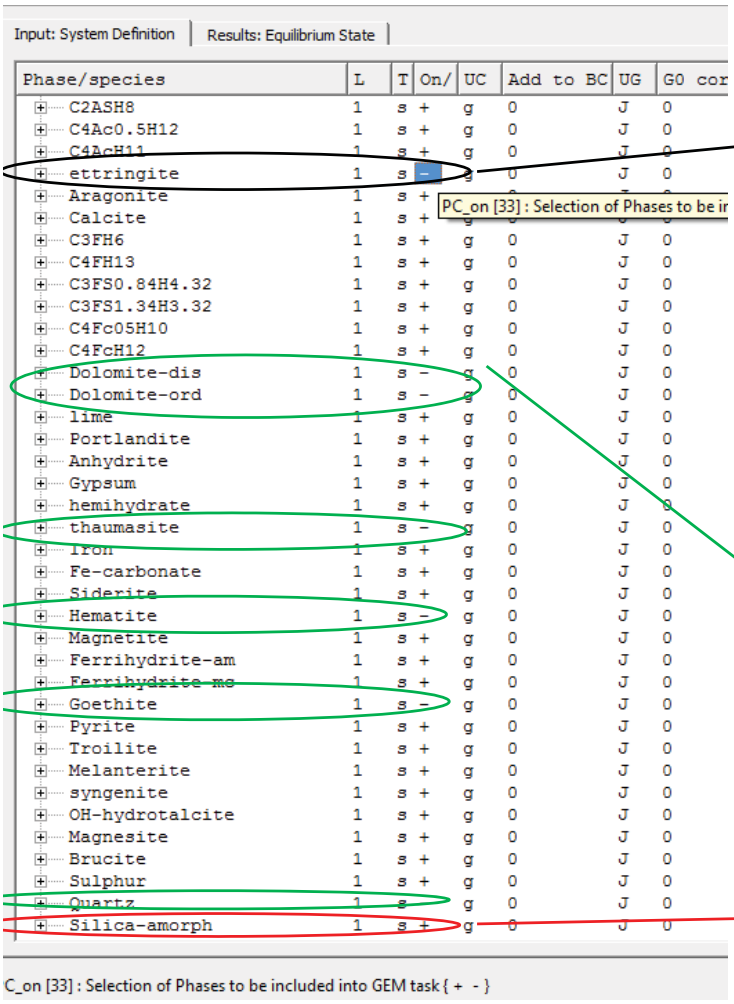


No siliceous hydrogarnet (C3(AF)S084H) dolomite, quartz, … formation at room temperature and short time frames

Quarternary solid solution model for C-S-H (Kulik 2010); Ca/Si varies from 0.67 to ≈1.5 (in the presence of portlandite)

Al-Fe monosulphate and Al-Fe-ettringite excluded for this example *(duplicates can cause mathematical problems; iron more stable in hydroandradite: $C_3FS_{0.84}H_{4.32}$)*

Single solids (ettringite/monosulphate) dectivated as already considered as solid solutions



Single solids dectivated as already considered as solid solutions

No thaumasite, hematite, dolomite, goethite, quartz, … formation at room temperature and short time frames

Amorphous SiO_2

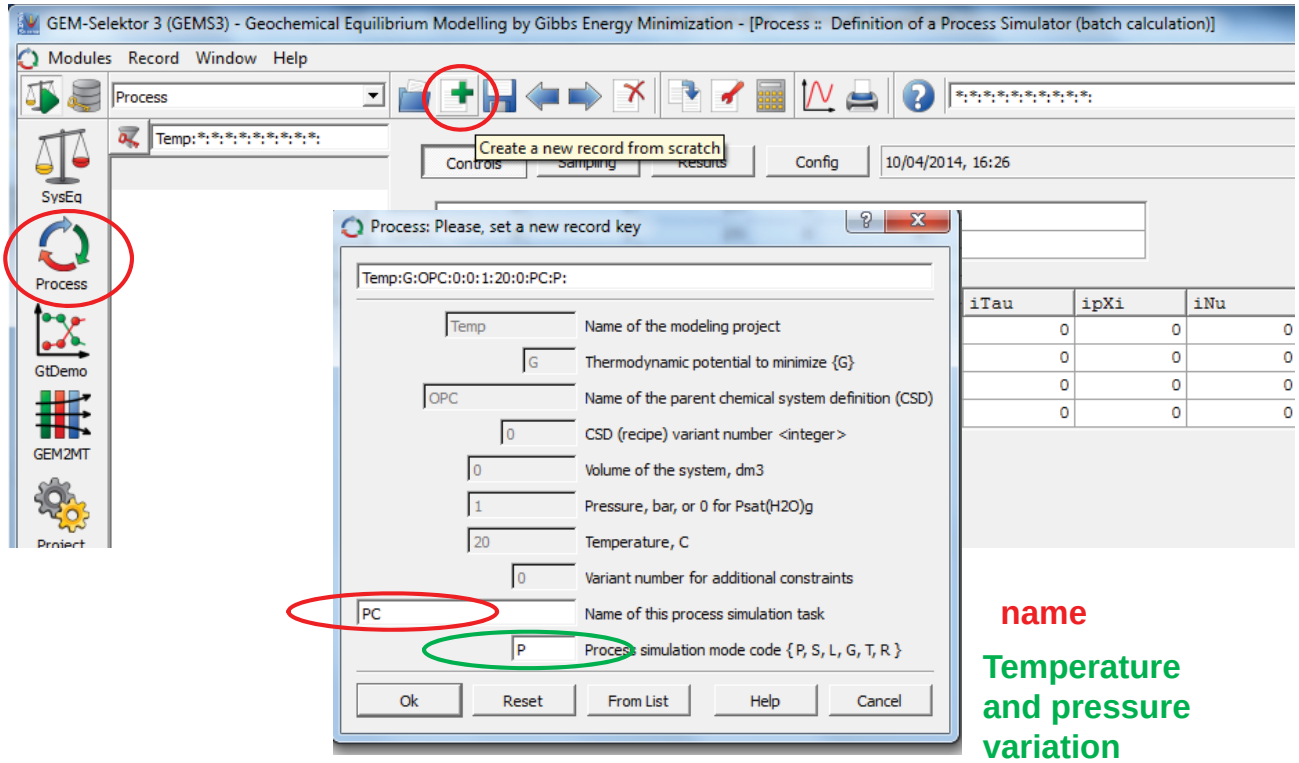
Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration
a aq_gen	69	a	0.43500338	2.192e-09	
g gas_gen	5	g	0.0031158762	-2.094e-11	
s CSHQ	4	s	0.46917649	1.379e-09	
s SO4_OH_AFm	2	s	0	-1	
s OH_SO4_AFm	2	s	0	-1	
s SO4_CO3_AFt	2	s	0.018717018	-3.32e-09	
s CO3_SO4_AFt	2	s	2.9848203e-007	0.0001596	
s hydrotalc-pyro	2	s	0	-8.646	
s Al(OH)3mic	1	s	0	-3.192	
s Gibbsite	1	s	0	-2.669	
s Kaolinite	1	s	0	-15.11	
s Graphite	1	s	0	-83.76	
s Mayenite	1	s	0	-145.1	
s Belite	1	s	0	-1.856	
s Aluminate	1	s	0	-38.91	
s Alite	1	s	0	-14.11	
s Ferrite	1	s	0	-36.62	
s CA	1	s	0	-13	
s CA2	1	s	0	-18.96	
s C2AH75	1	s	0	-4.162	
s C3AH6	1	s	0	-2.668	
s C4AH13	1	s	0	-3.239	
s CAH10	1	s	0	-5.212	
s C2ASH8	1	s	0	-2.895	
s C4Ac0.5H12	1	s	0	-0.7397	
s C4AcH11	1	s	0.024117778	2.299e-09	
s Aragonite	1	s	0	-0.1441	
s Calcite	1	s	0.01959412	5.851e-09	
s C3FH6	1	s	0	-2.316	
s C4FH13	1	s	0	-2.476	
s C3FS0.84H4.32	1	s	0.0062622026	0	
s C3FS1.34H3.32	1	s	0	-0.6439	
s C4Fc05H10	1	s	0	-4.76	
s C4FcH12	1	s	0	-2.433	
s lime	1	s	0	-9.956	
s Portlandite	1	s	0.36532113	-3.761e-10	
s Anhydrite	1	s	0	-3.092	
s Gypsum	1	s	0	-2.838	

Solution
C-S-H
CH
Ettringite
Monocarbonate
Calcite
Hydroandradite ($C_3FS_{0.84}H_{4.32}$)
Hydrotalcite

Influence of temperature: tutorial

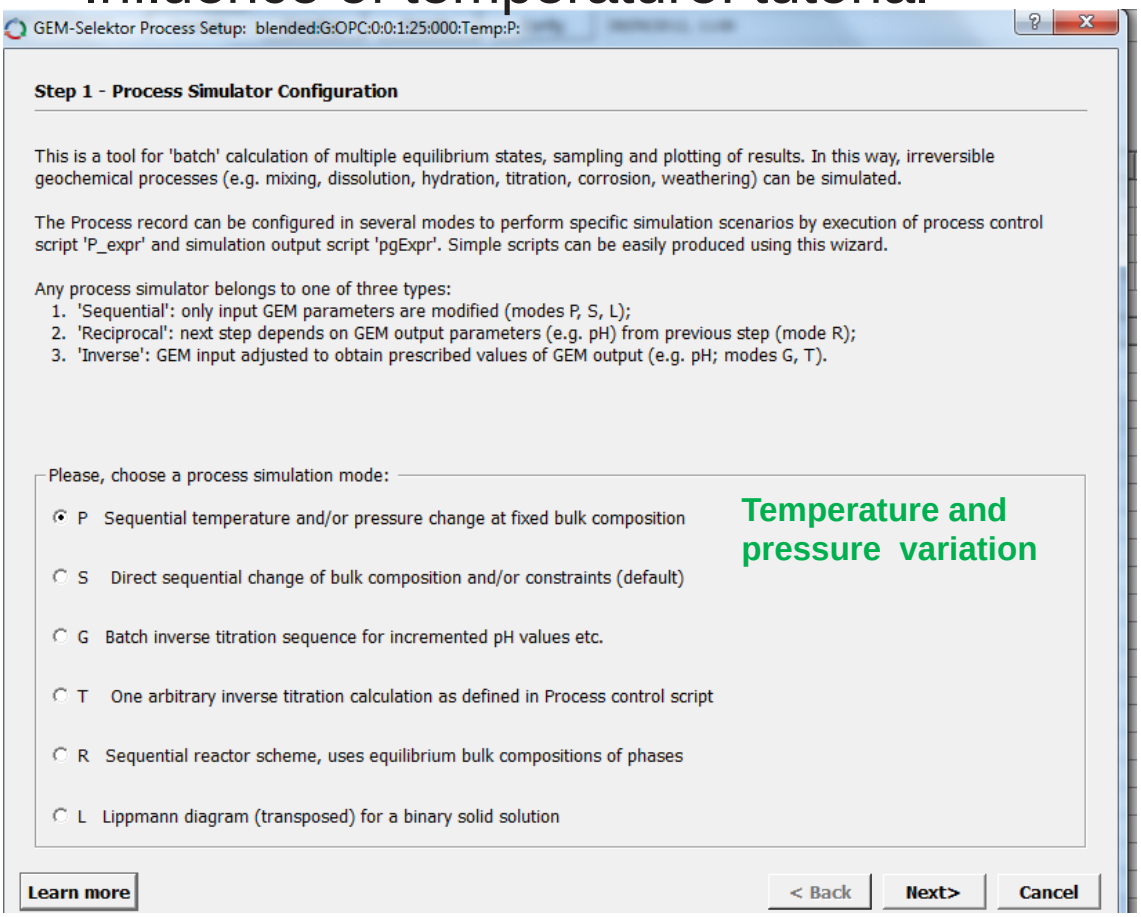
- New process file to calculate variation of temperature



