Oregon State University

Empa
Materials Science and Technology

Lecture 10
Hydrated Portland cement

Effect of temperature

Frank Winnefeld

NTNU – Trondheim
Norwegian University of Science and Technology

Software development/fitting tools/kinetic:
Dmitrii Kulik
Dan Miron

PAUL SCHERRER INSTITUT
PSI

Tutorial: Effect of temperature on PC hydration

Empa
Materials Science and Technology

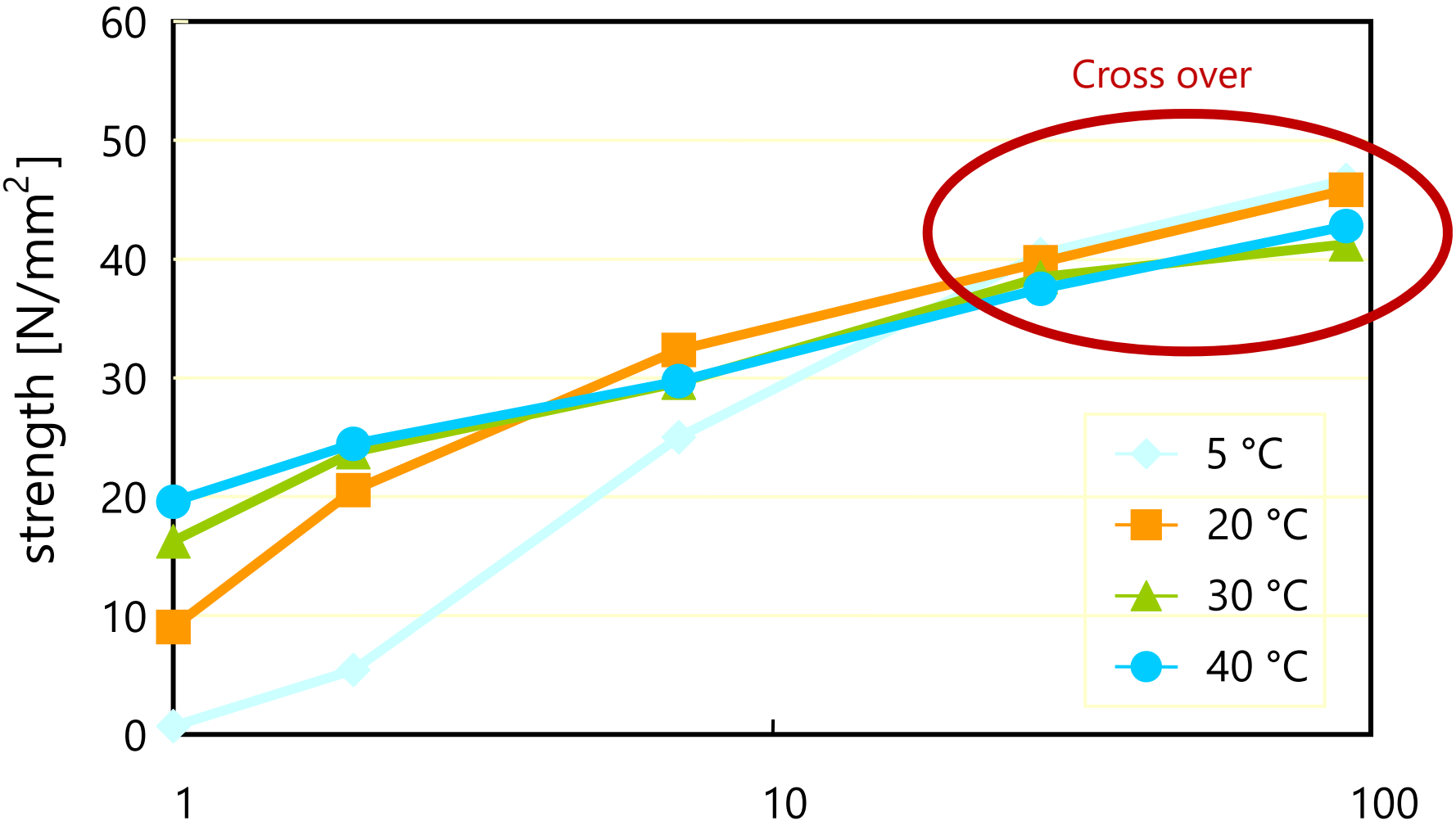
Hydration of Portland cement at different temperatures

1) Experimental evidences

2) Temperature calculation in GEMS
   (Limestone-blended cement)

Tutorial: Effect of temperature on PC hydration

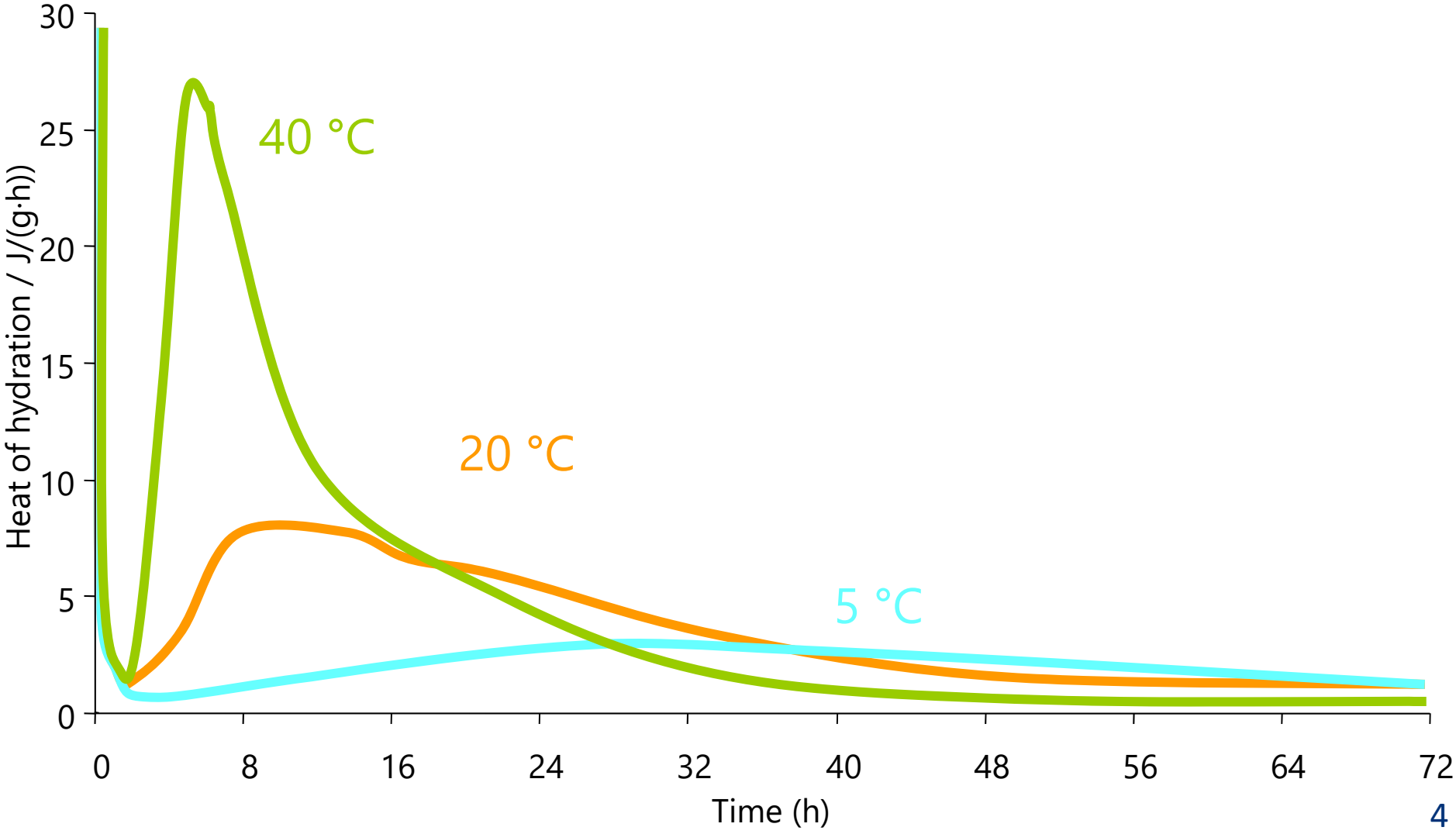
Influence of temperature: Compressive strength



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

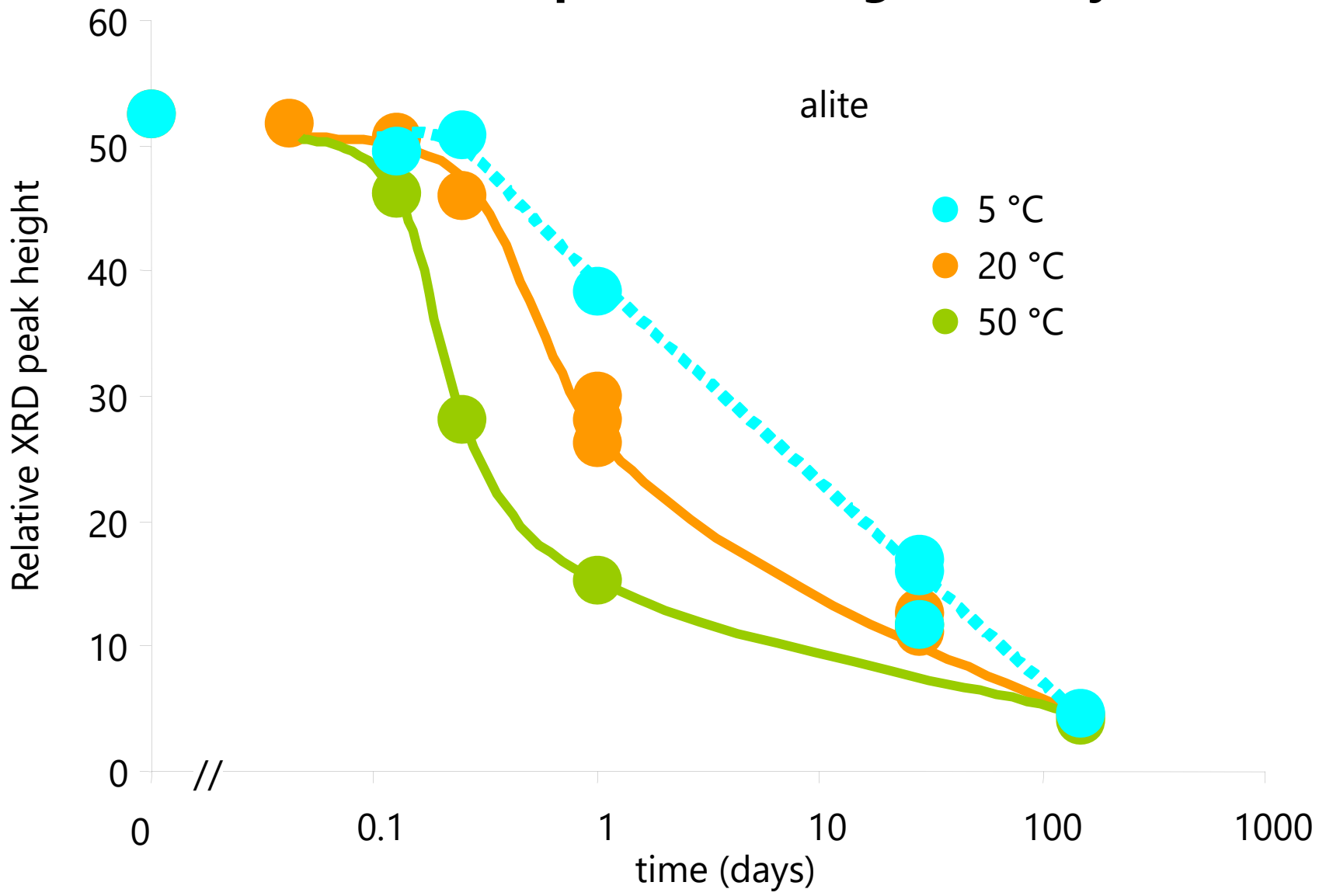
Tutorial: Effect of temperature on PC hydration

Influence of temperature: Isothermal calorimetry



Tutorial: Effect of temperature on PC hydration

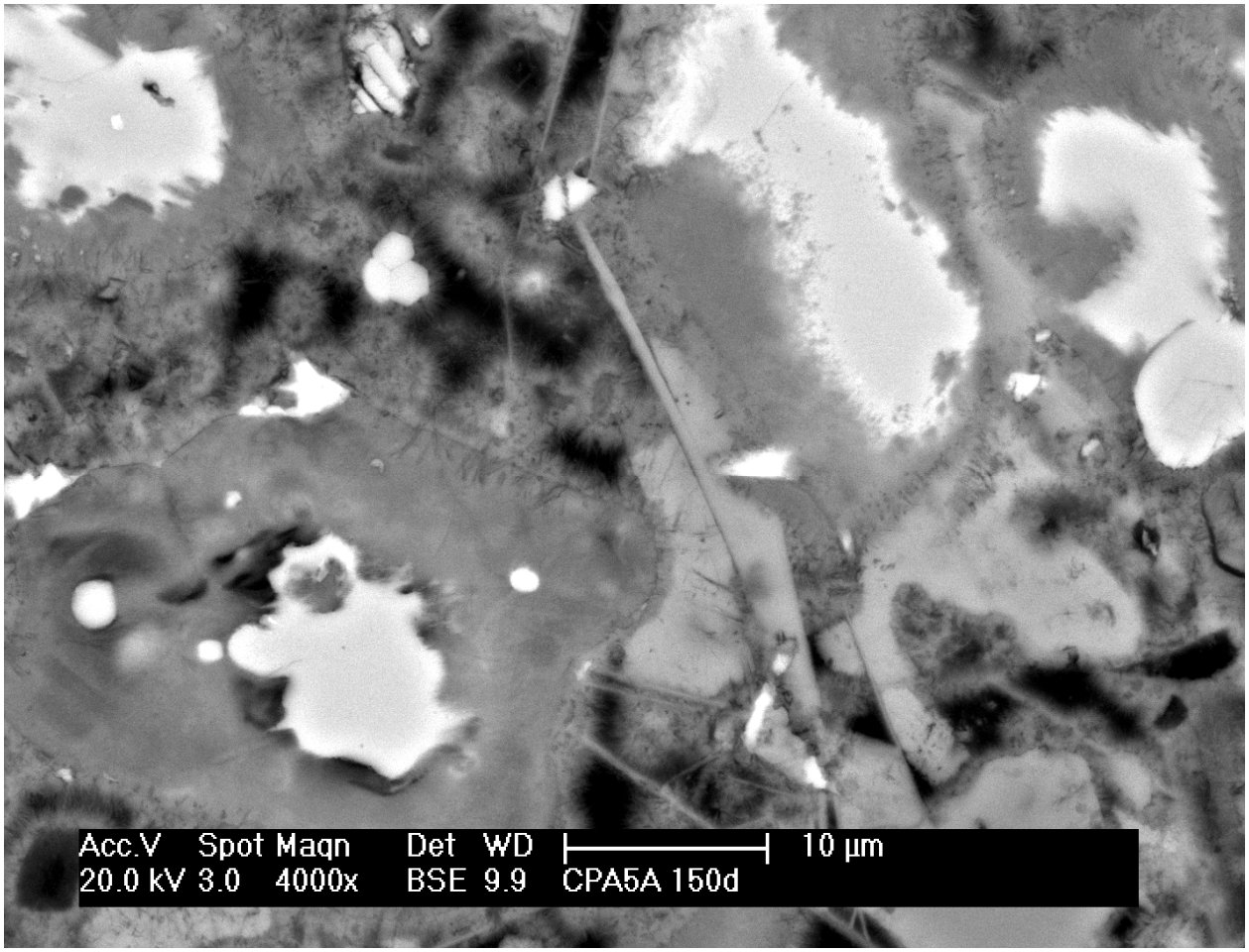
Influence of temperature: Progress of hydration



Tutorial: Effect of temperature on PC hydration

Influence of temperature: Microstructure

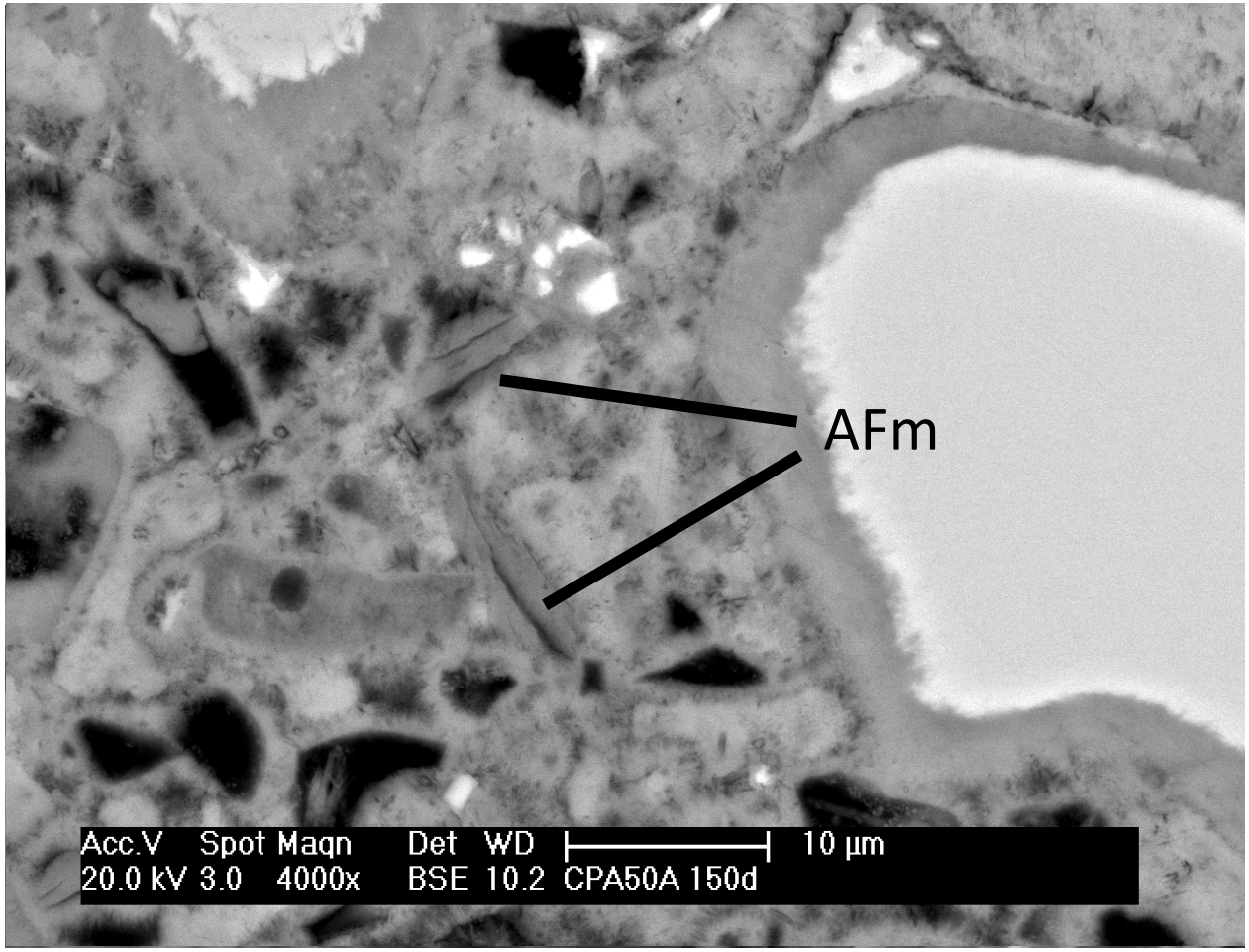
5°C, 150 days



Tutorial: Effect of temperature on PC hydration

Influence of temperature: Microstructure

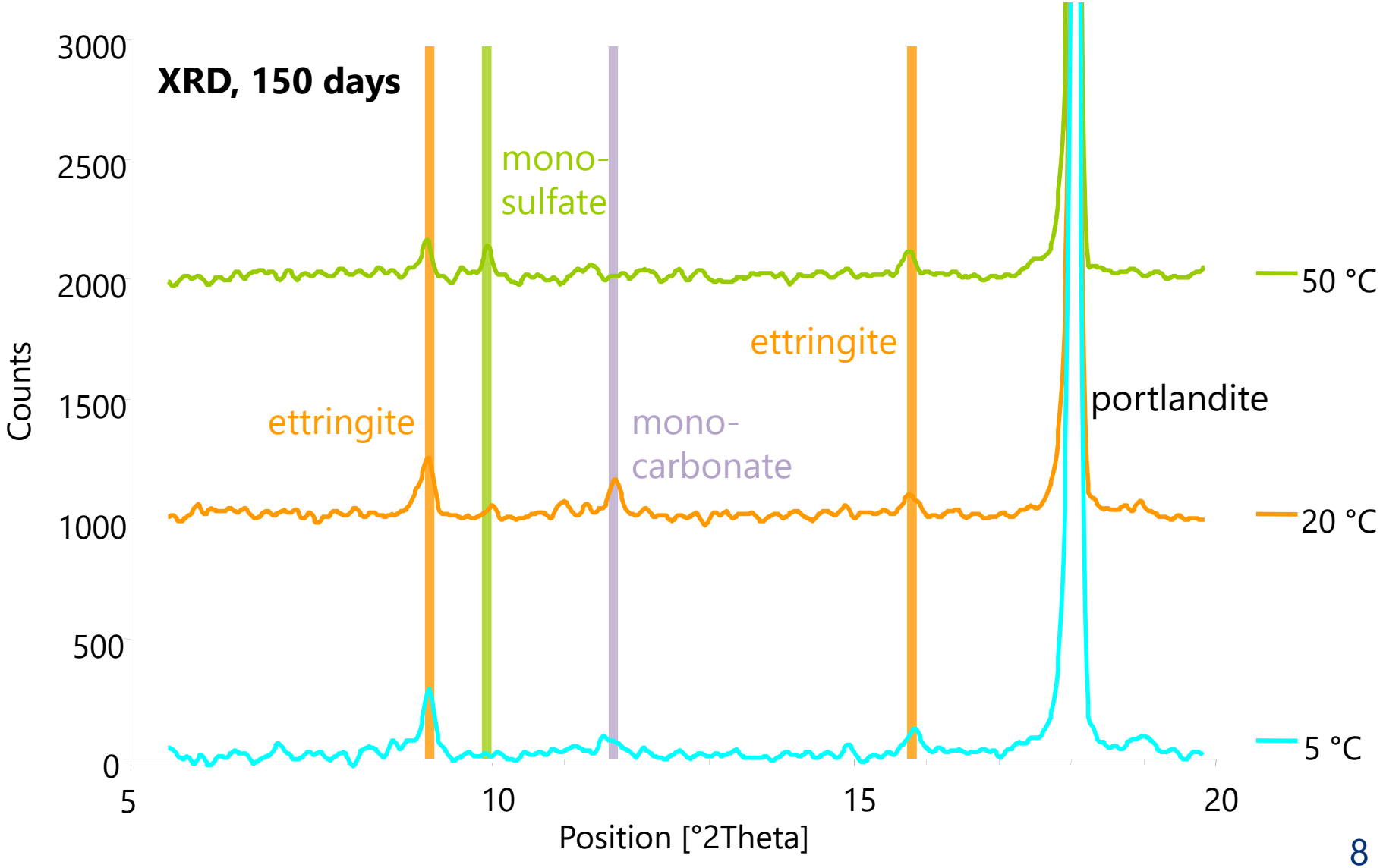
50°C, 150 days



Tutorial: Effect of temperature on PC hydration

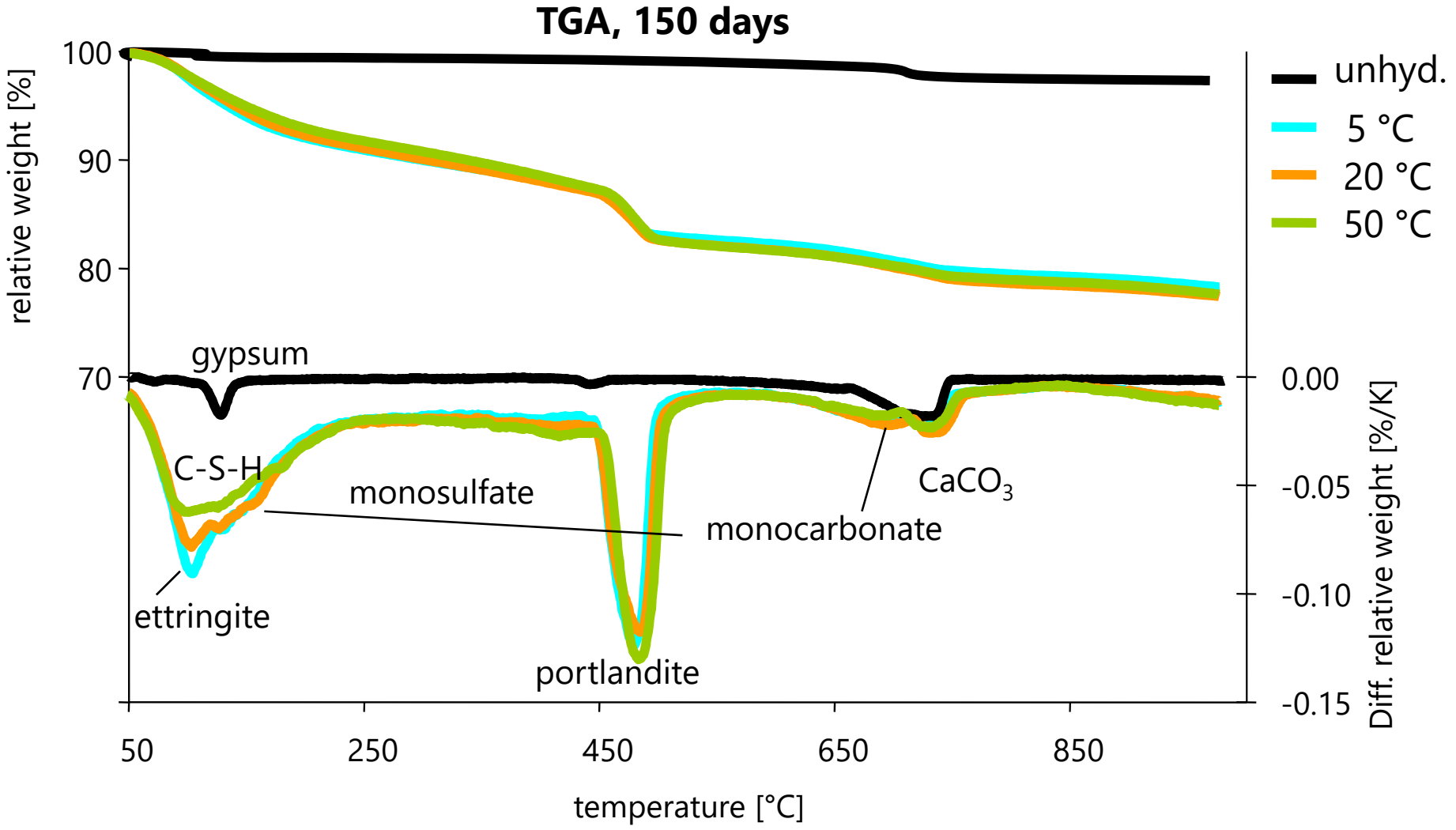
Empa
Materials Science and Technology

Influence of temperature: Hydrate assemblage



Tutorial: Effect of temperature on PC hydration

Influence of temperature: Hydrate assemblage



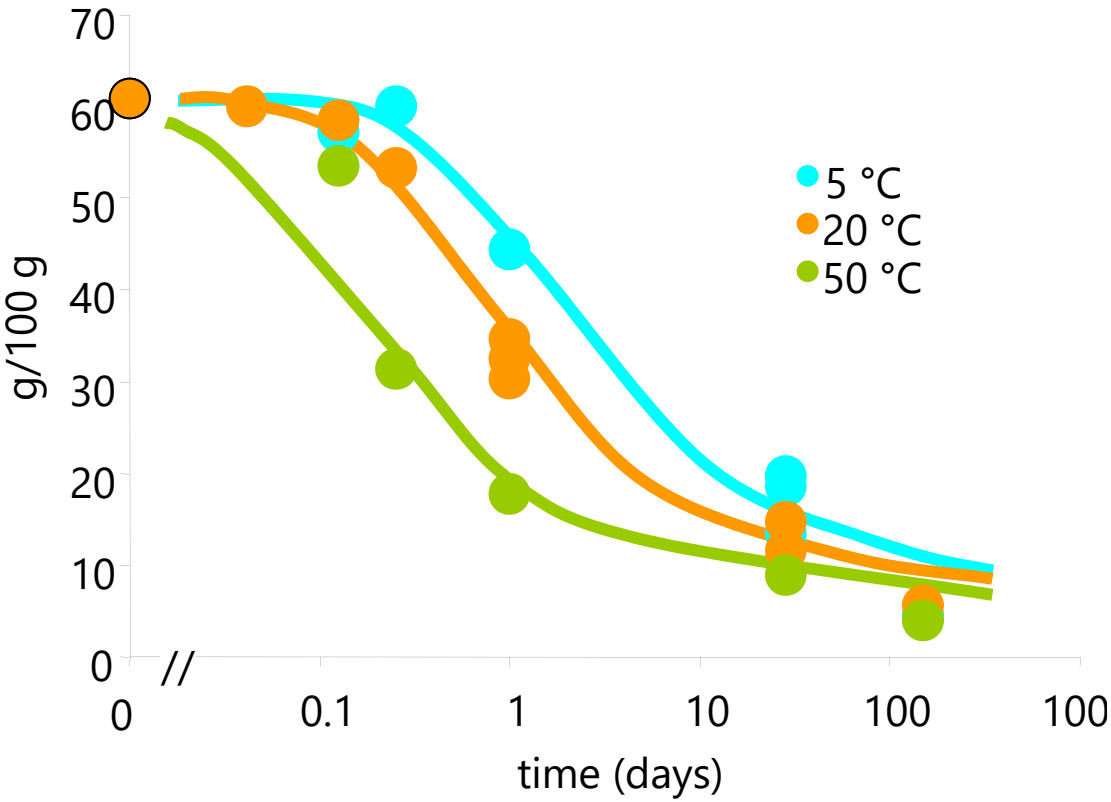
Tutorial: Effect of temperature on PC hydration