name

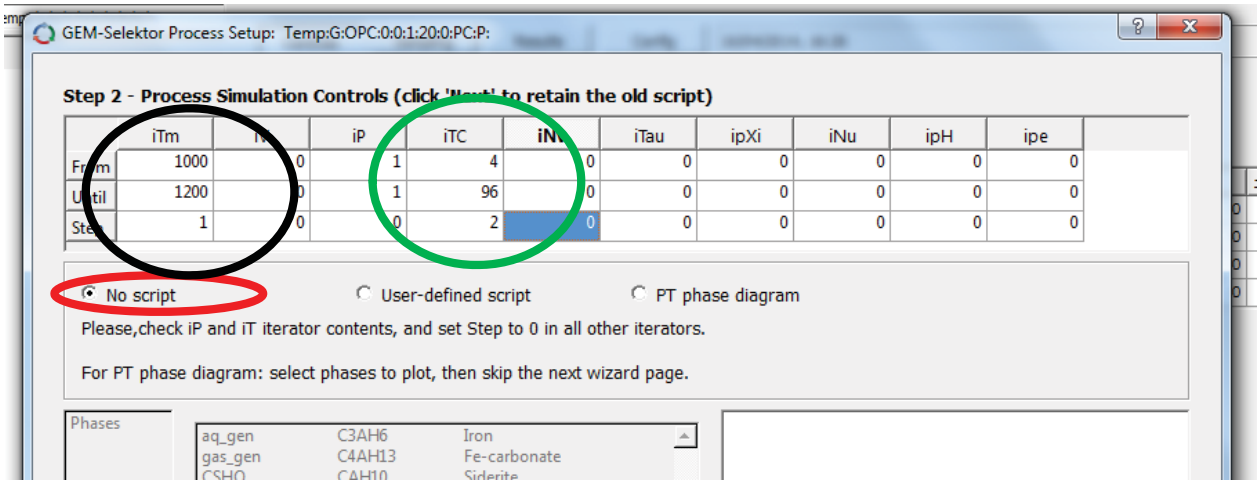
Temperature and pressure variation

Influence of temperature: tutorial



Temperature and pressure variation

Influence of temperature: tutorial

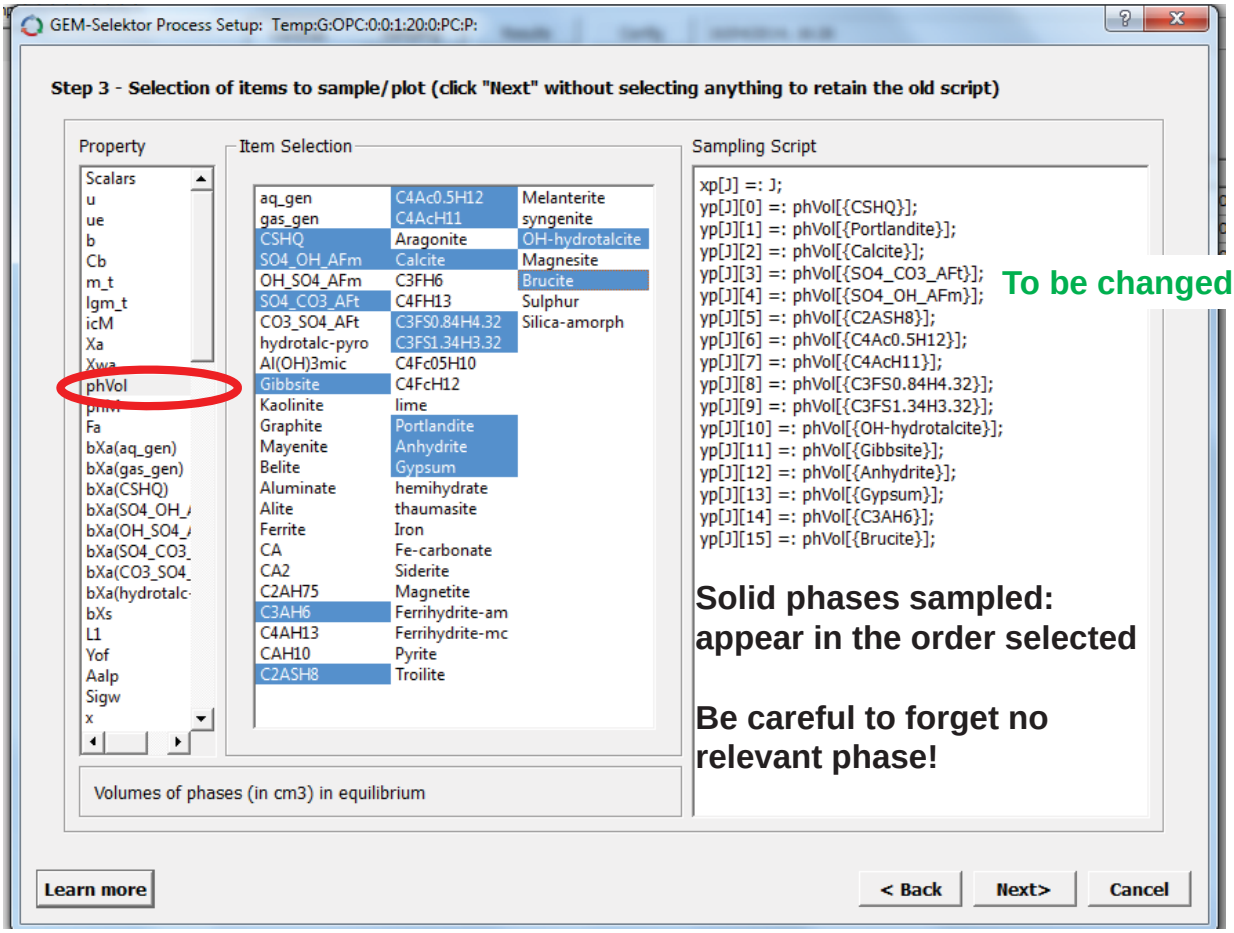


Numbering of the single calculations

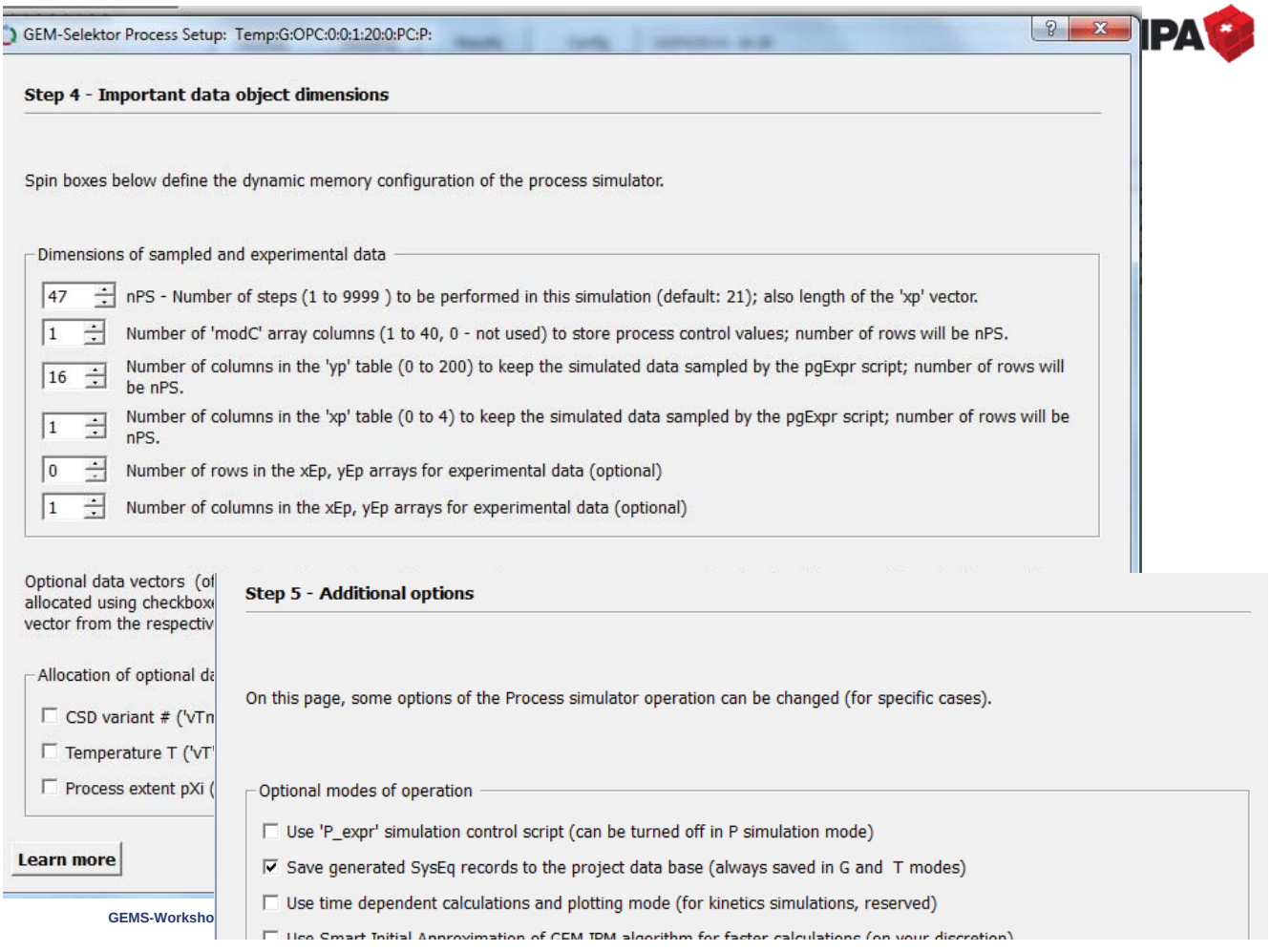
Start temperature
Stop temperature
Step size

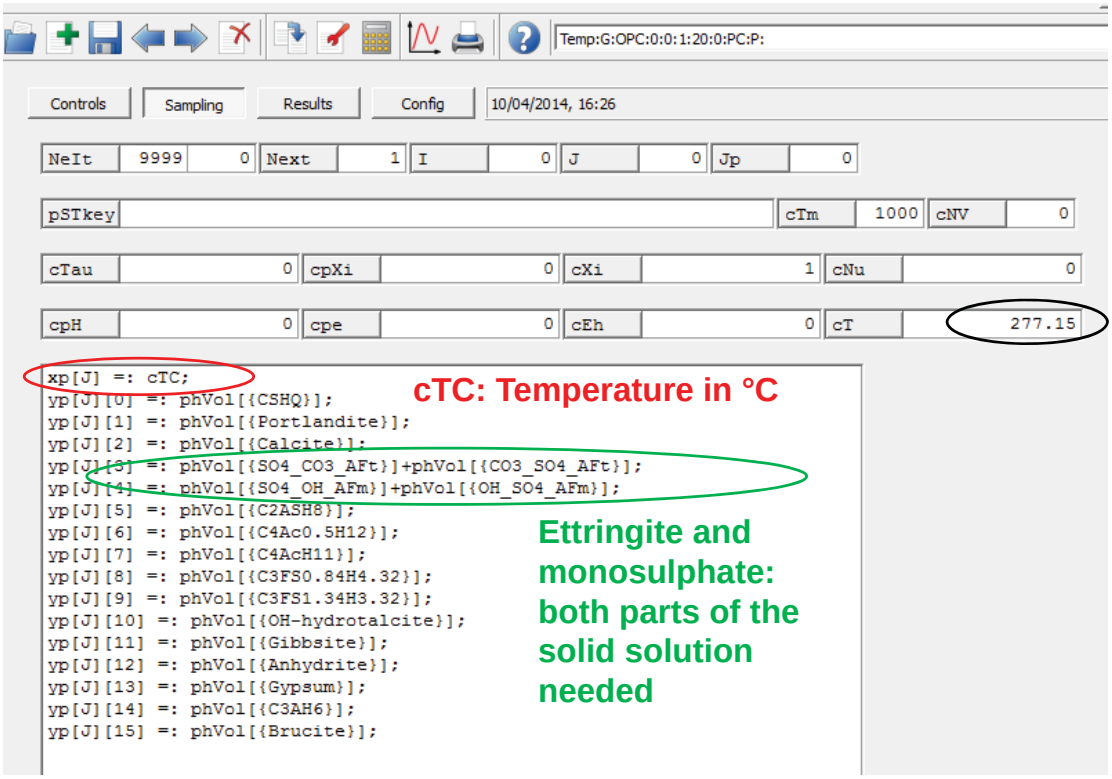
No script needed

Volume in cm3



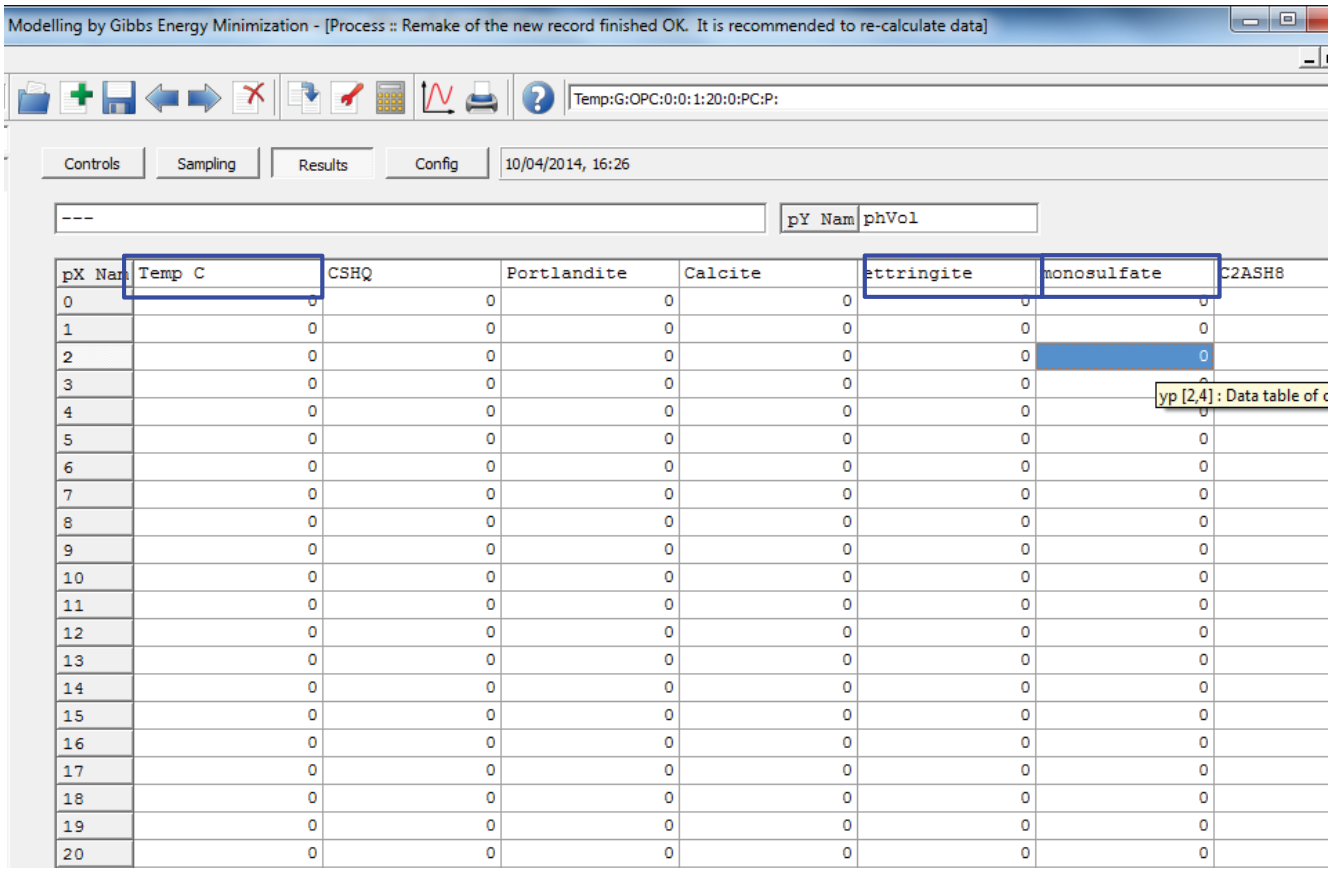
To be changed later



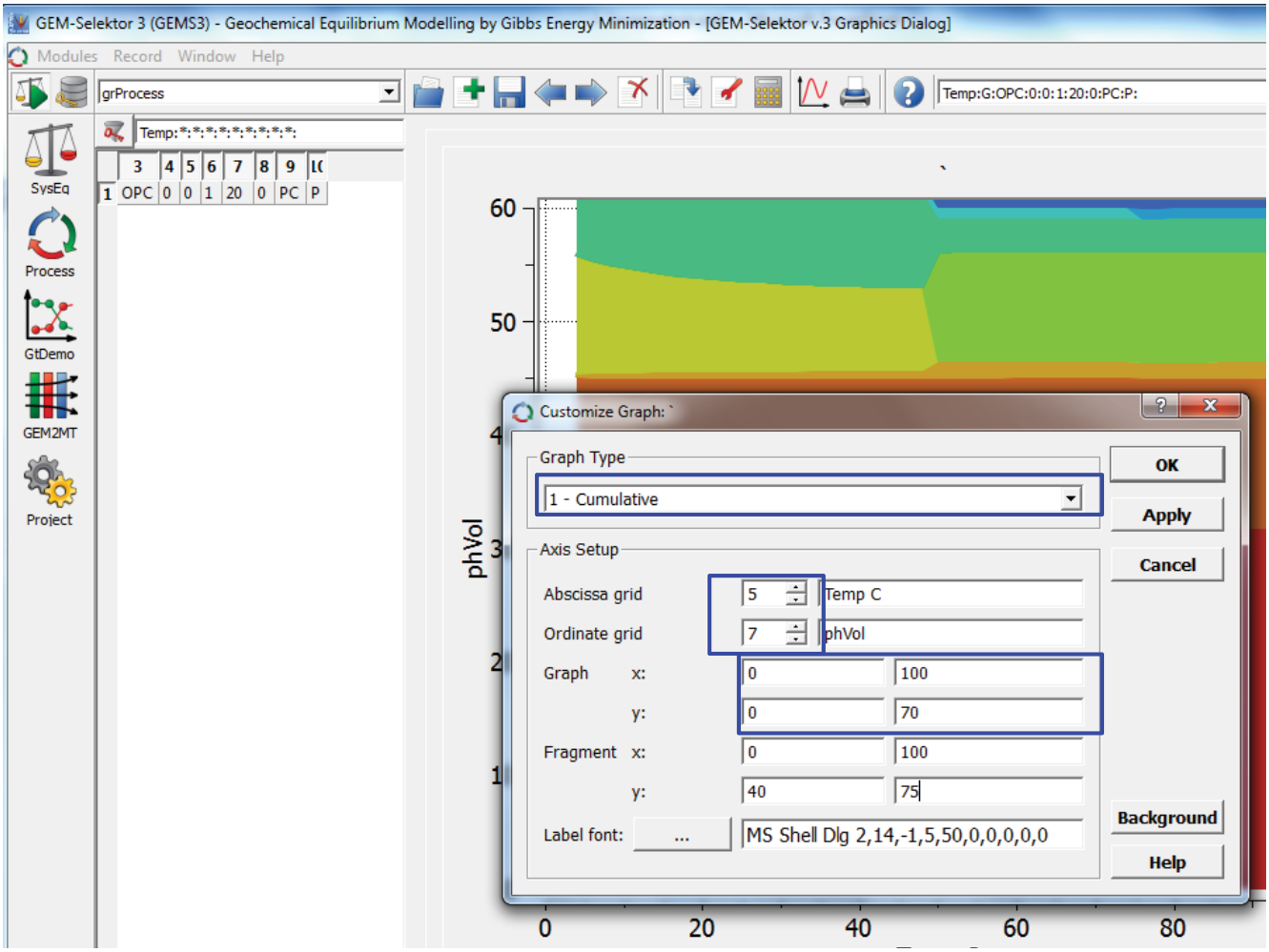


cT temperature in K

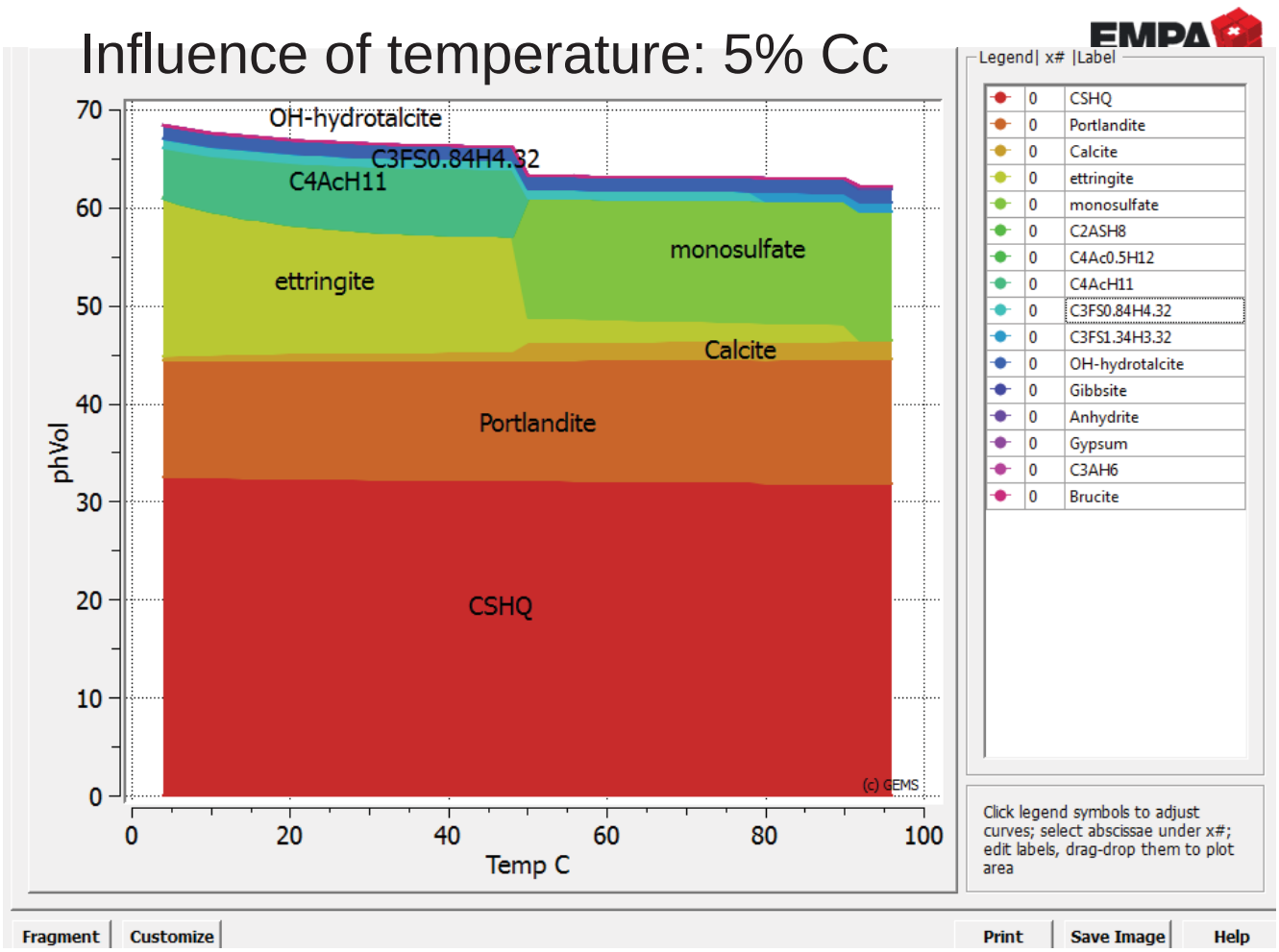
Influence of temperature: tutorial



pX Nam	Temp C	CSHQ	Portlandite	Calcite	ettringite	monosulfate	C2ASH8
0	0	0	0	0	0	0	
1	0	0	0	0	0	0	
2	0	0	0	0	0	0	
3	0	0	0	0	0		
4	0	0	0	0	0		
5	0	0	0	0	0	0	
6	0	0	0	0	0	0	
7	0	0	0	0	0	0	
8	0	0	0	0	0	0	
9	0	0	0	0	0	0	
10	0	0	0	0	0	0	
11	0	0	0	0	0	0	
12	0	0	0	0	0	0	
13	0	0	0	0	0	0	
14	0	0	0	0	0	0	
15	0	0	0	0	0	0	
16	0	0	0	0	0	0	
17	0	0	0	0	0	0	
18	0	0	0	0	0	0	
19	0	0	0	0	0	0	
20	0	0	0	0	0	0	