Modelling: Temperature

Arrhenius equation

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

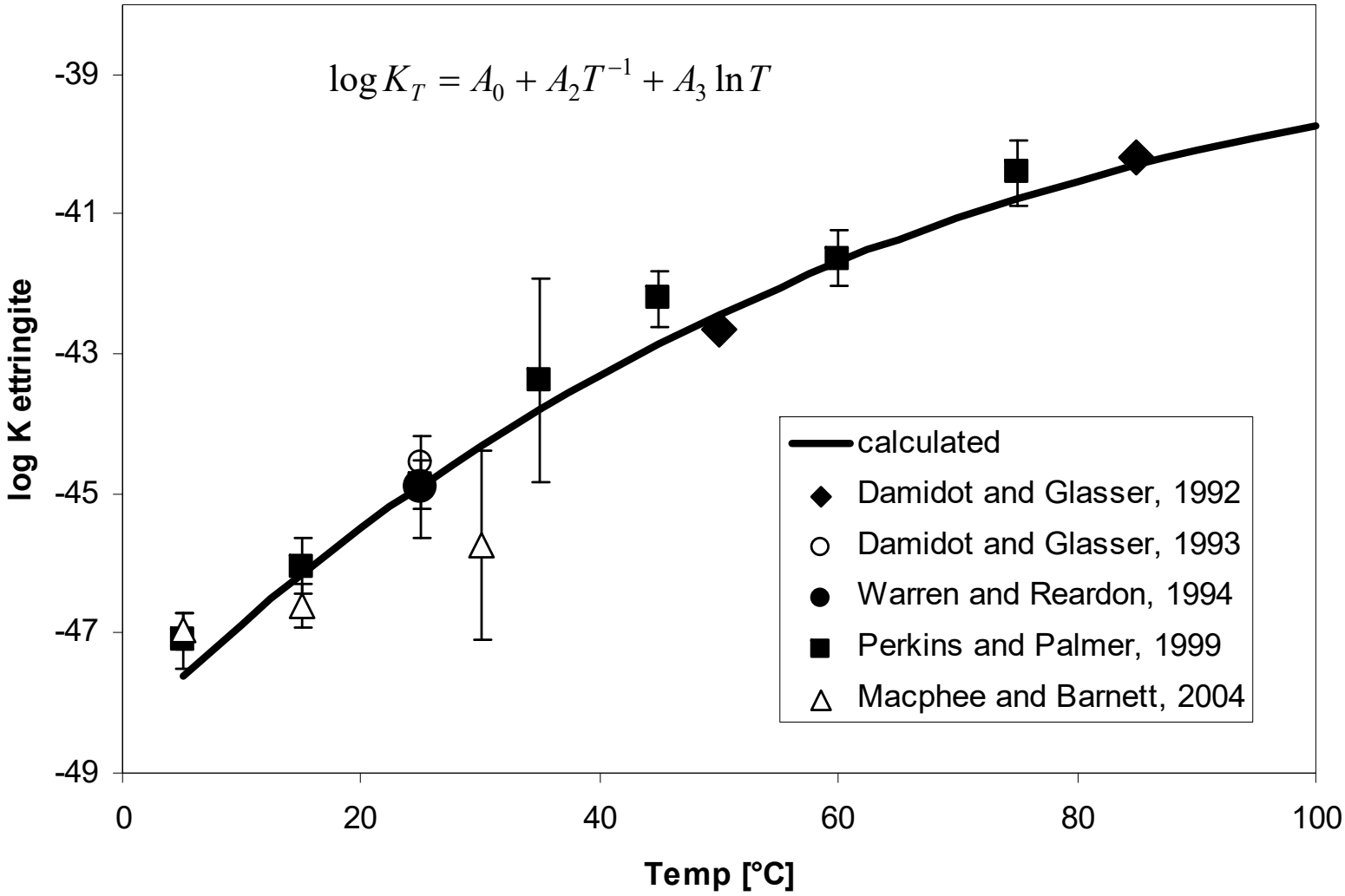
E_a: *activation energy*



Chemical reactions accelerate with increasing temperature

Tutorial: Effect of temperature on PC hydration

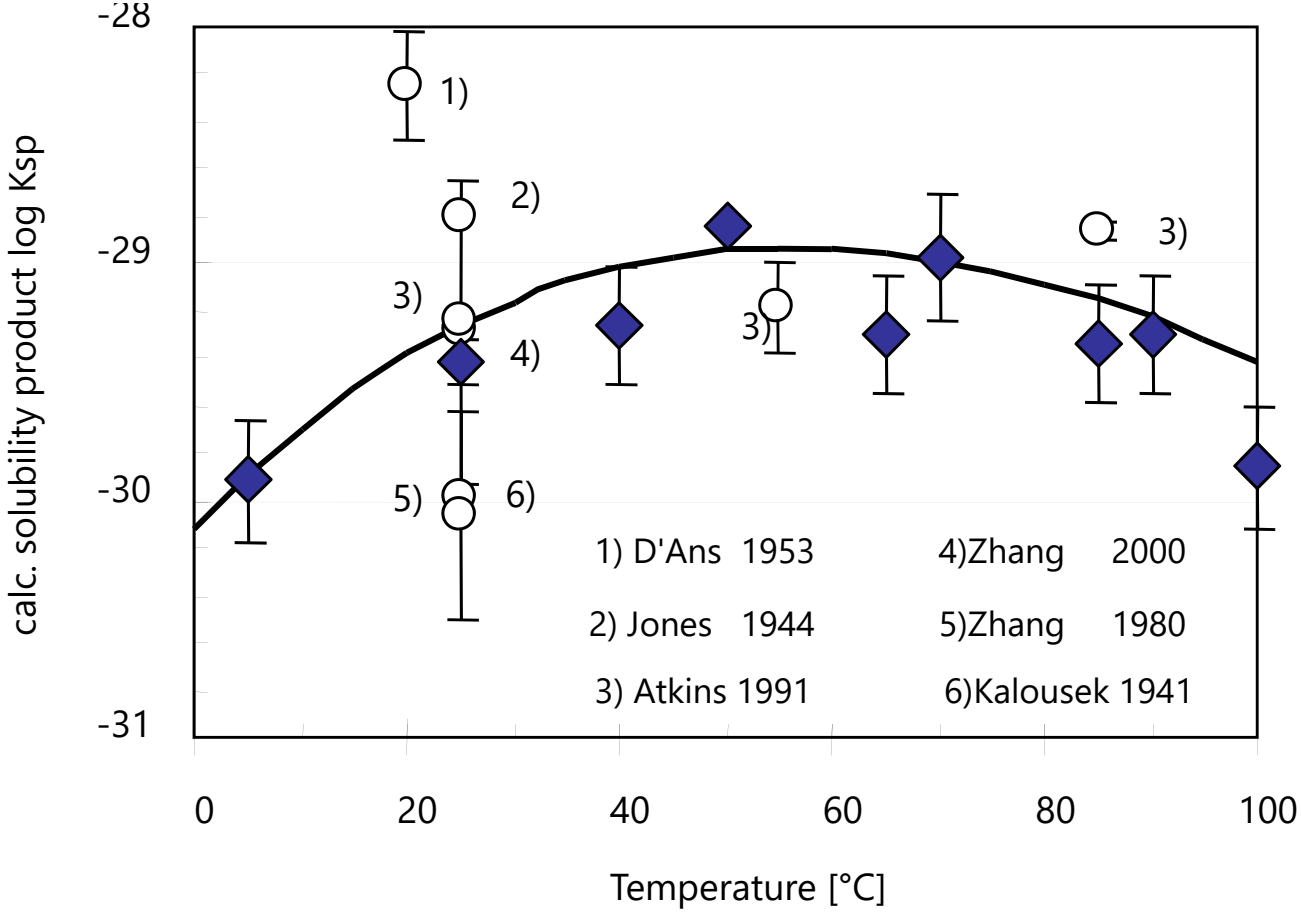
Solubility of ettringite as f(T)



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

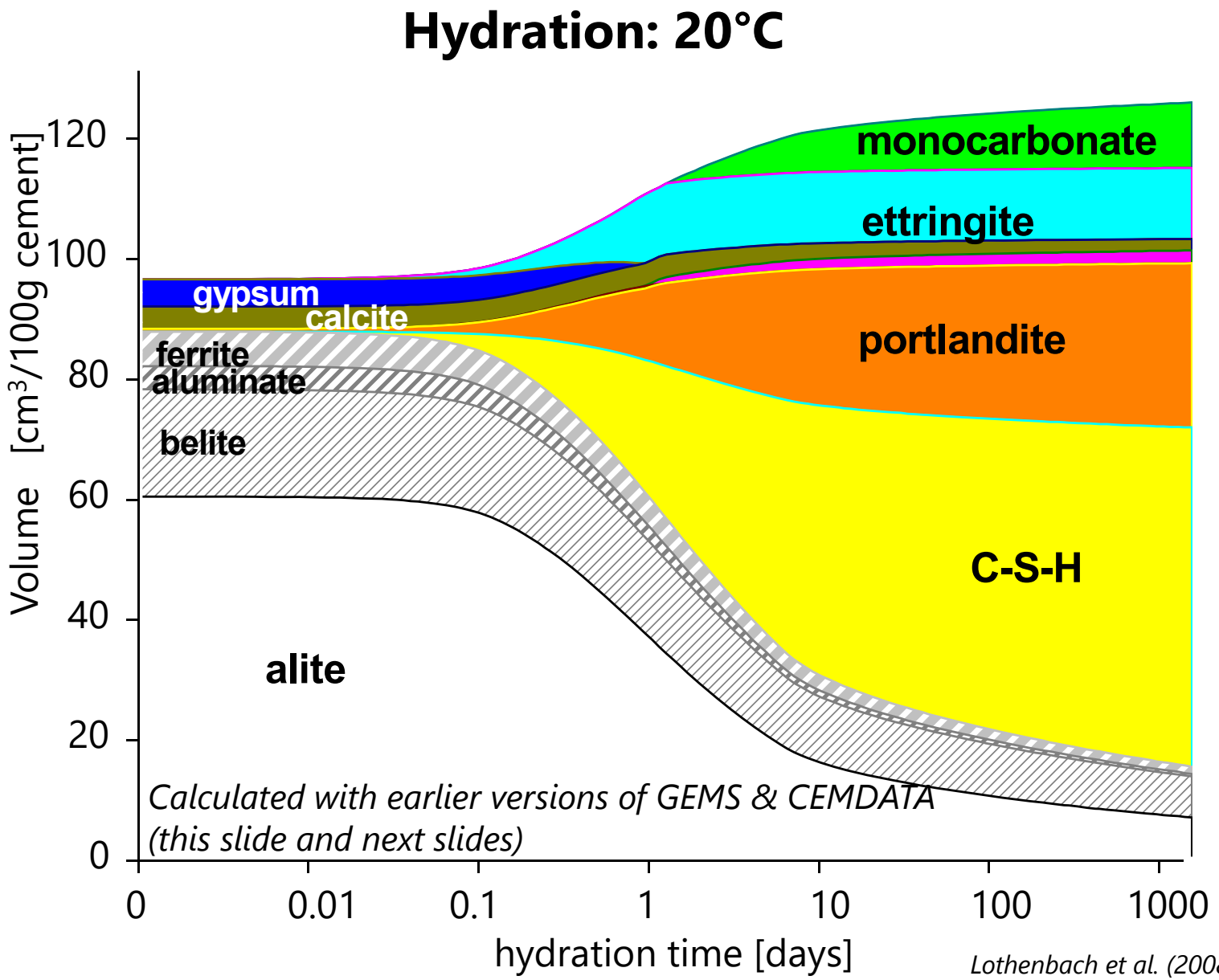
Tutorial: Effect of temperature on PC hydration

Solubility of monosulfate as f(T)



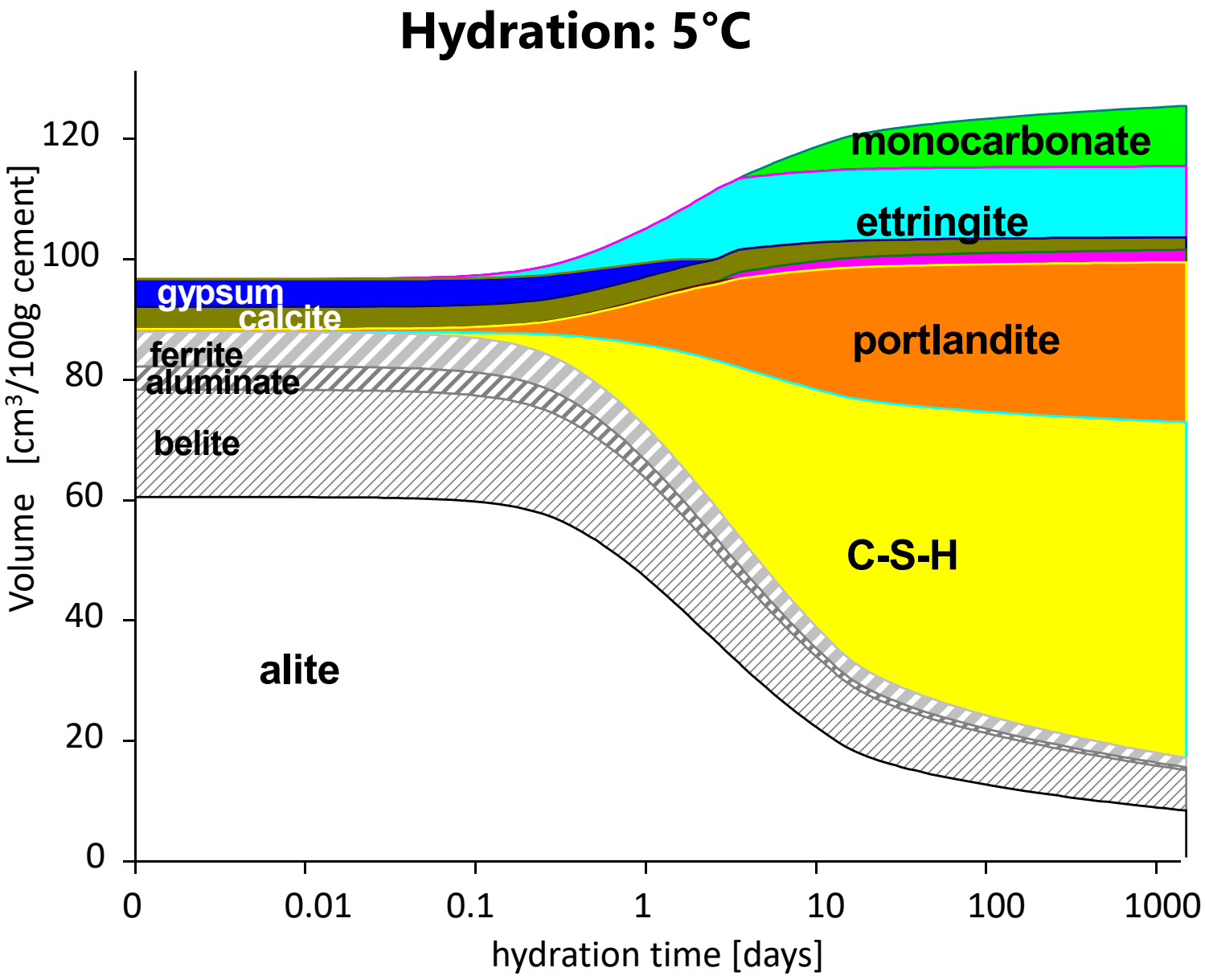
Matschei et al. (2007), CCR 37, 1379-1410

Tutorial: Effect of temperature on PC hydration

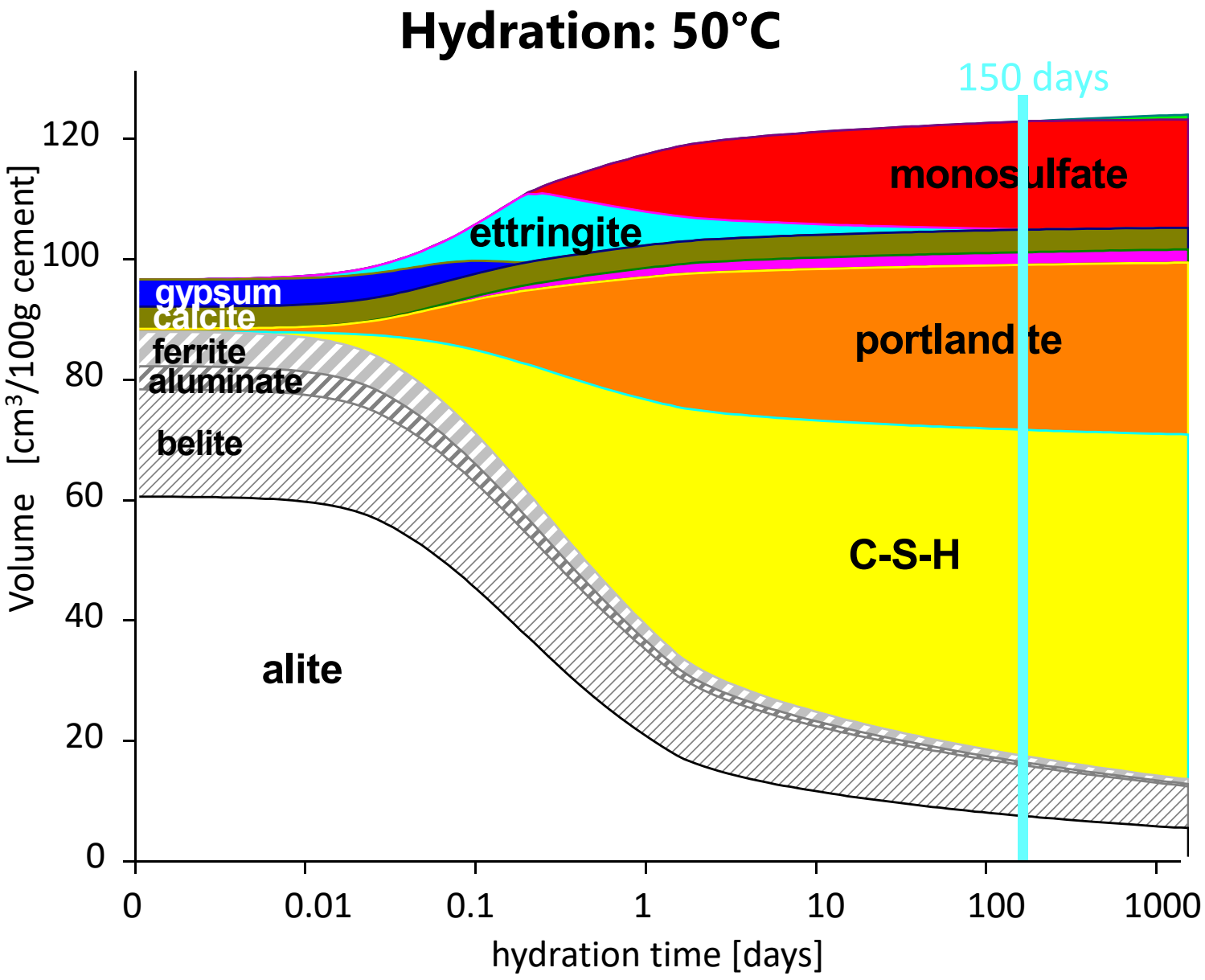


Lothenbach et al. (2008), CCR 38, 1-18

Tutorial: Effect of temperature on PC hydration



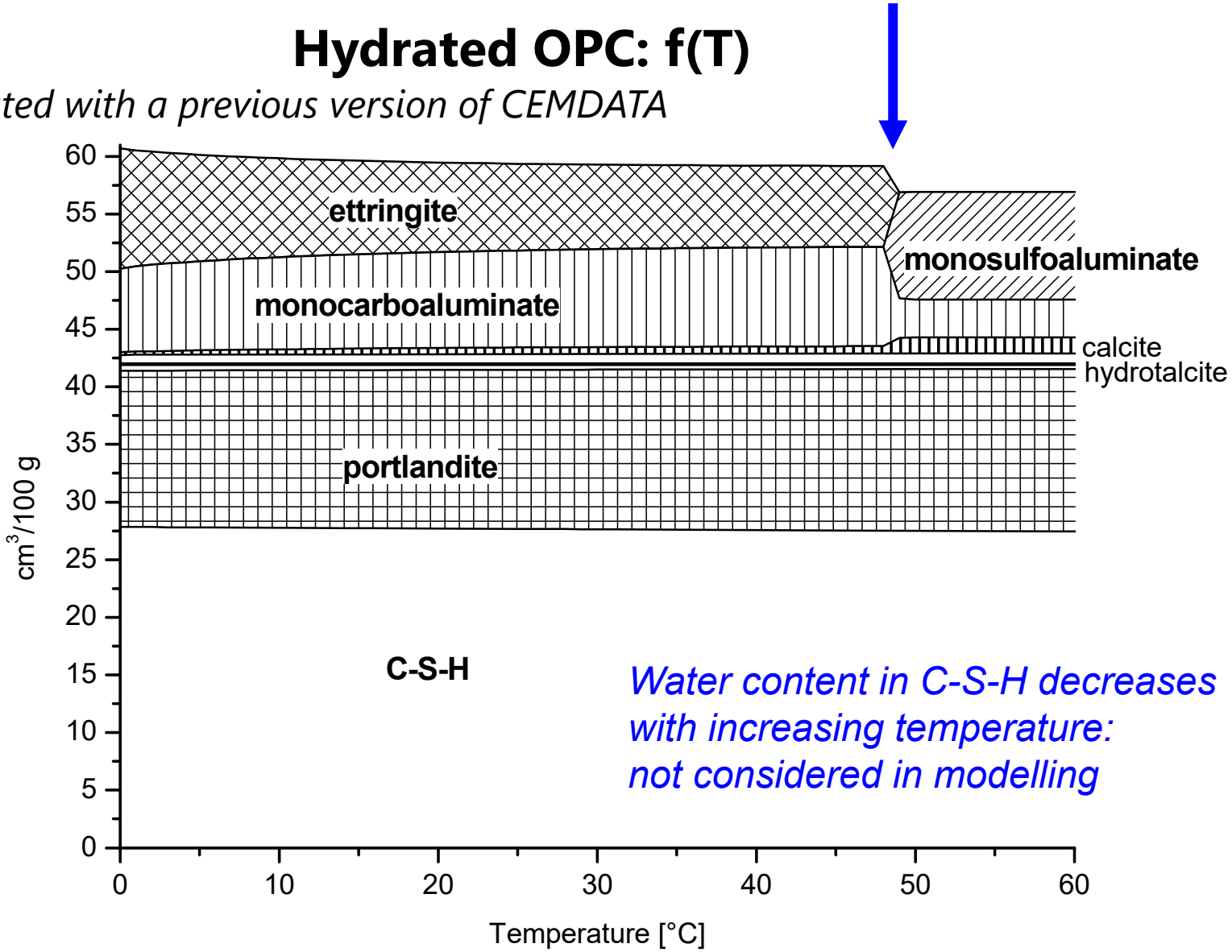
Tutorial: Effect of temperature on PC hydration



Tutorial: Effect of temperature on PC hydration

Hydrated OPC: f(T)

Calculated with a previous version of CEMDATA

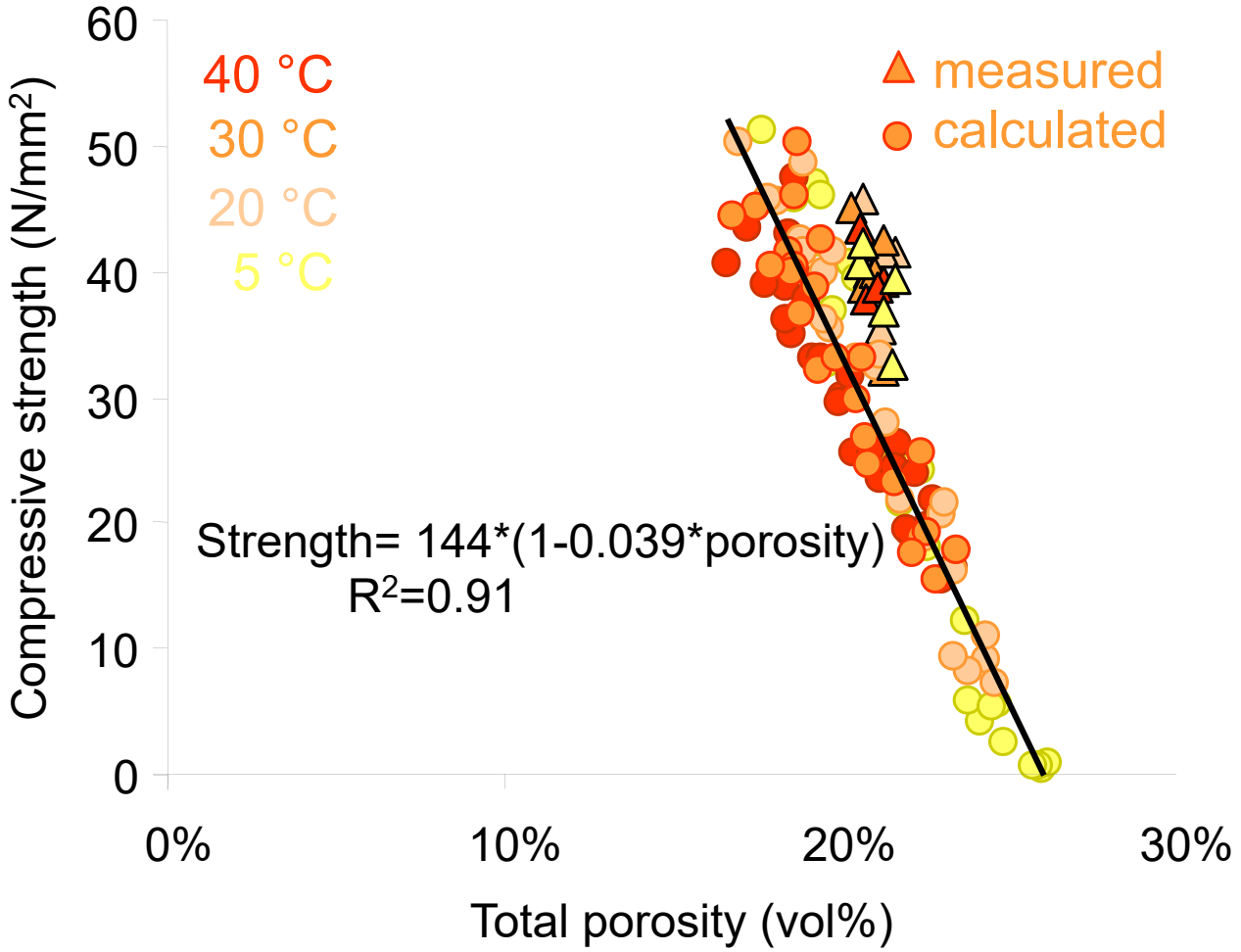


Water content in C-S-H decreases with increasing temperature: not considered in modelling