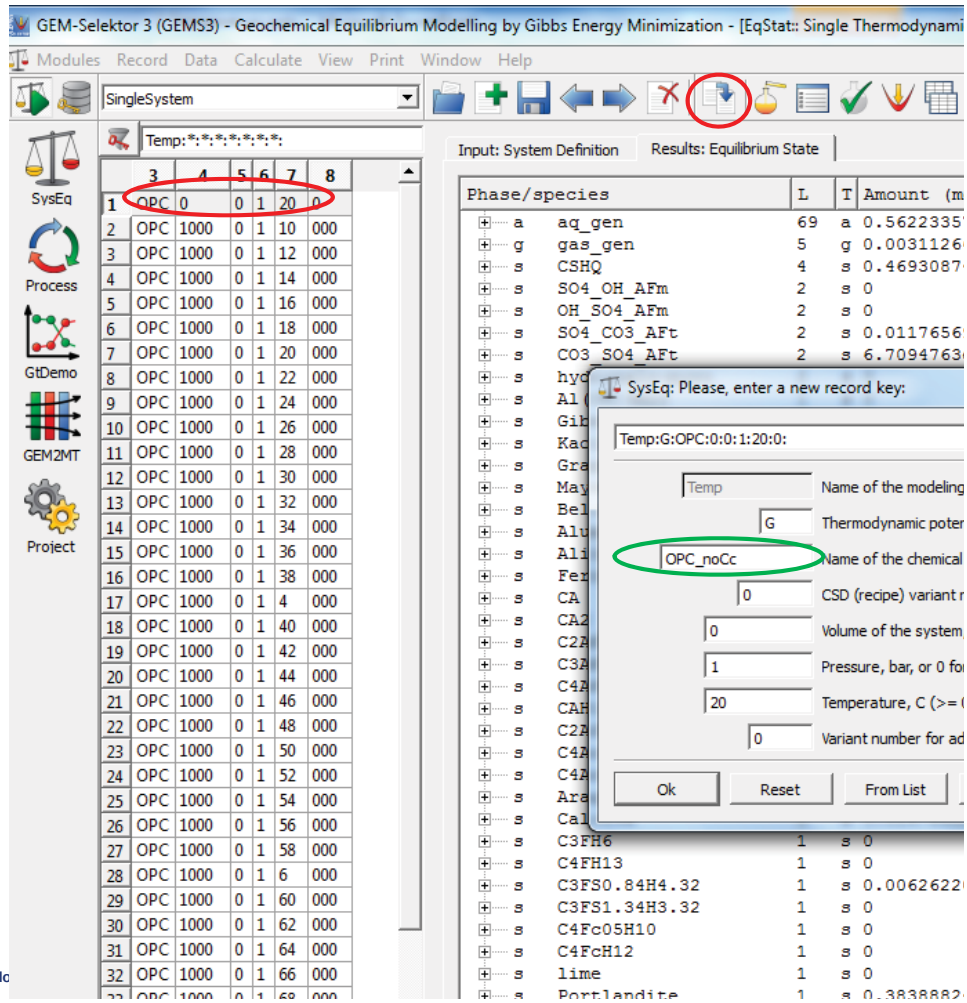
Influence of temperature: 5% Cc



Cement: «OPC_noCc» in project «Temp»

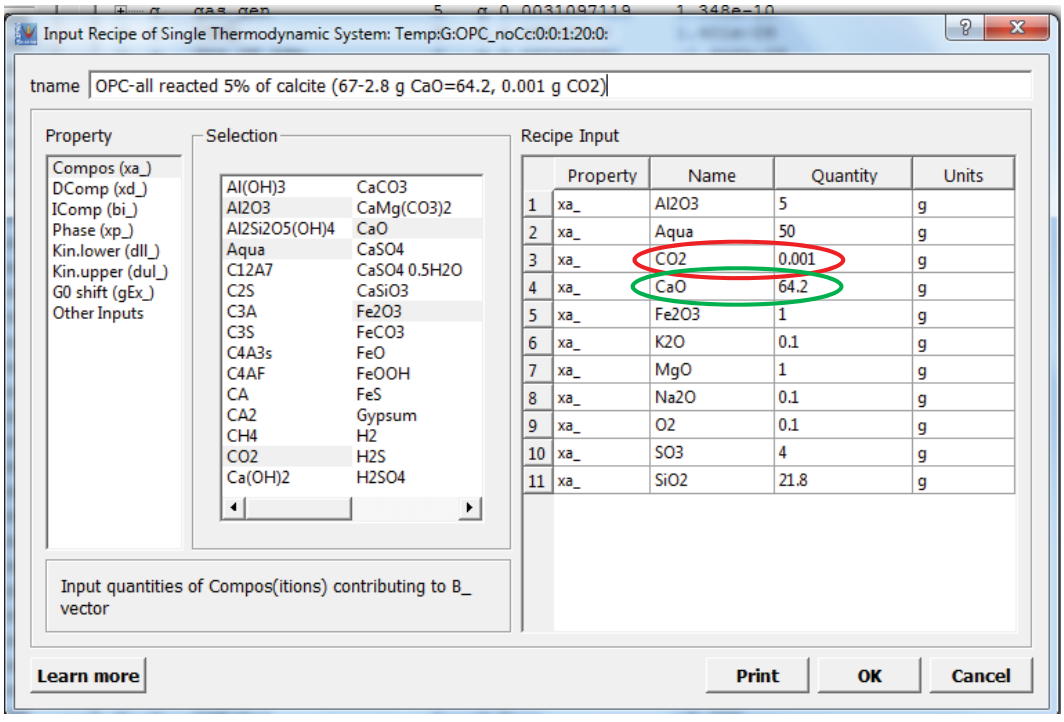
Clone existing OPC

OPC without calcite



Influence of temperature: tutorial

- Cement: «OPC_noCc» in project «Temp»

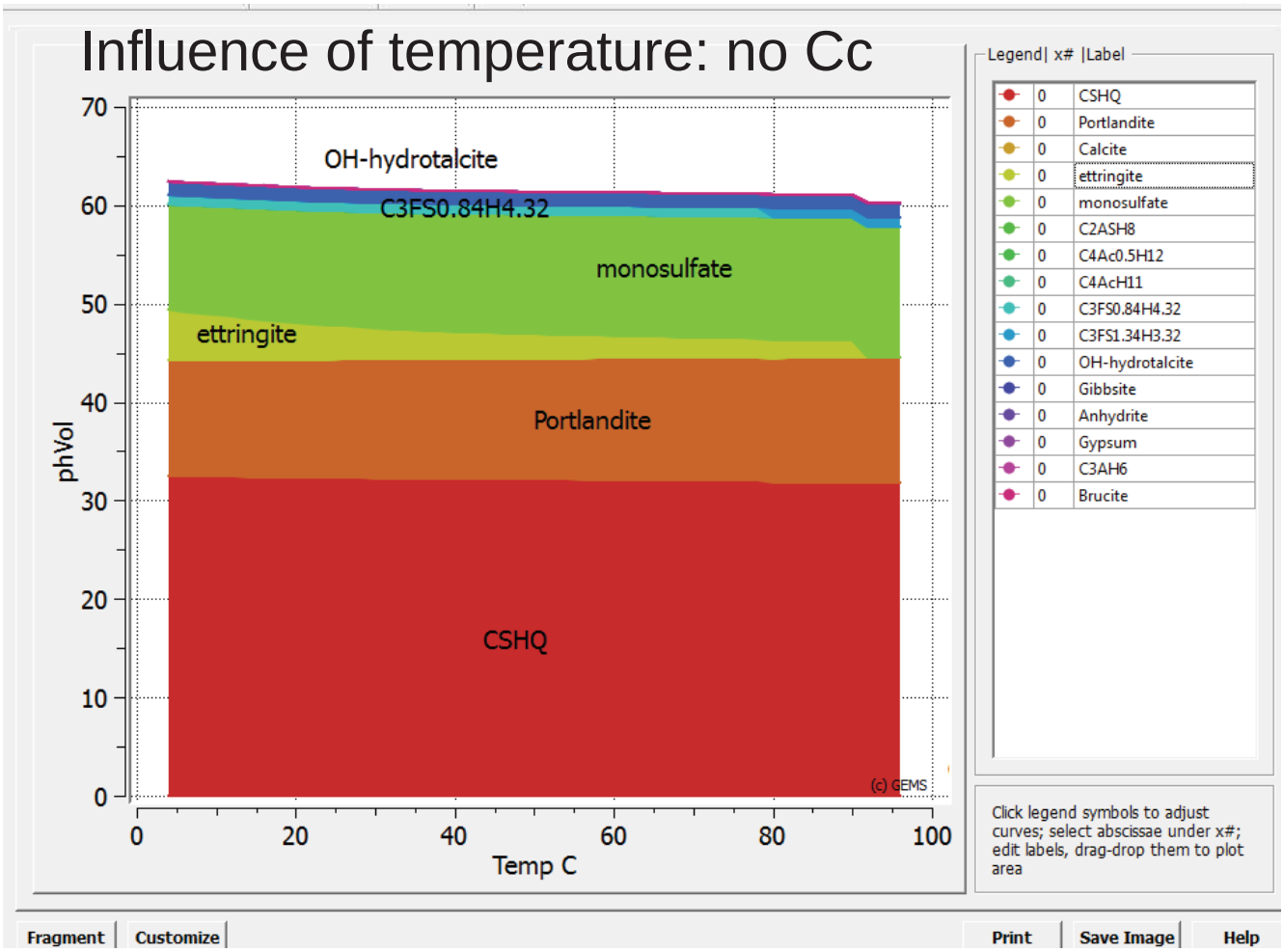


Cement composition in g/100 g: => All reacts!