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

Tutorial: Effect of temperature on PC hydration

Hydrated OPC: strength vs. calculated porosity (GEMS)



Tutorial: Effect of temperature on PC hydration

Empa
Materials Science and Technology

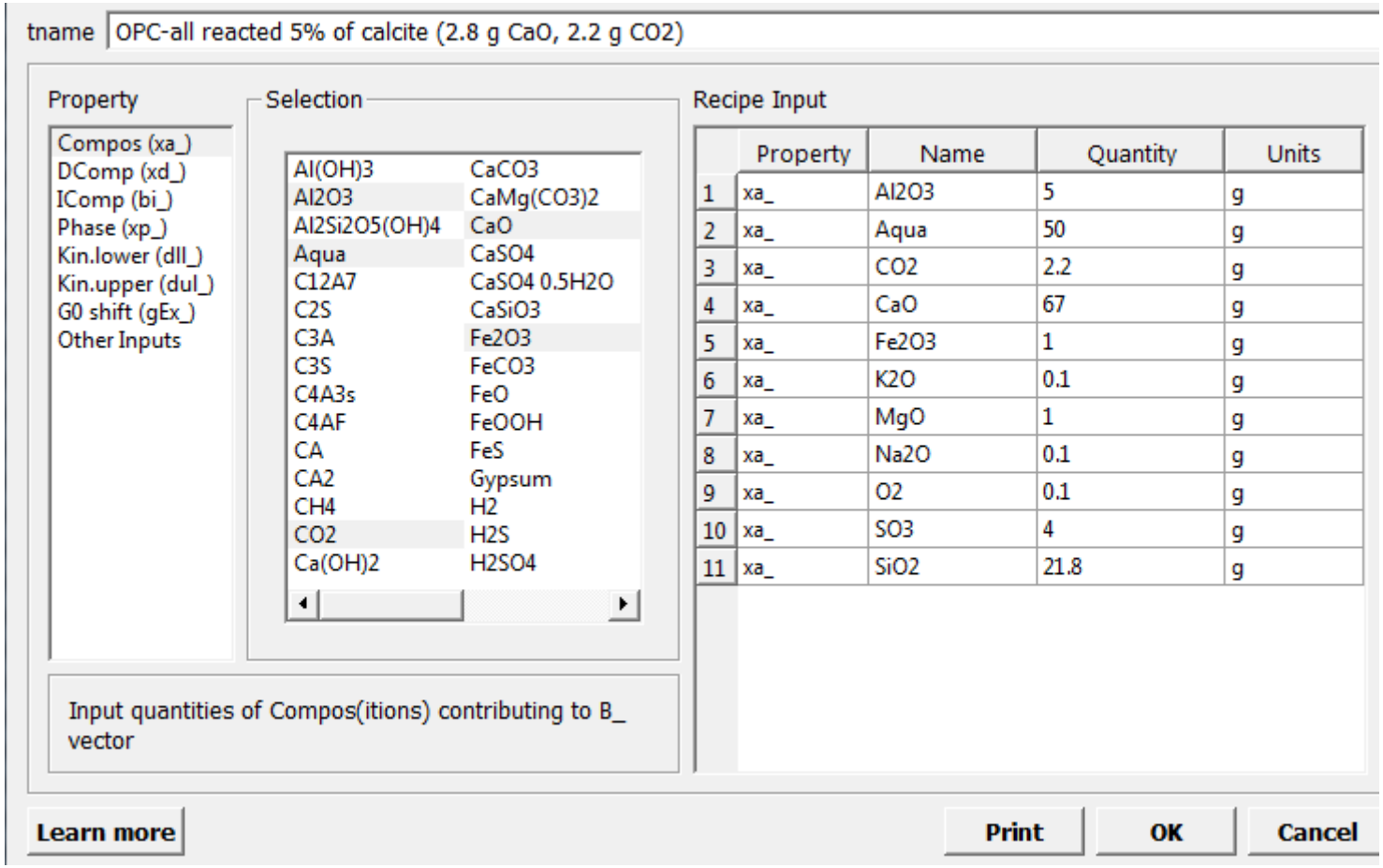
Summary

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

Tutorial: Effect of temperature on PC hydration

- Open Project „PC“ (Lessons L03 & L04)
- Clone the single file „PC“ and name it e.g. „PC2“ (will preserve deactivation of phases)
- Enter its composition as listed below und calculate



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

w/b = 0.5

Some O_2 to ensure oxidizing conditions

Tutorial: Effect of temperature on PC hydration

Empa
Materials Science and Technology

Input: System Definition | Results: Equilibrium State

Phase/species		L	T	Amount (mol)	logSI/Activity
a	aq_gen	69	a	0.45860346	8.75e-10
g	gas_gen	6	g	0.0031903426	-1.74e-09
s	C3(AF)S0.84H	2	s	0.011119501	-9.423e-09
s	CSHQ	6	s	0.47205288	-8.479e-09
s	straetlingite	2	s	0	-2.862
s	ettringite	2	s	0	-0.09211
s	SO4_OH_AFm	2	s	0	-1
s	OH_SO4_AFm	2	s	0	-1
s	SO4_CO3_AFt	2	s	0.056752341	1.495e-08
s	CO3_SO4_AFt	2	s	2.7503032e-07	1.495e-08
s	hydrotalc-pyro	2	s	0	-8.634
s	C4Ac0.5H9	1	s	0	-5.651
s	C4AcH11	1	s	0.019060554	-6.597e-09
s	C6AsH13	1	s	0	-29.71
s	C6AsH9	1	s	0	-37.95
s	Aragonite	1	s	0	-0.1441
s	Calcite	1	s	0.024134813	-2.393e-08
s	C3FH6	1	s	0	-3.179
s	lime	1	s	0	-9.966
s	Portlandite	1	s	0.37407254	7.363e-09
s	Anhydrite	1	s	0	-3.186
s	Gypsum	1	s	0	-2.913
s	hemihydrate	1	s	0	-3.959
s	Iron	1	s	0	-65.72
s	Fe-carbonate	1	s	0	-28.2
s	Siderite	1	s	0	-27.81
s	Magnetite	1	s	0	-15.6
s	Ferrihydrite-am	1	s	0	-3.965
s	Ferrihydrite-mc	1	s	0	-1.298
s	Pyrite	1	s	0	-92.94
s	Troilite	1	s	0	-92.94
s	Melanterite	1	s	0	-35.46
s	arcanite	1	s	0	-6.698
s	syngenite	1	s	0	-8.79
s	K-oxide	1	s	0	-63.2
s	OH-hydrotalcite	1	s	0.0062027966	0
s	Magnesite	1	s	0	-7.238

Fe-containing siliceous hydrogarnet

C-S-H

Ettringite

Monocarbonate

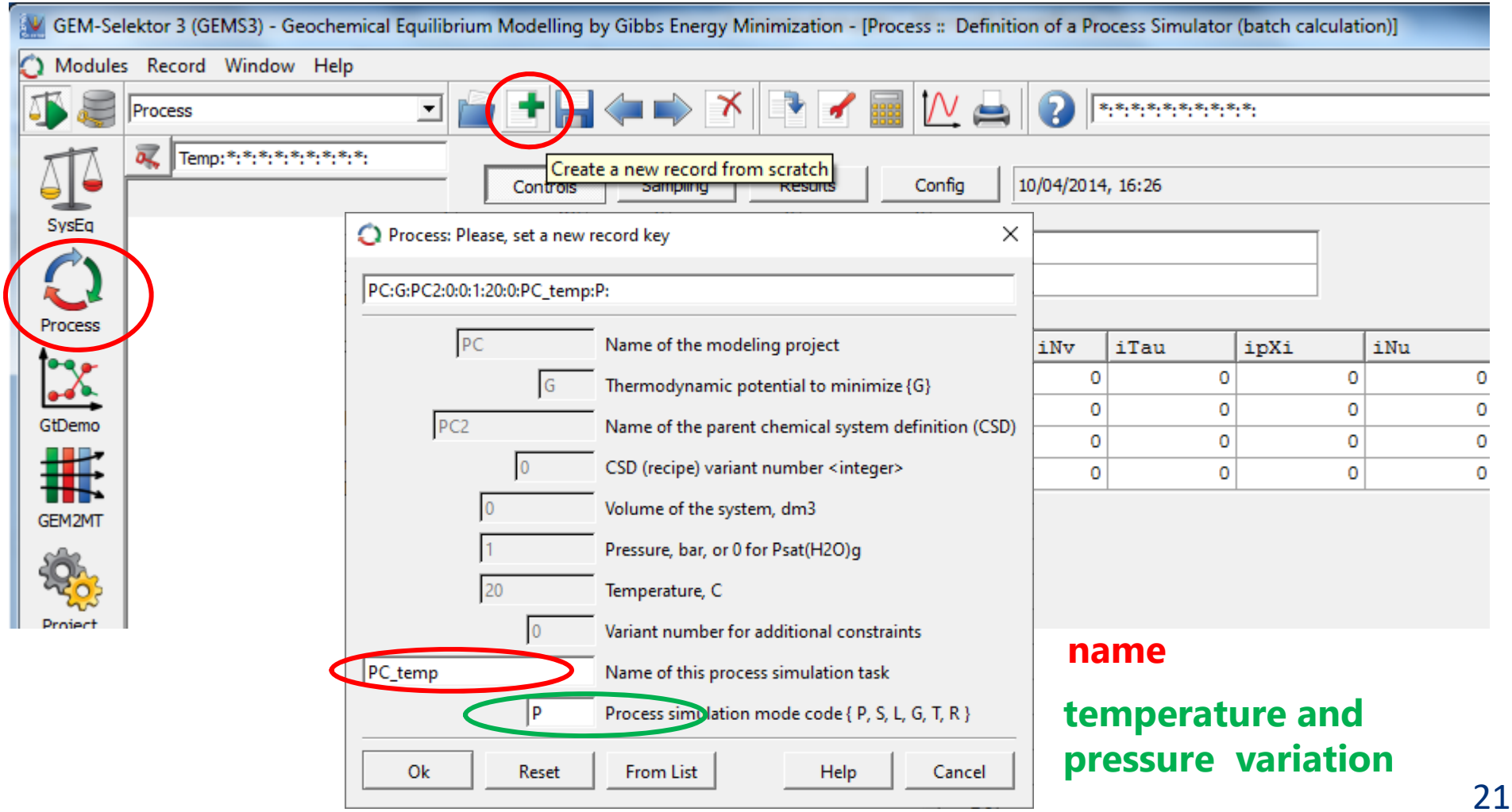
Calcite

Portlandite

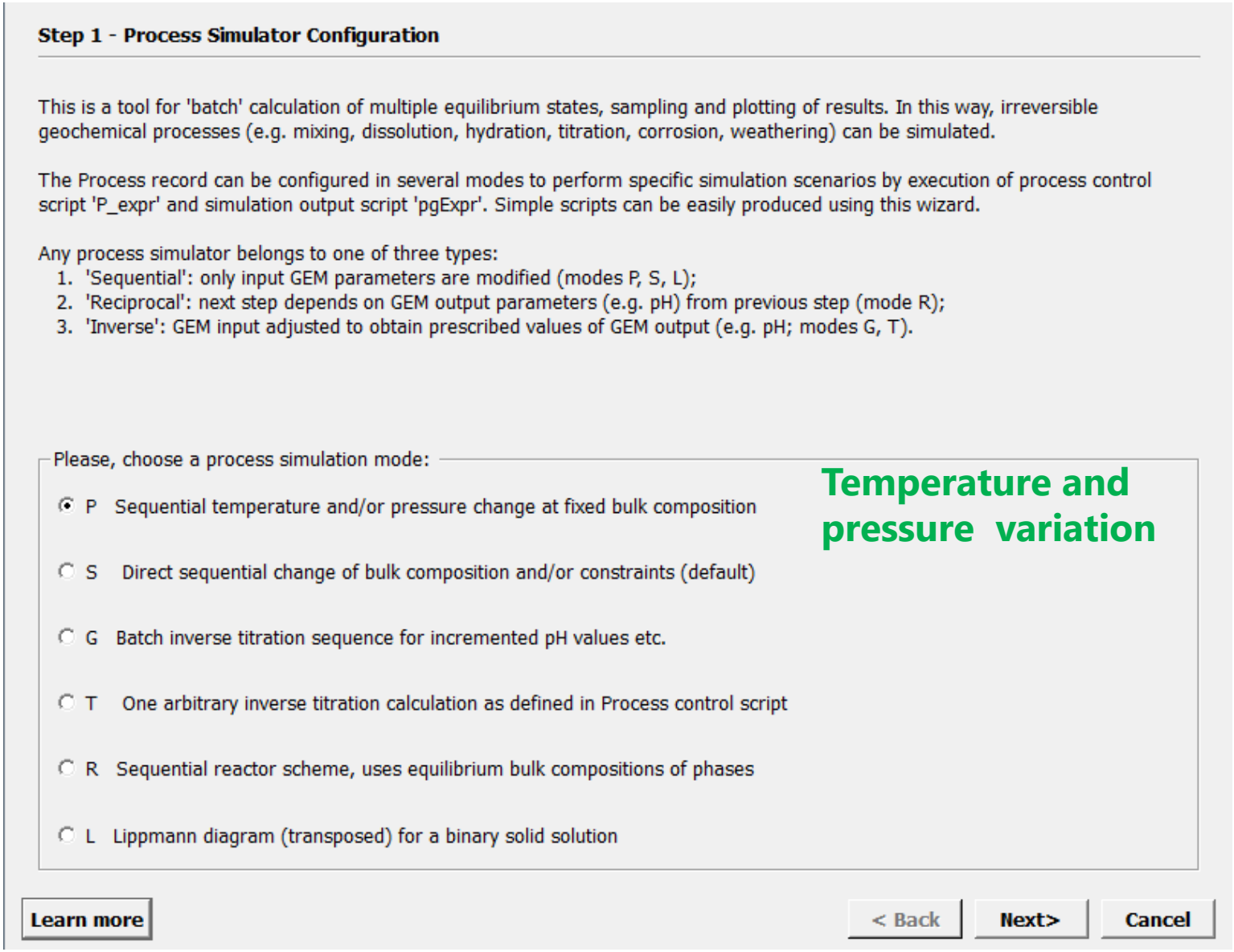
Hydrotalcite

Tutorial: Effect of temperature on PC hydration

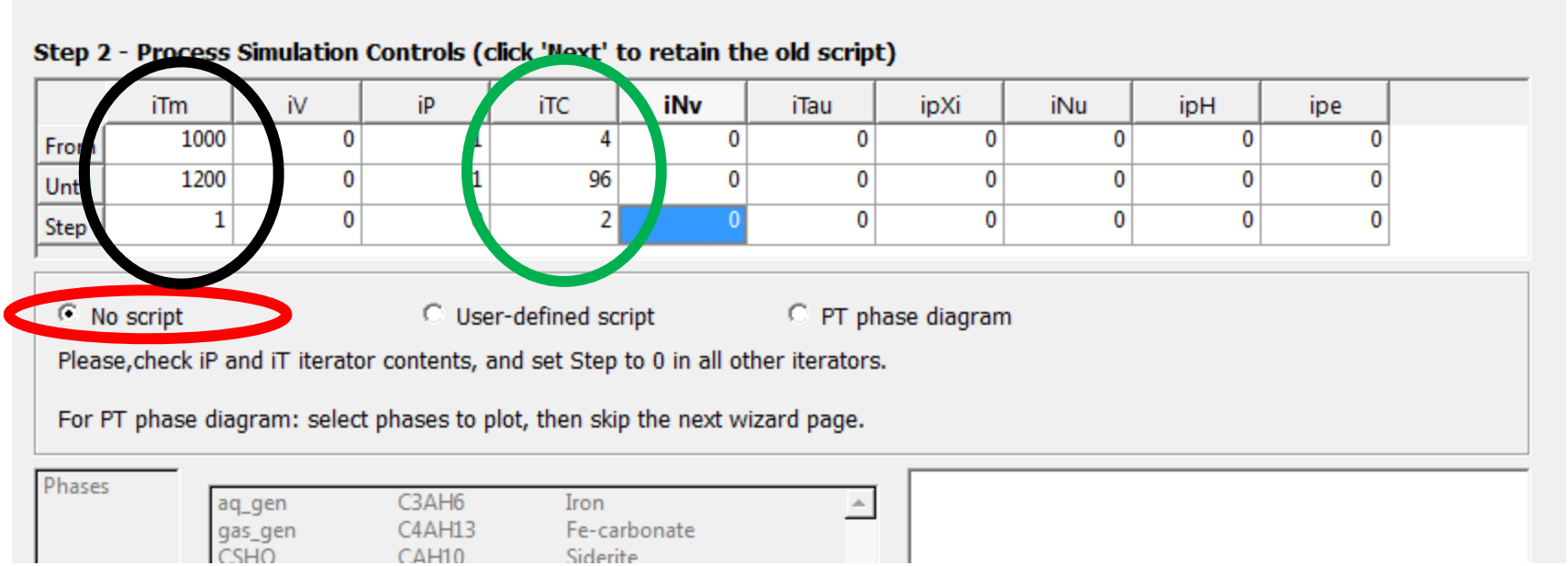
- Clone process file „LS_Vol“ as we will re-use the output part to simplify our work