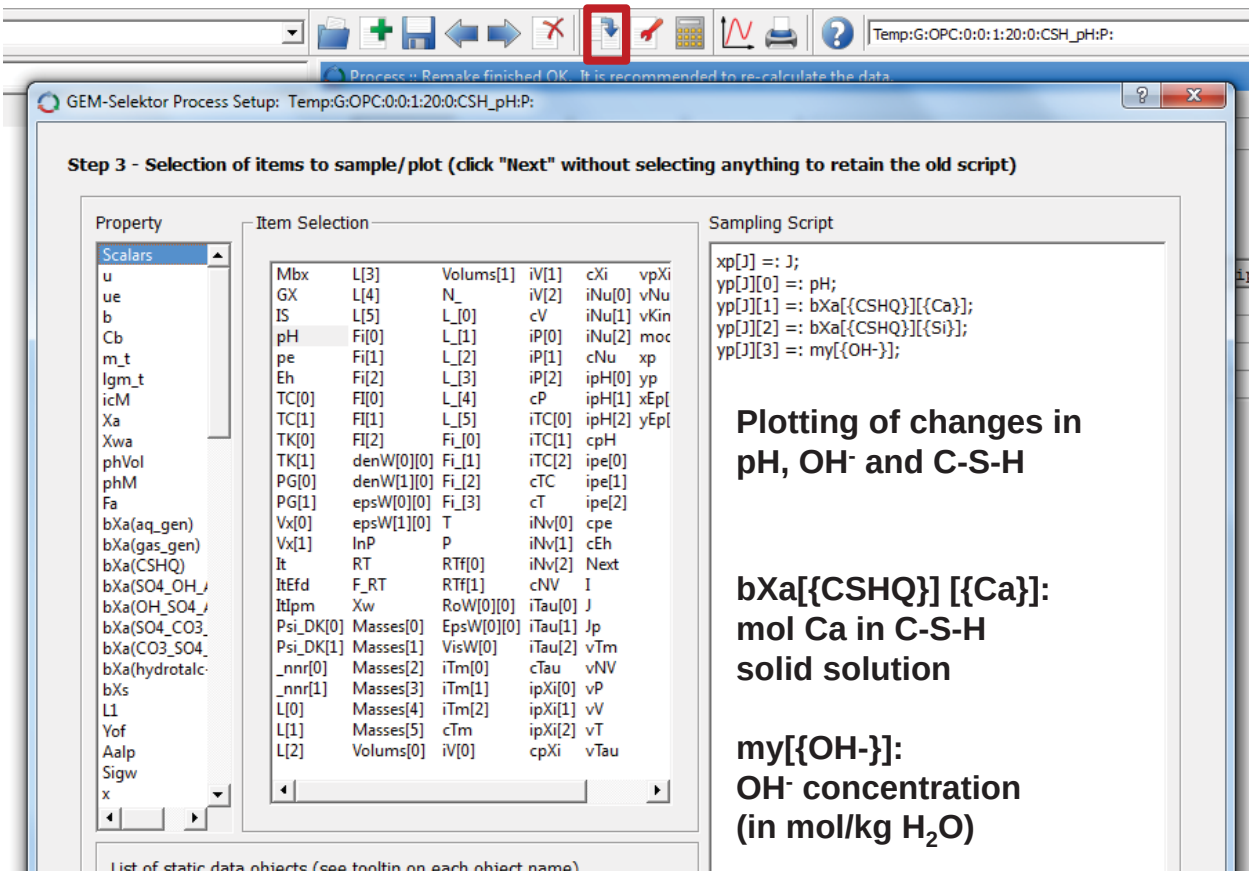
Remove CO2

Reduce CaO

Influence of temperature: no Cc



Influence of temperature: 5% Cc



Influence of temperature: 5% Cc

Controls | Sampling | Results | Config | 17/04/2014, 11:19

NeIt	9999	47	Next	0	I	0	J	46	Jp	46

pSTkey	Temp:G:OPC:0:0:1:20:0:	cTm	1000	cNV	0

cTau	0	cpXi	0	cXi	1	cNu	0

cpH	0	cpe	0	cEh	0	cT	369.15

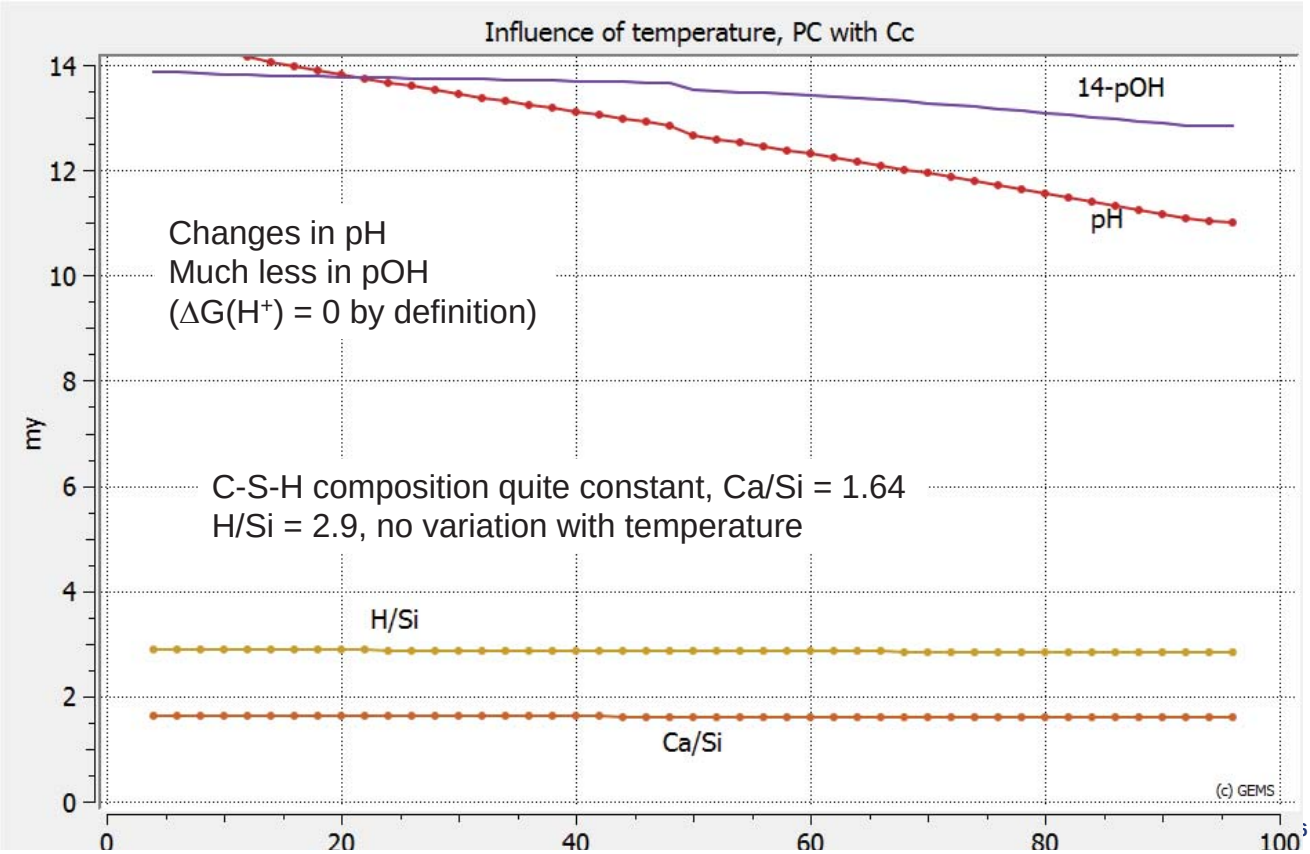
```
xp[J] =: cTC;
yp[J][0] =: pH;
$ plotting Ca/Si in CSH
yp[J][1] =: bXa[{CSHQ}][{Ca}]/bXa[{CSHQ}][{Si}];
$ plotting H/Si in CSH: H/2 = H2O
yp[J][2] =: bXa[{CSHQ}][{H}]/2/bXa[{CSHQ}][{Si}];
$ log OH- conc
yp[J][3] =: 14+lg(my[{OH-}]);
```

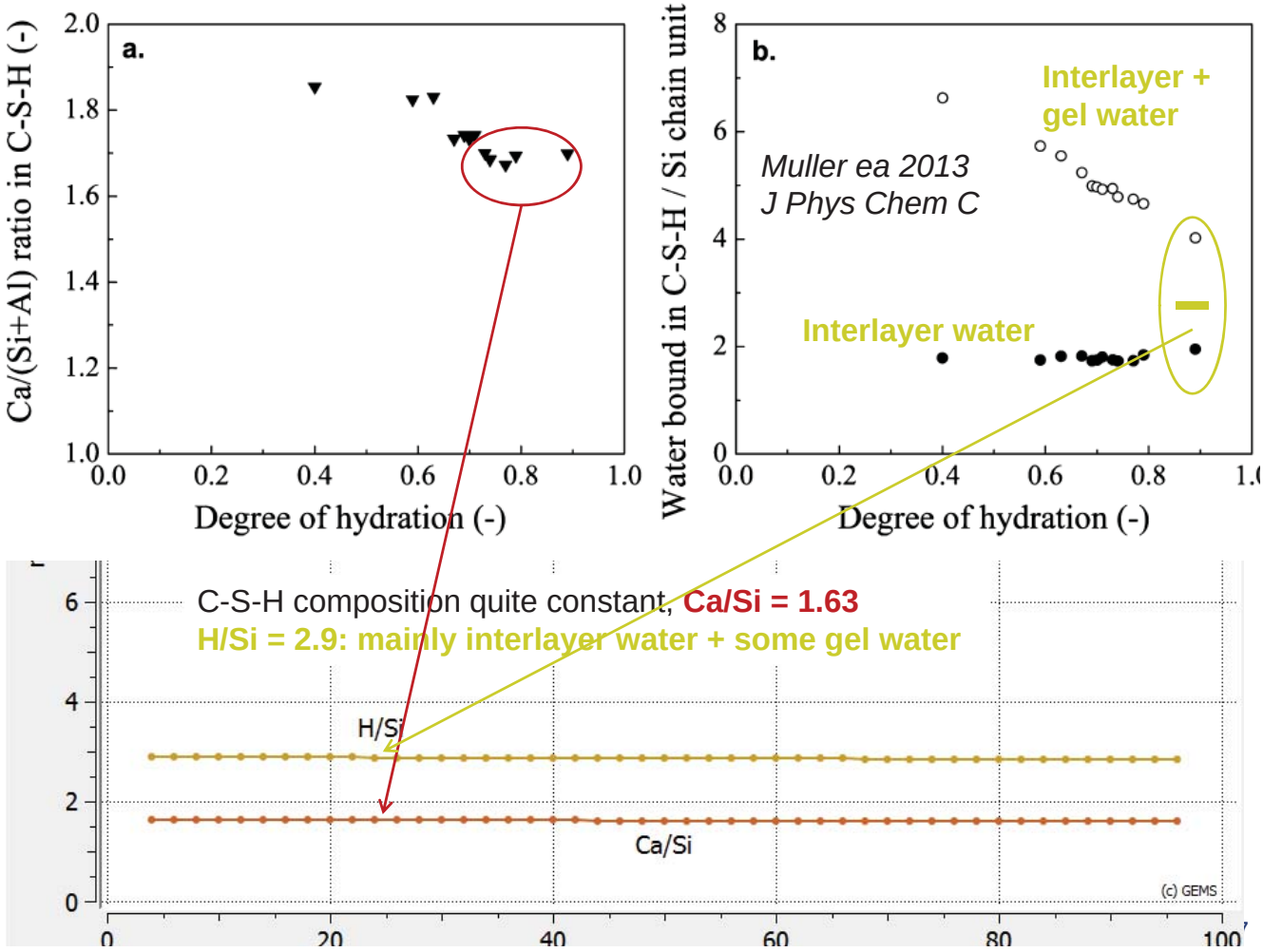
Plotting of changes in pH, OH- and C-S-H

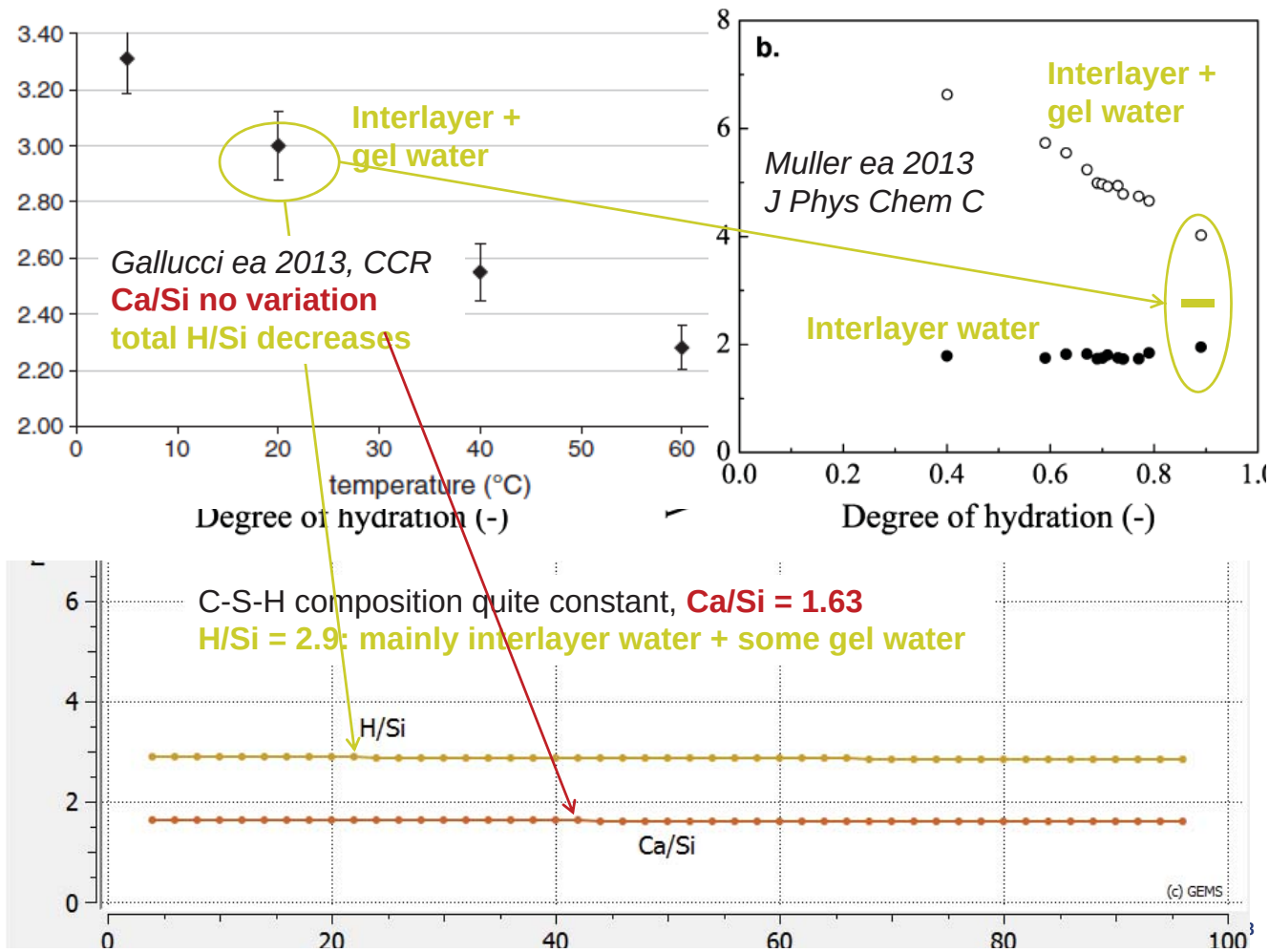
bXa[{CSHQ}][{Ca}]/bXa[{CSHQ}][{Si}]:
molar Ca/Si in C-S-H solid solution
bXa[{CSHQ}][{H}]2/bXa[{CSHQ}][{Si}]:
molar H/Si in C-S-H solid solution (H/2 = H2O)

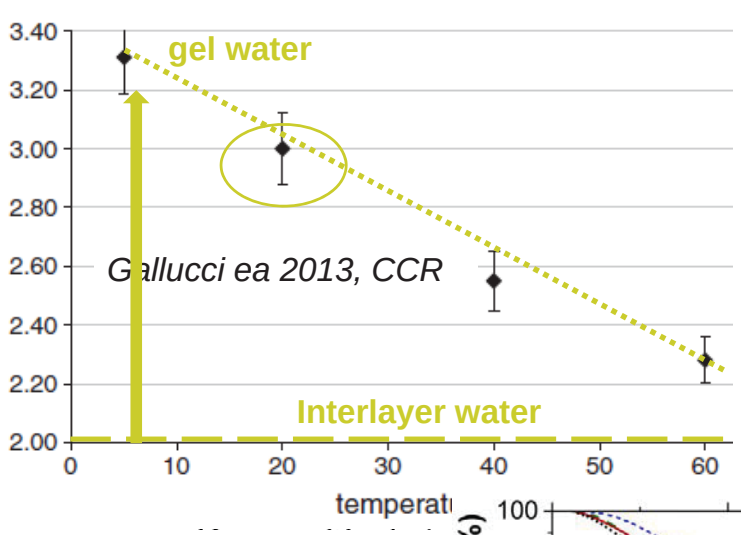
14+lg(my[{OH-}]) equals pH at 25 °C
=> to illustrate temperature effect on pH:

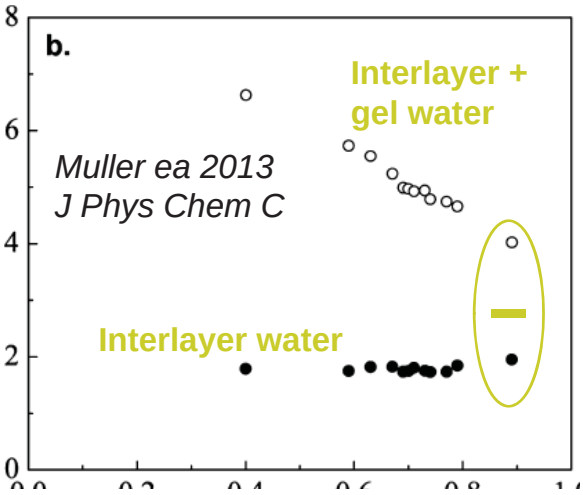
Influence of temperature: 5% Cc




a.
Ca/(Si+Al) ratio in C-S-H (-)
Degree of hydration (-)
b.
Water bound in C-S-H / Si chain unit
Interlayer + gel water
Muller ea 2013
J Phys Chem C
Interlayer water
Degree of hydration (-)
C-S-H composition quite constant, Ca/Si = 1.63
H/Si = 2.9: mainly interlayer water + some gel water
H/Si
Ca/Si
(c) GEMS

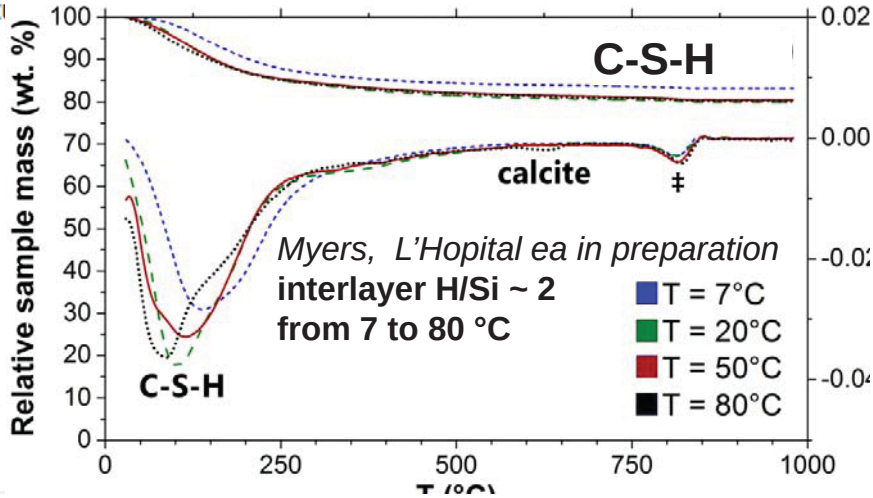

Interlayer + gel water
Gallucci ea 2013, CCR
Ca/Si no variation
total H/Si decreases
temperature (°C)
Degree of hydration (-)
b.
Interlayer + gel water
Muller ea 2013
J Phys Chem C
Interlayer water
Degree of hydration (-)
C-S-H composition quite constant, Ca/Si = 1.63
H/Si = 2.9: mainly interlayer water + some gel water
H/Si
Ca/Si
(c) GEMS



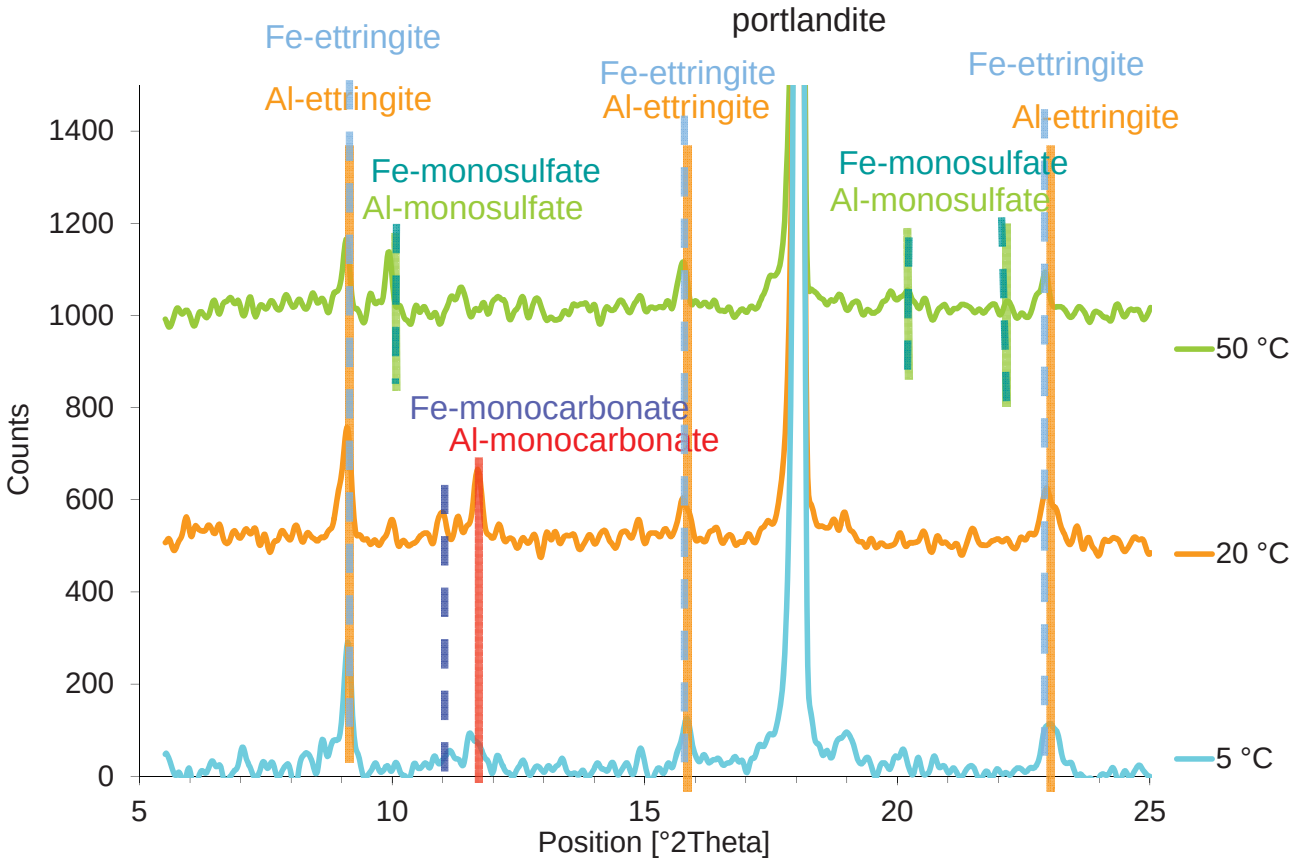


⇒ **Variations in gel water difficult to include**

⇒ **Temperature effect on composition and interlayer water, on aluminium, anion and alkali uptake:**
work in progress
L'Hopital, Myers, Plusquellec, Kulik, Lothenbach, Nonat, …



What happens with the iron?



Lothenbach ea 2007, CCR 37

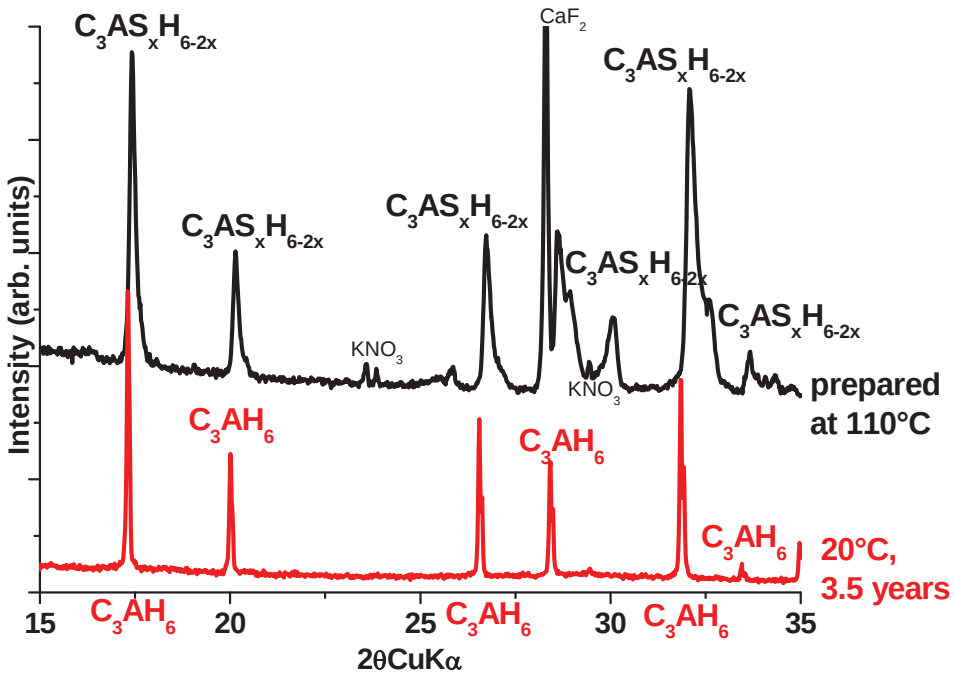
Stability of Fe and Al-hydrates at 25 °C

(Solubility products refer to Ca^{2+}, OH^-, $Fe,Al(OH)_4^-$, $HSiO_3^-$, SO_4^{2-}, CO_3^{2-})

Fe-hydrates		Al-hydrates		Δ Al-Fe
FH	-11.2	-1.3	AH_3	**-10**
C_6FsH_{32}	-44.0	-45.0	C_6AsH_{32}	1
C_4FsH_{12}	-31.6	-29.3	C_4AsH_{12}	-2
C_4FcH_{12}	-34.6	-31.5	C_4AcH_{11}	-3
$C_4Fc_{0.5}H_{10}$	-30.8	-29.1	$C_4Ac_{0.5}H_{10}$	-2
C_3FH_6	-26.3	-20.5	C_3AH_6	-6
$C_3FS_{0.84}H_{4.32}$	-34.2	-26.7	$C_3AS_{0.84}H_{4.32}$	**-8**

- Lower solubility product => higher stability
- **Stability Fe-ettringite < Fe-AFm < FH_3/Fe-siliceous hydrogarnet**
- **Formation of Al-containing siliceous hydrogarnet kinetically hindered at room temperature**

Al siliceous hydrogarnet



Room temperature: only C_3AH_6 + C-S-H forms; $C_3AS_xH_{6-2x}$ forms at 110 C°, but remains stable at 20 °C

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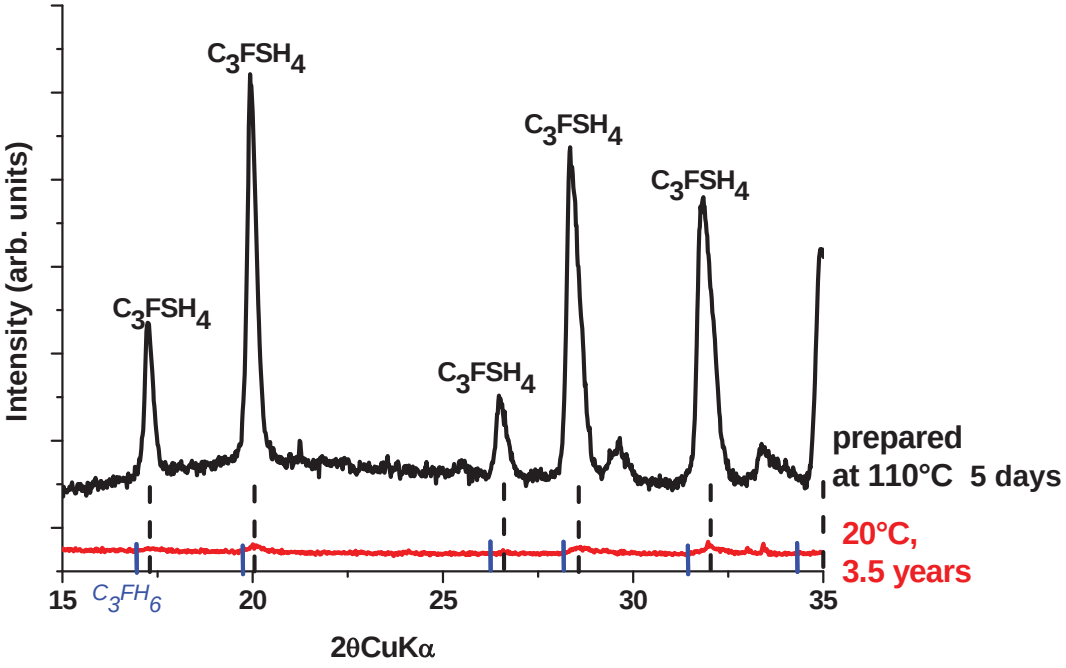
Fe siliceous hydrogarnet