Tutorial: Effect of temperature on PC hydration



Tutorial: Effect of temperature on PC hydration



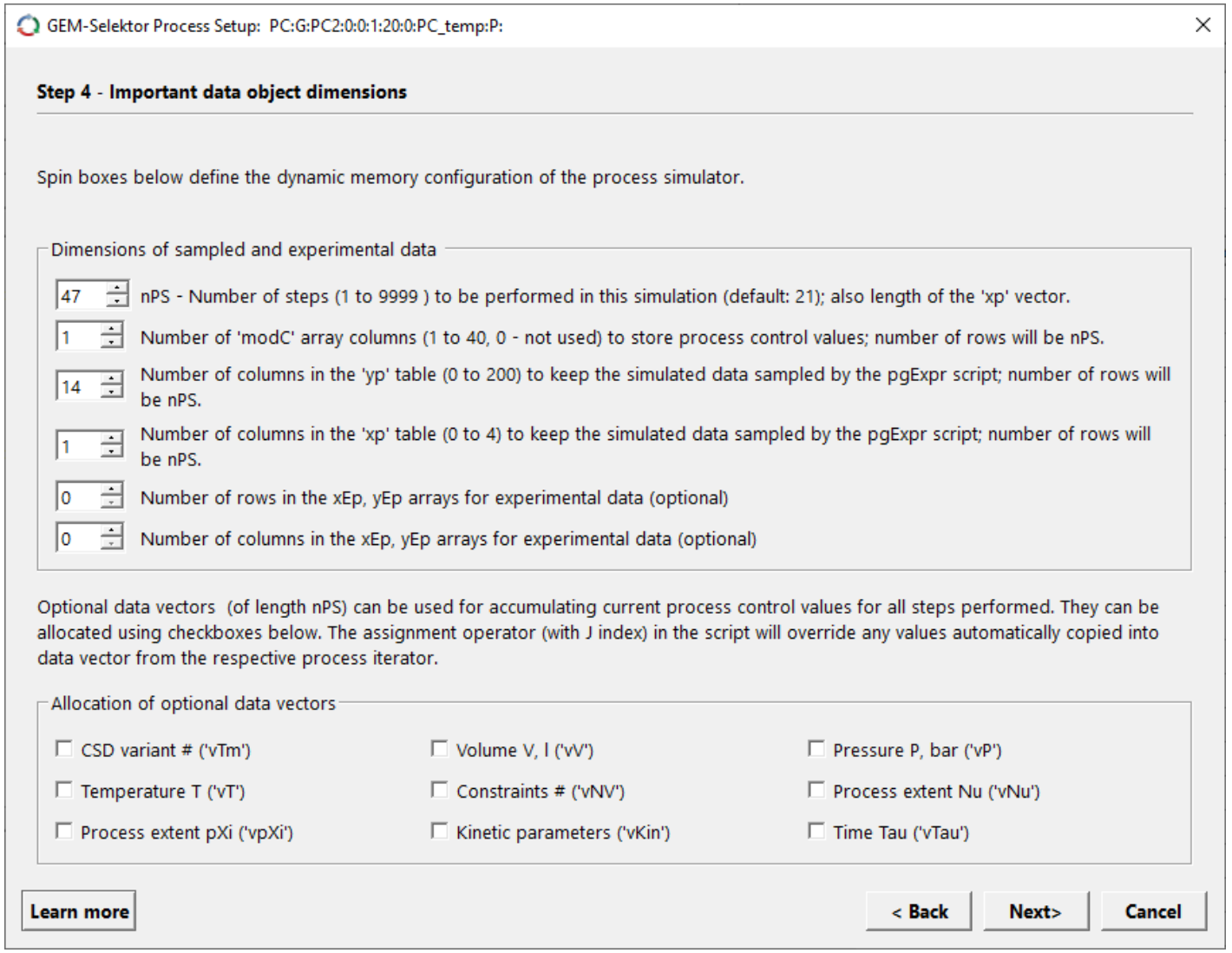
Numbering of the single calculations

Start temperature
Stop temperature
Step size

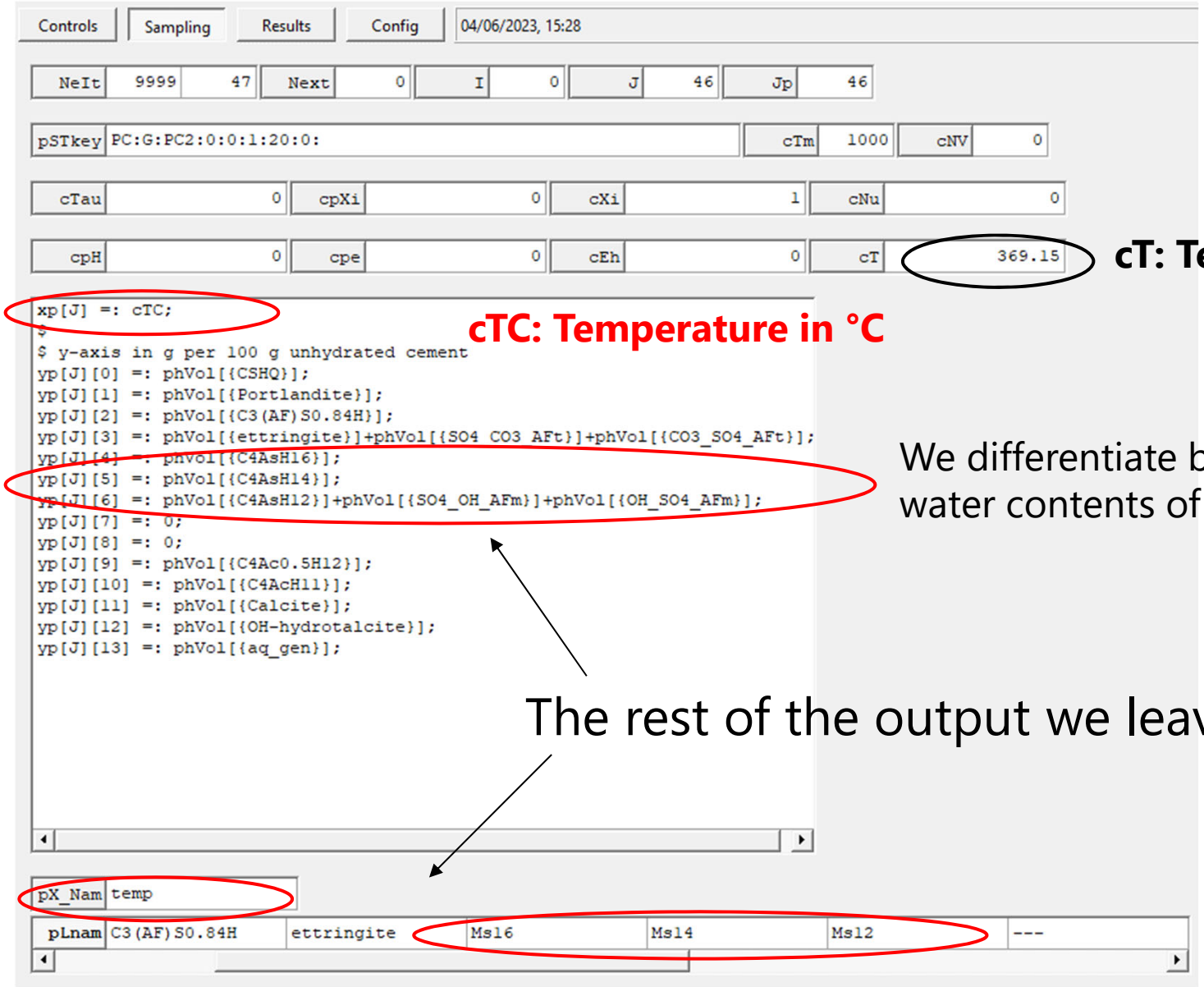
No script needed

We leave the output file like it is and change it later

Tutorial: Effect of temperature on PC hydration



Tutorial: Effect of temperature on PC hydration



cT: Temperature in K

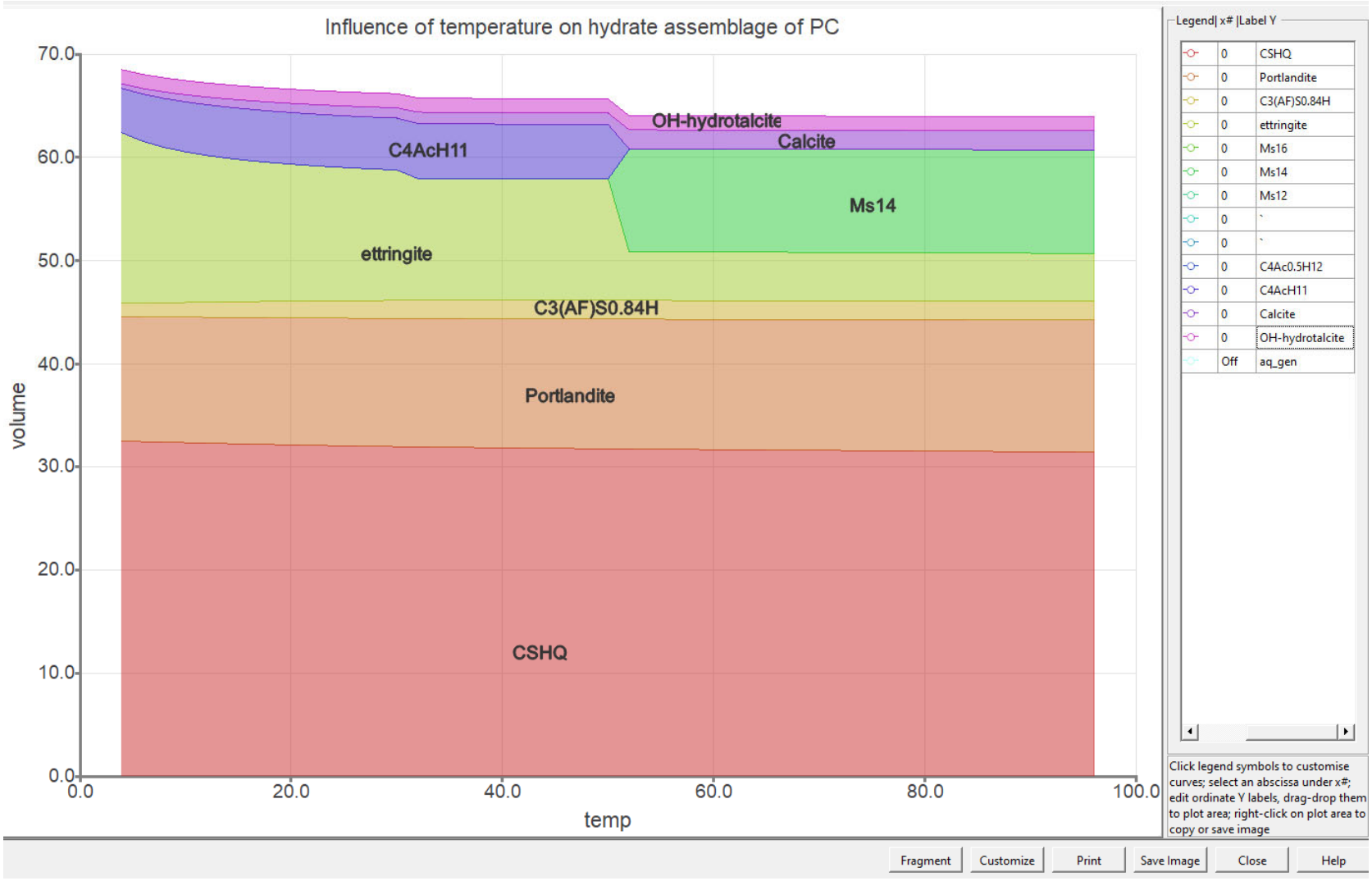
cTC: Temperature in °C

We differentiate between the water contents of monosulfate

The rest of the output we leave like it is

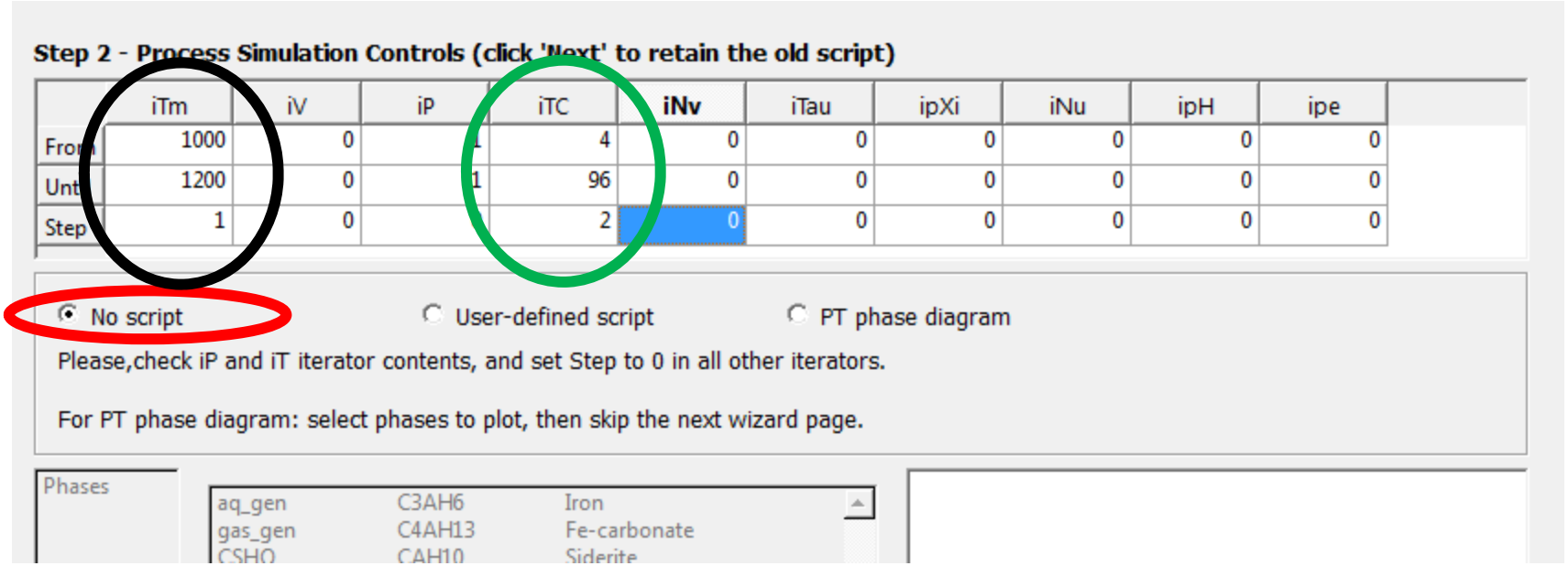
Tutorial: Effect of temperature on PC hydration

- Calculate and make a nice cumulative plot



Tutorial: Effect of temperature on PC hydration

- Plotting changes of pH, OH^- and C-S-H composition
- Make new process „PC_temp_CSH“ with PC2 as parent file

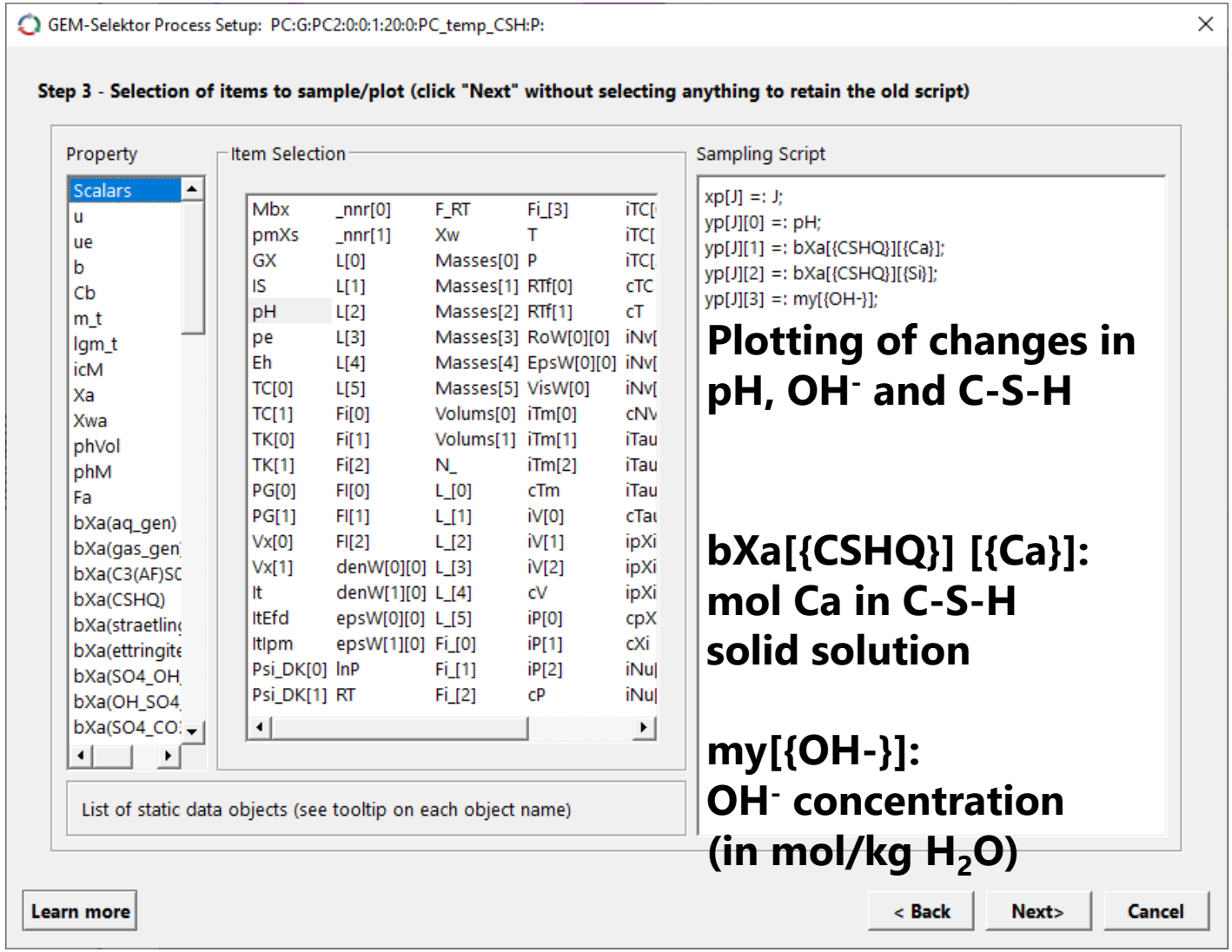


Numbering of the single calculations

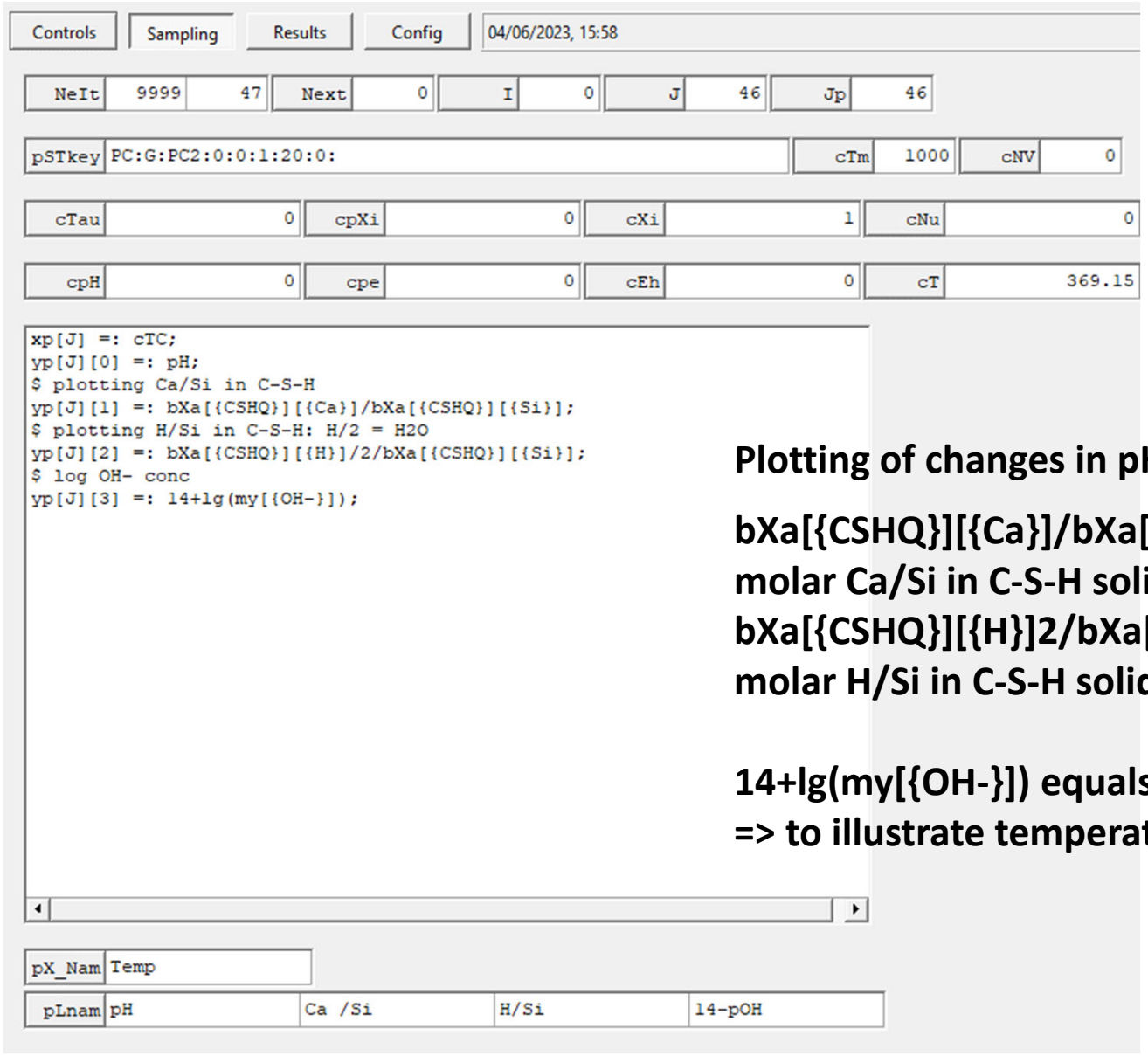
Start temperature
Stop temperature
Step size