Low temperature Fe-siliceous hydrogarnet poorly crystalline
=> difficult to detect by XRD

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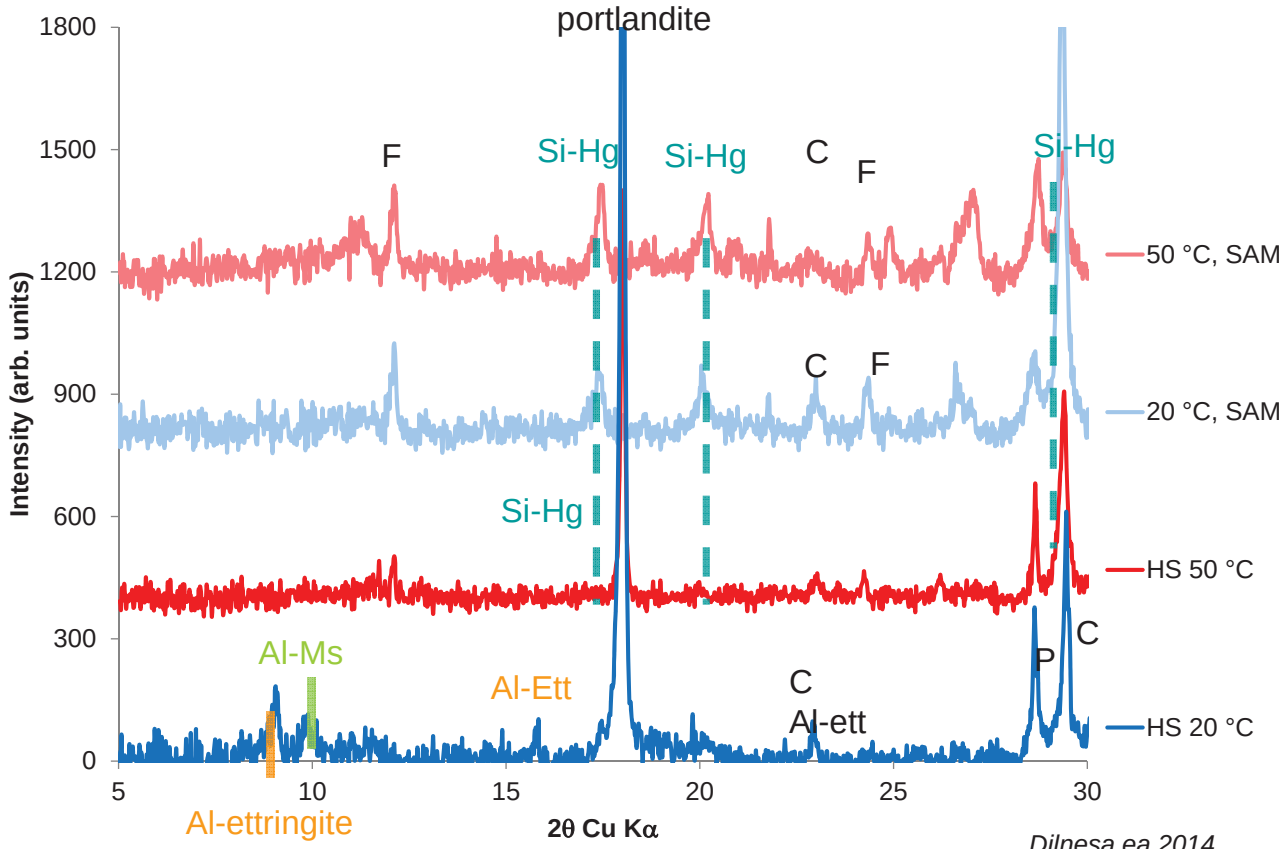
Selective Dissolution using SAM

Salicylic Acid/Methanol Extraction (SAM)

Better identification of minor phases

- Dissolves
  - alite, belite, lime
  - CH, C-S-H, AFt and AFm phases
- Not affected:
  - $C_2(A,F)$, periclase, calcite,
  - $C_3(A,F)SH_4$, hydrotalcite, …

XRD OPC, 150 days: Siliceous hydrogarnet observed



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EXAFS: Fe in siliceous hydrogarnet in the hydrated cement

At 20 °C								
Age	$C_2(A,F)$	$Fe(OH)_3$	C_3FSH_4	$C_3(A,F)SH_4$	Fe-Htl	C_4FcH_{12}	$C_6Fs_3H_{32}$	R-factor
Unhyd	1.00*	-				-	-	0.12
4 hrs	0.78(3)	0.20(3)	First hours			-	-	0.08
16 hrs	0.56(3)	0.44(3)	-	-	-	-	-	0.09
1 day	0.62(2)	-	-	0.38(2)	-	-	-	0.18
28 days	0.57(2)	-	-	0.43(2)	At ≥ 1 days			0.09
150 days	0.56(2)	-	-	0.44(2)	-	-	-	0.09
1 year	0.56(2)	-	-	0.44(2)	-	-	-	0.07
At 50 °C								
Age	C_4AF	$Fe(OH)_3$	C_3FSH_4	$C_3(A,F)SH_4$	Fe-Ht	C_4FcH_{12}	$C_6Fs_3H_{32}$	R-factor
Unhyd	1.00*							0.12
1 hrs	0.70(4)	0.30(4)	First hours					0.14
4 hrs	0.65(2)	0.35(2)						0.09
16 hrs	0.64(2)			0.36(2)				0.18
150 days	0.59(1)			0.41(1)	At ≥ 16 hours			0.09
1 year	0.58(2)			0.42(2)				0.07

20 °C

50 °C

>1 day:
iron present only in Fe siliceous hydrogarnet $C_3(A,F)S_xH_{6-2x}$

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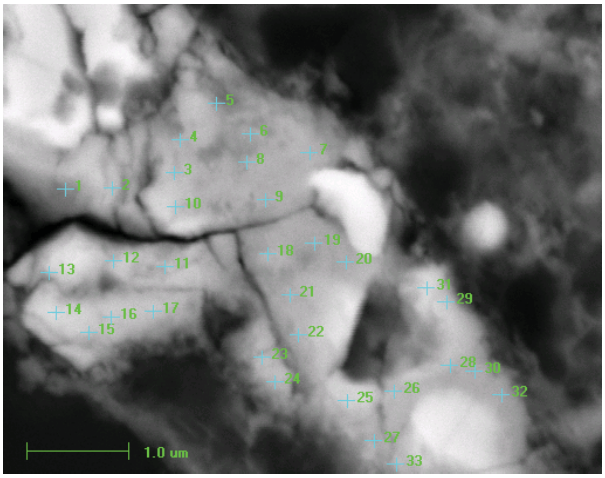
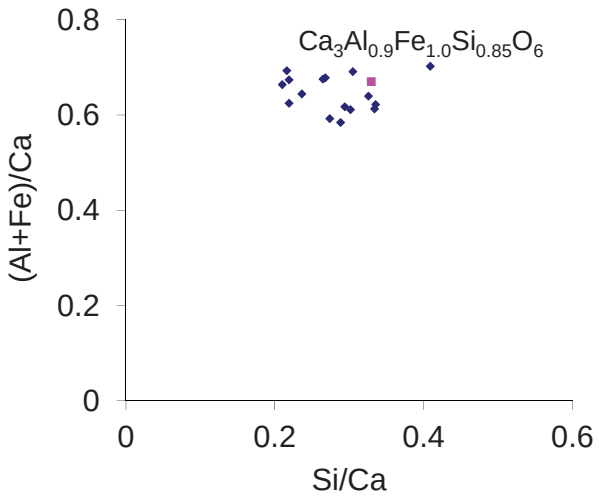
SEM/EDX analysis of OPC





- Siliceous hydrogarnet observed in all samples
- Mixed siliceous hydrogarnet ($C_3(A,F)S_{0.9}H_{4.2}$

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Conclusion: Fate of iron oxides

Thermodynamic modelling:
C_3FSH_4 stable from 1 to 60 °C
C_3ASH_4 stable but formation kinetically hindered (suppressed in calculations)

Experimental evidence:
XAFS spectroscopy => Fe associated with $C_3(A,F)S_xH_{6-2x}$
Similar amount of siliceous hydrogarnet at 20 and 50 °C

XRD, TGA, $C_3(A,F)SH_4$ present in hydrated cements
but difficult to detect; more crystalline at 50°C

SEM: Mixed Al/Fe siliceous hydrogarnet

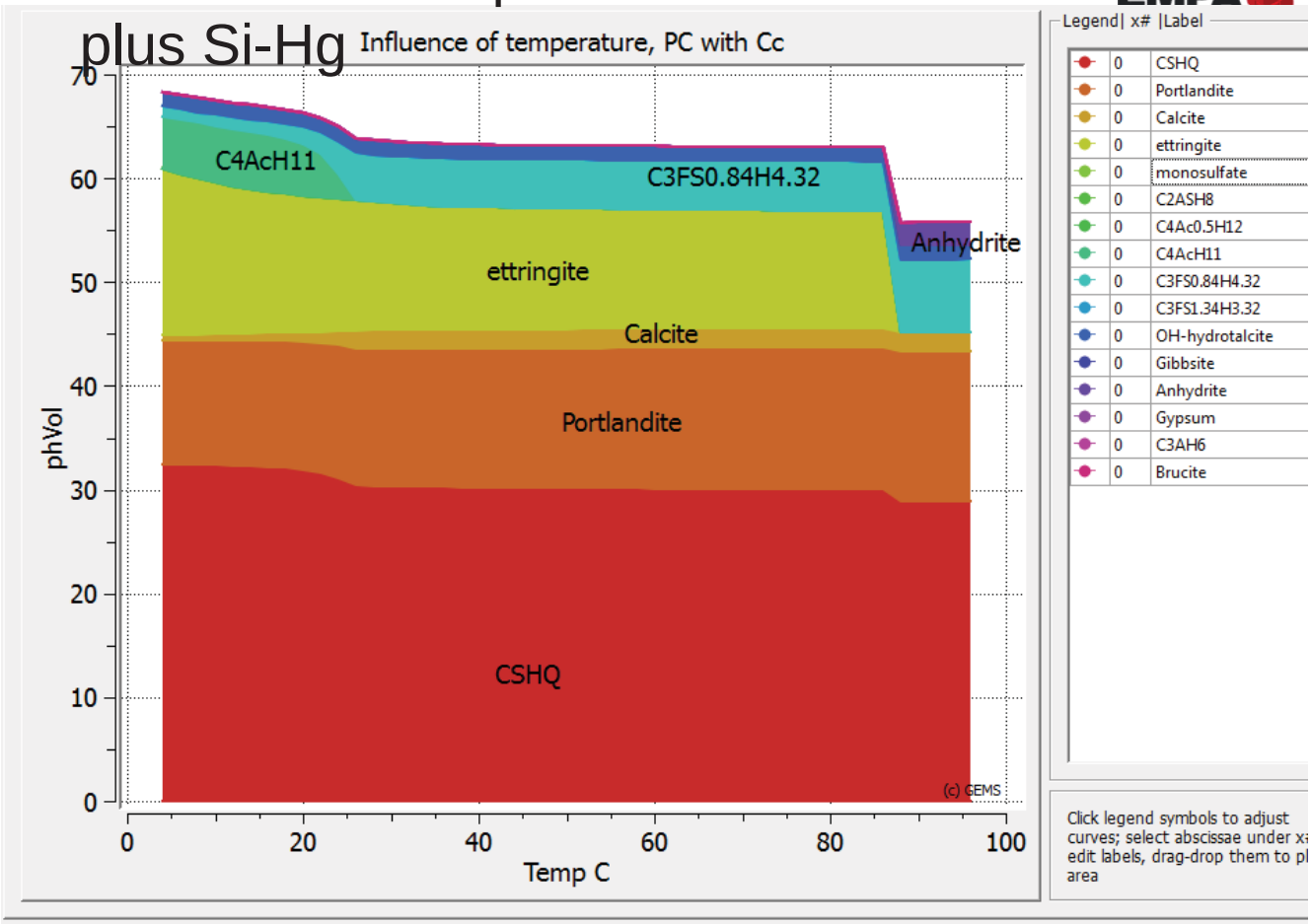
Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	A
a aq_gen	69	a	0.47421475	8.907e-10		
g gas_gen	5	g	0.0031148901	1.938e-10		
s C3(AF)S0.84H	2	s	0.011454257	-3.416e-09		
C3AS0.84H4.32		I	0.005192054	0.453286	0.45328598	1
C3FS0.84H4.32		I	0.0062622028	0.546714	0.54671402	1
s CSHQ	4	s	0.46350181	2.004e-09		
s SO4_OH_AFm	2	s	0	-1		
s OH_SO4_AFm	2	s	0	-1		
s SO4_CO3_AFt	2	s	0.018760835	-1.991e-09		
s CO3_SO4_AFt	2	s	3.9158123e-009	0.004993		
s hydrotalc-pyro	2	s	0	-8.645		
s Al(OH)3mic	1	s	0	-3.194		
s Gibbsite	1	s	0	-2.671		
s Kaolinite	1	s	0	-15.12		
s Graphite	1	s	0	-83.75		
s Mayenite	1	s	0	-145.1		
s Belite	1	s	0	-1.859		
s Aluminate	1	s	0	-38.92		
s Alite	1	s	0	-14.12		
s Ferrite	1	s	0	-36.89		
s CA	1	s	0	-13		
s CA2	1	s	0	-18.97		
s C2AH75	1	s	0	-4.164		
s C3AH6	1	s	0	-2.672		
s C4AH13	1	s	0	-3.238		
s C4AH19	1	s	0	-2.835		
s CAH10	1	s	0	-5.211		
s C2ASH8	1	s	0	-2.898		
s C4Ac0.5H12	1	s	0	-0.7393		
s C4AcH11	1	s	0.0188822	5.777e-09		
s Aragonite	1	s	0	-0.1441		
s Calcite	1	s	0.0247094	3.357e-09		
s C3FH6	1	s	0	-2.576		
s C4FH13	1	s	0	-2.731		
s C3FS0.84H4.32	1	s	0	-0.2622		
s C3FS1.34H3.32	1	s	0	-0.9075		
s C4Fc05H10	1	s	0	-5.017		
s C4FcH12	1	s	0	-2.688		
s lime	1	s	0	-9.957		

ystem: T = 293.15 K; P = 1.00 bar; V = 0.1506 L; Aqueous: built-in EDH(H); pH = 13.785; pe = 7.365; IS = 0.568 m

Solution
Hydrogarnet/hydroandradite (C3(A,F)S0.84H4.32)
C-S-H
CH
Ettringite
Monocarbonate
hydrotalcite

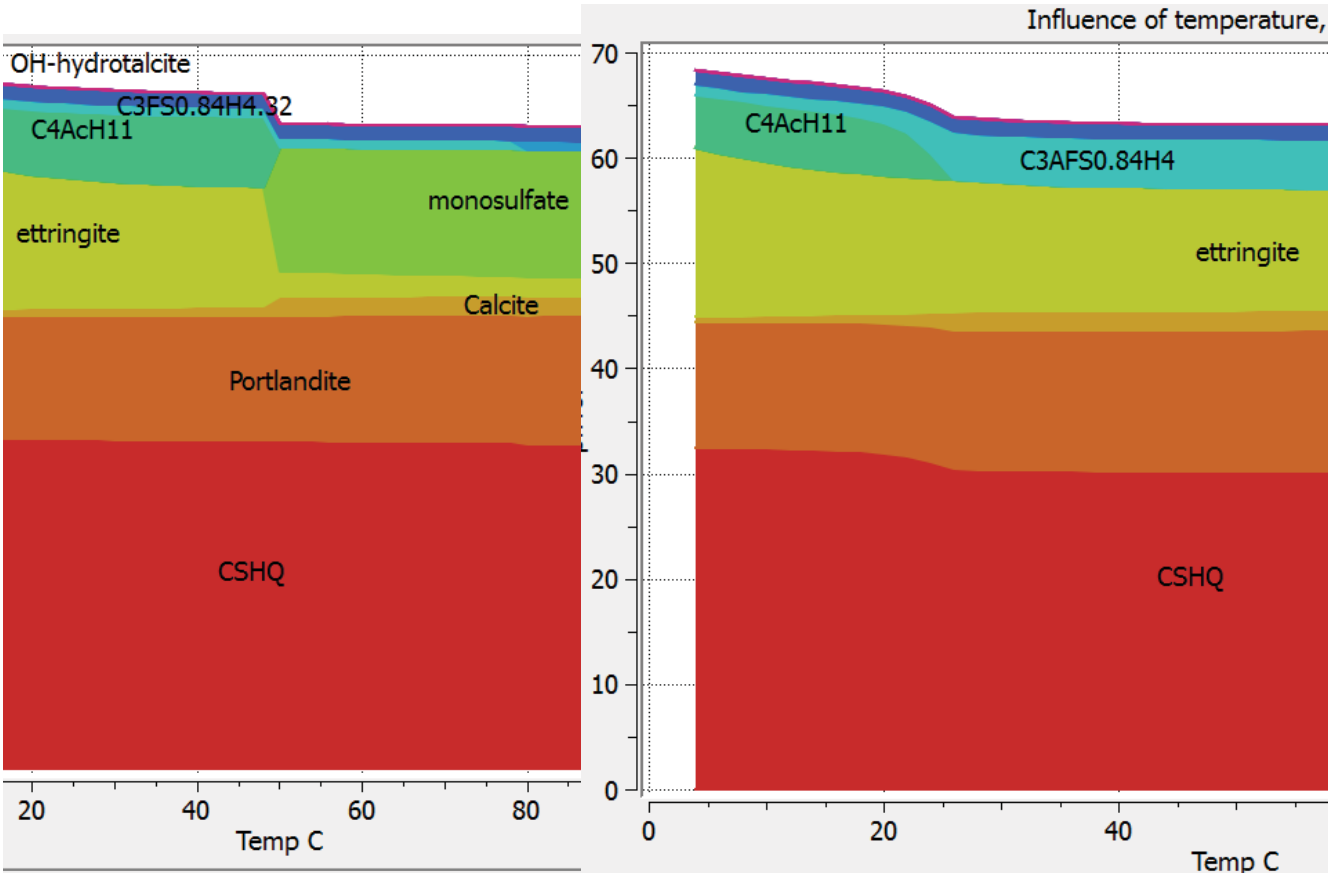
Note $C_3AS_{0.42}H_{5.16}$: not activated in database => supressed during all calculations as its formation not observed at ambient conditions (to include create an additional Phase refering to Dcomp: $C_3AS_{0.42}H_{5.16}$)

Influence of temperature: 5% Cc plus Si-Hg



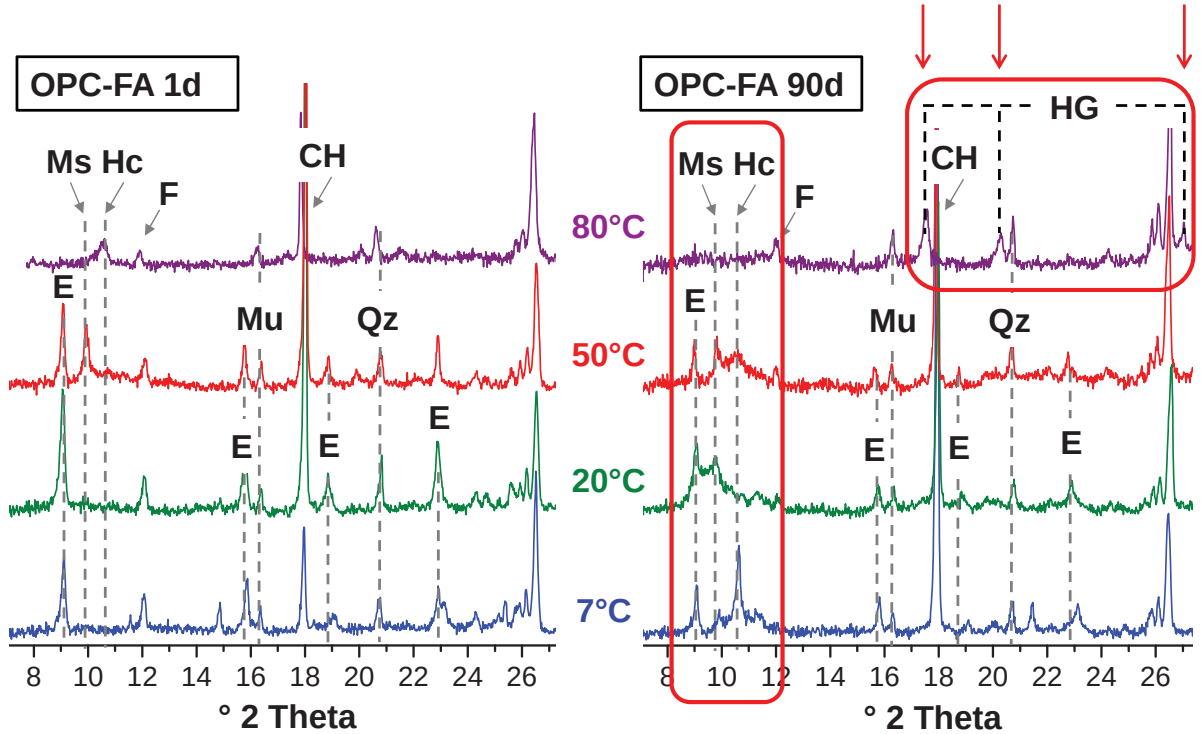
No $C_3AS_{0.84}H_{4.32}$

With $C_3AS_{0.84}H_{4.32}$



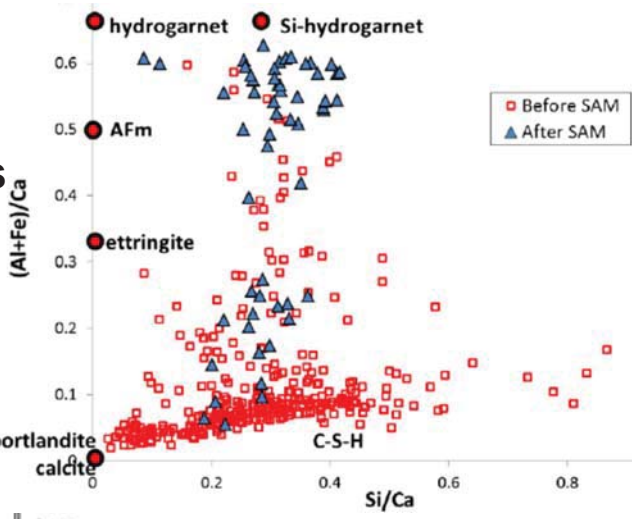
siliceous hydrogarnet

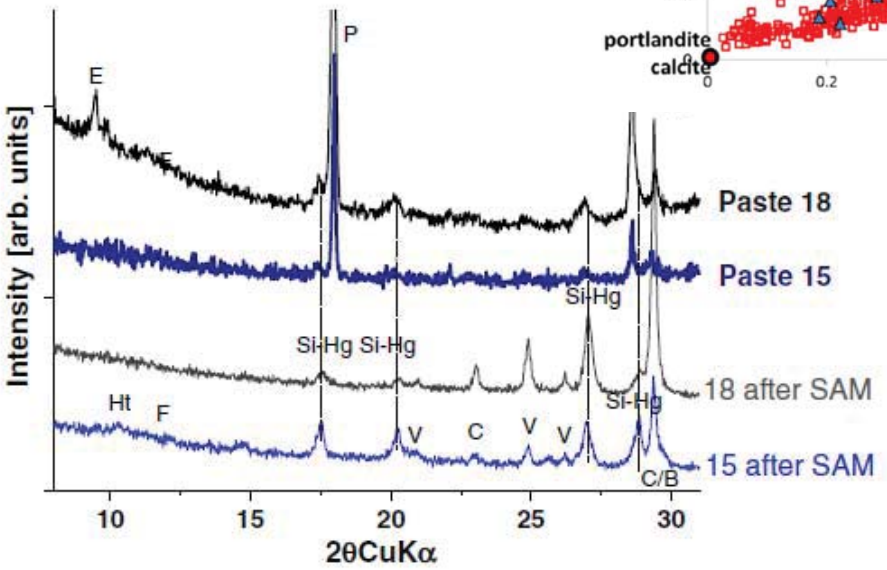
siliceous hydrogarnet in OPC blended with fly ash)



Deschner ea, 2013

Si-hydrogarnet / no AFm observed in very old cements hydrated 50 years at 20 °C





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Influence of temperature

Higher temperature:
→ faster kinetic of PC hydration and SiO_2 reaction:

OPC
→ **47 °C**: ettringite, monocarb. → monosulfate
→ volume decrease => decrease in strength

longterm
→ **Hydrogarnet-hydrogrossular instead of AFm**

In addition changes in CSH volume (water content);
Not captured in present CSH model (no gel water present)!