No script needed

Tutorial: Effect of temperature on PC hydration



Tutorial: Effect of temperature on PC hydration

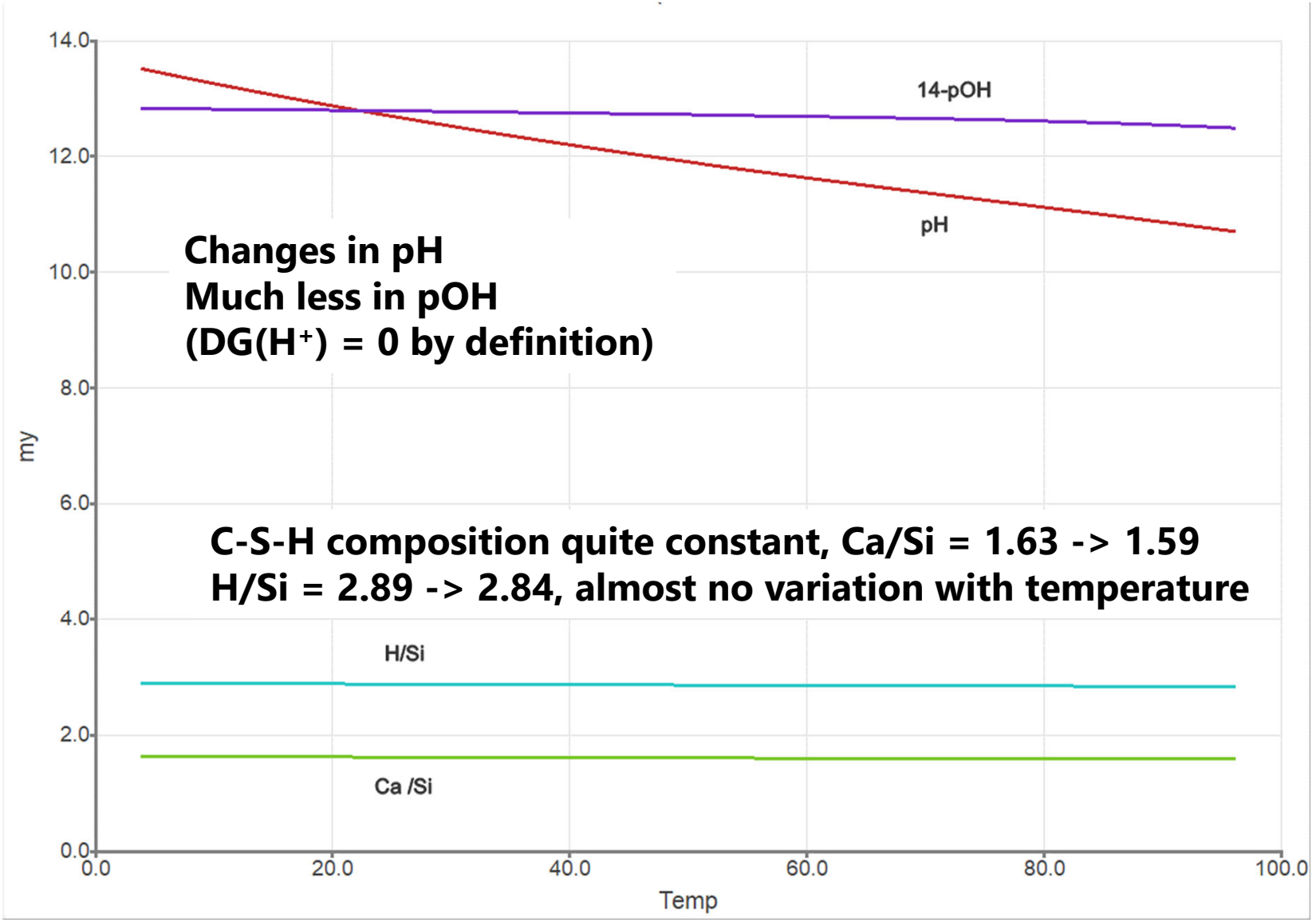


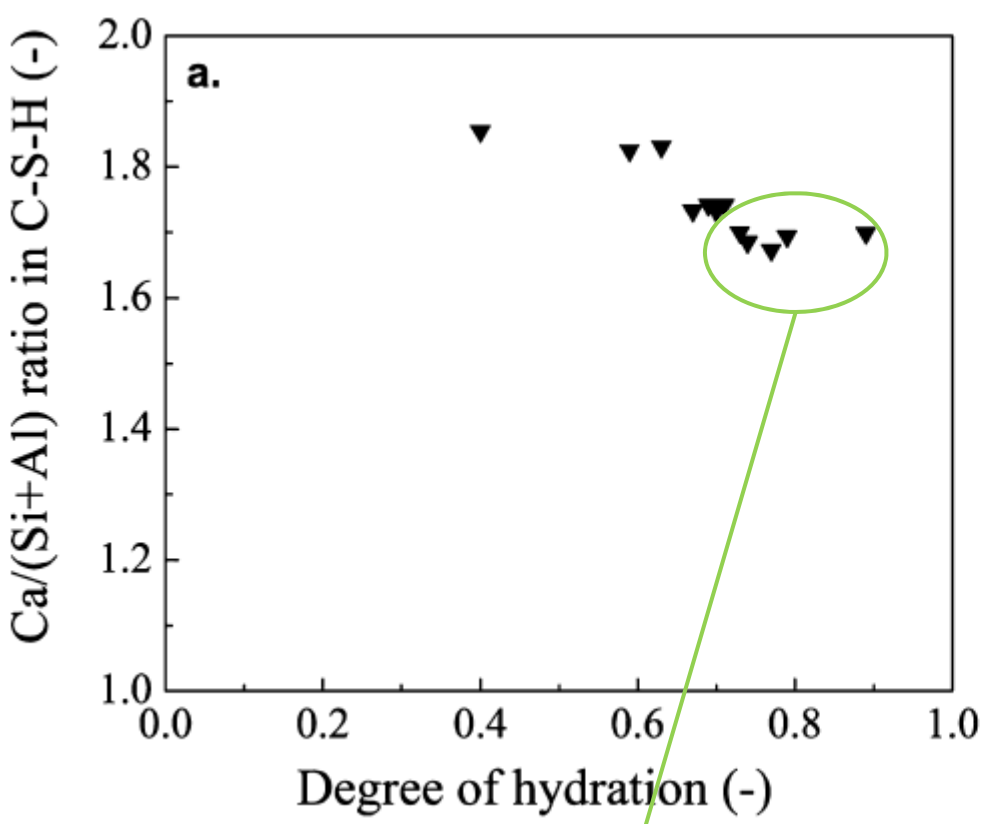
Plotting of changes in pH, OH- and C-S-H

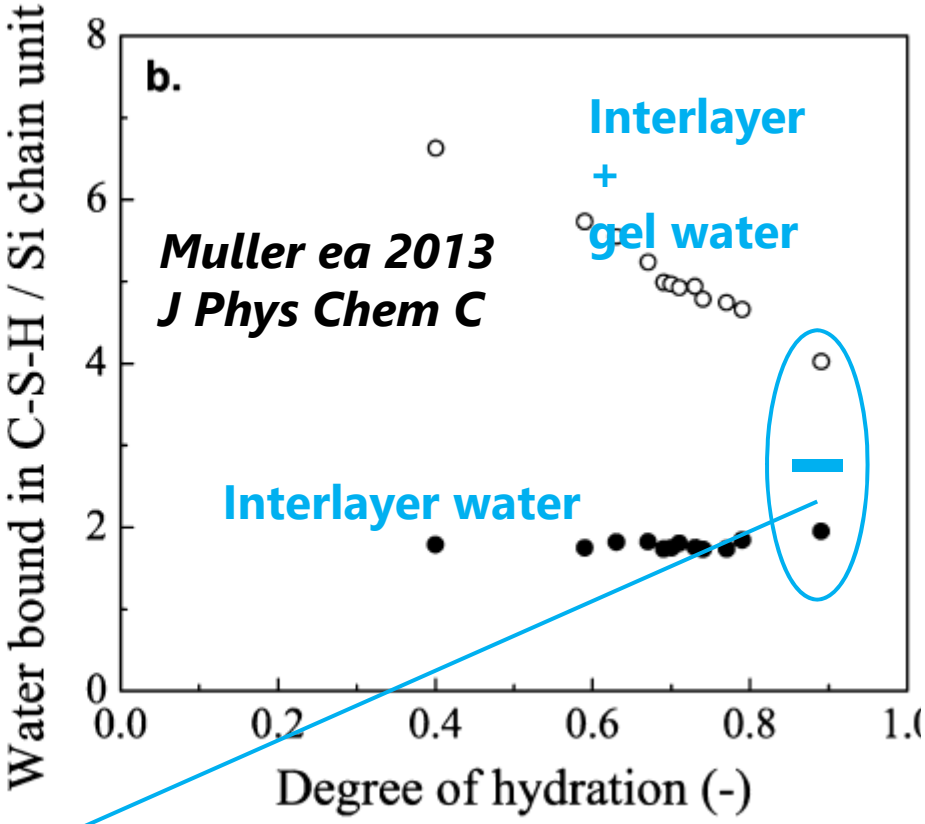
bXa[{CSHQ}][{Ca}]/bXa[{CSHQ}][{Si}]:
molar Ca/Si in C-S-H solid solution
bXa[{CSHQ}][{H}]2/bXa[{CSHQ}][{Si}]:
molar H/Si in C-S-H solid solution (H/2 = H2O)

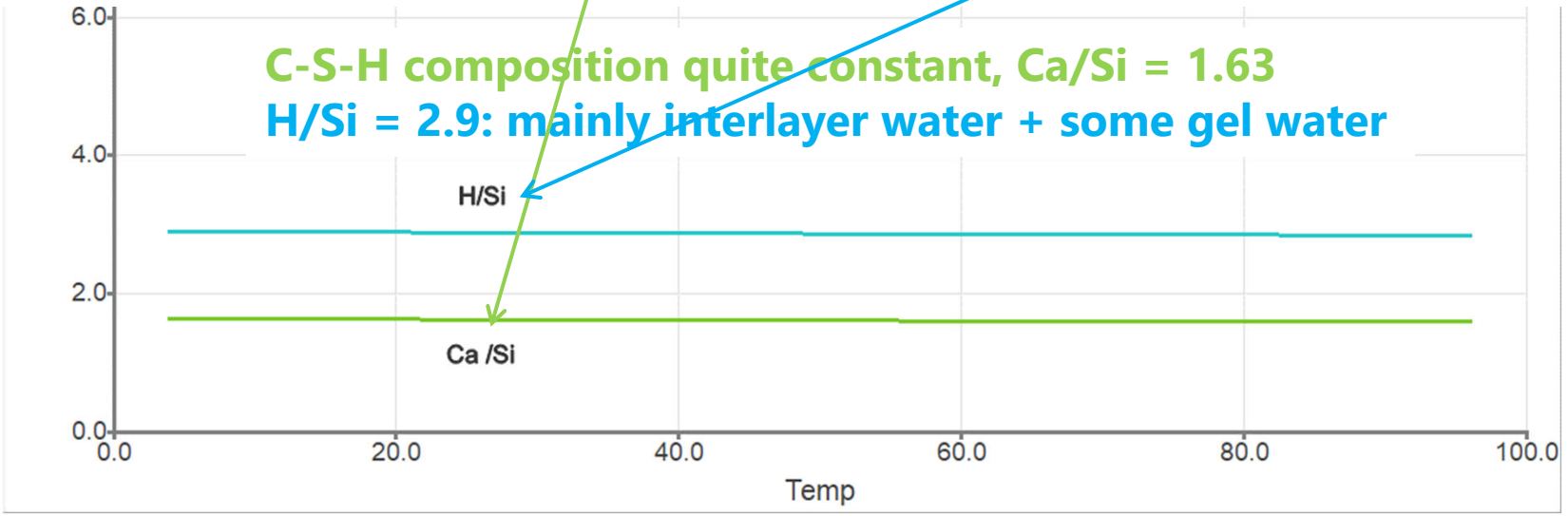
14+lg(my[{OH-}]) equals pH at 25 °C
=> to illustrate temperature effect on pH:

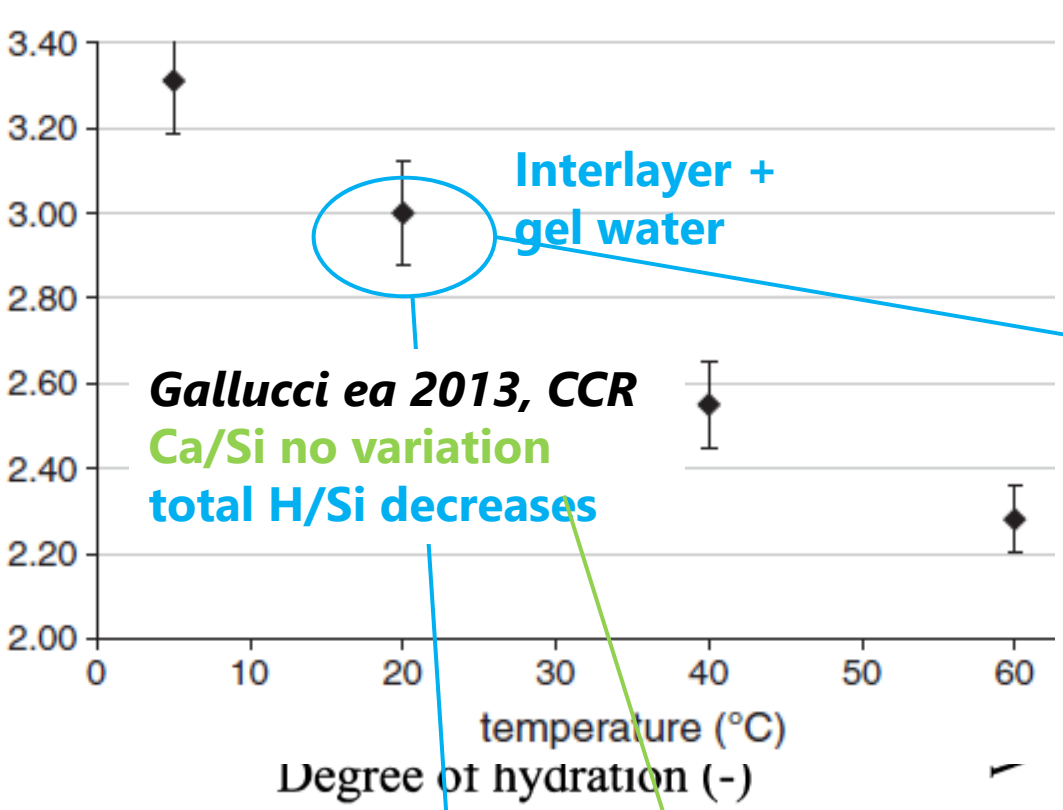
Tutorial: Effect of temperature on PC hydration




a.
Ca/(Si+Al) ratio in C-S-H (-)
Degree of hydration (-)
2.0
1.8
1.6
1.4
1.2
1.0
0.0
0.2
0.4
0.6
0.8
1.0


b.
Water bound in C-S-H / Si chain unit
Degree of hydration (-)
Interlayer
+
gel water
Muller ea 2013
J Phys Chem C
Interlayer water
8
6
4
2
0
0.0
0.2
0.4
0.6
0.8


C-S-H composition quite constant, Ca/Si = 1.63
H/Si = 2.9: mainly interlayer water + some gel water
H/Si
Ca /Si
Temp
6.0
4.0
2.0
0.0
0.0
20.0
40.0
60.0
80.0
100.0

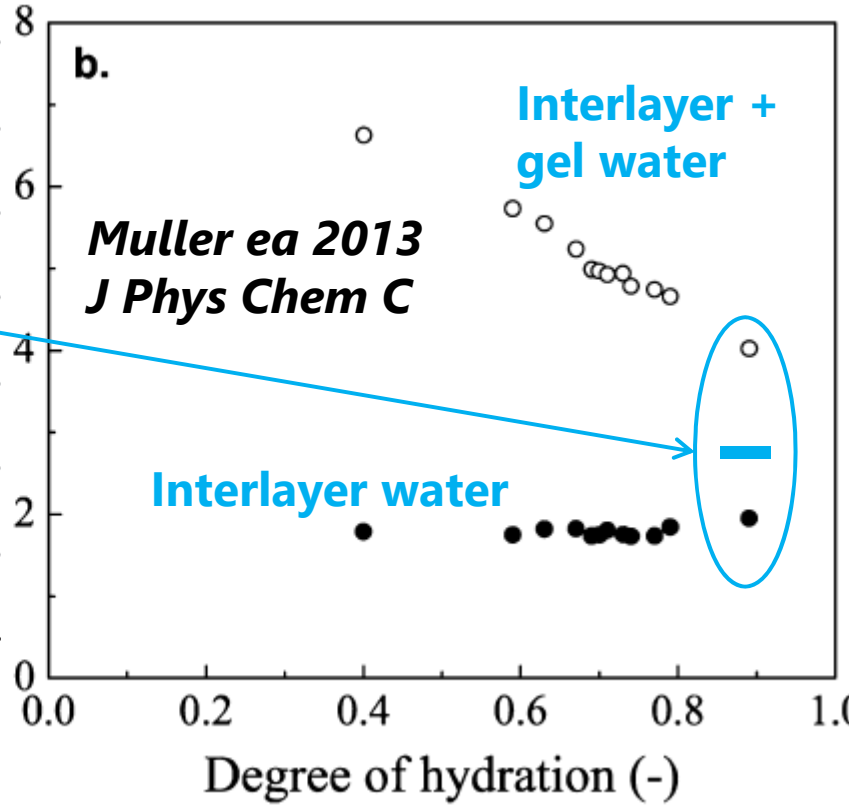


Interlayer + gel water

Gallucci ea 2013, CCR

Ca/Si no variation

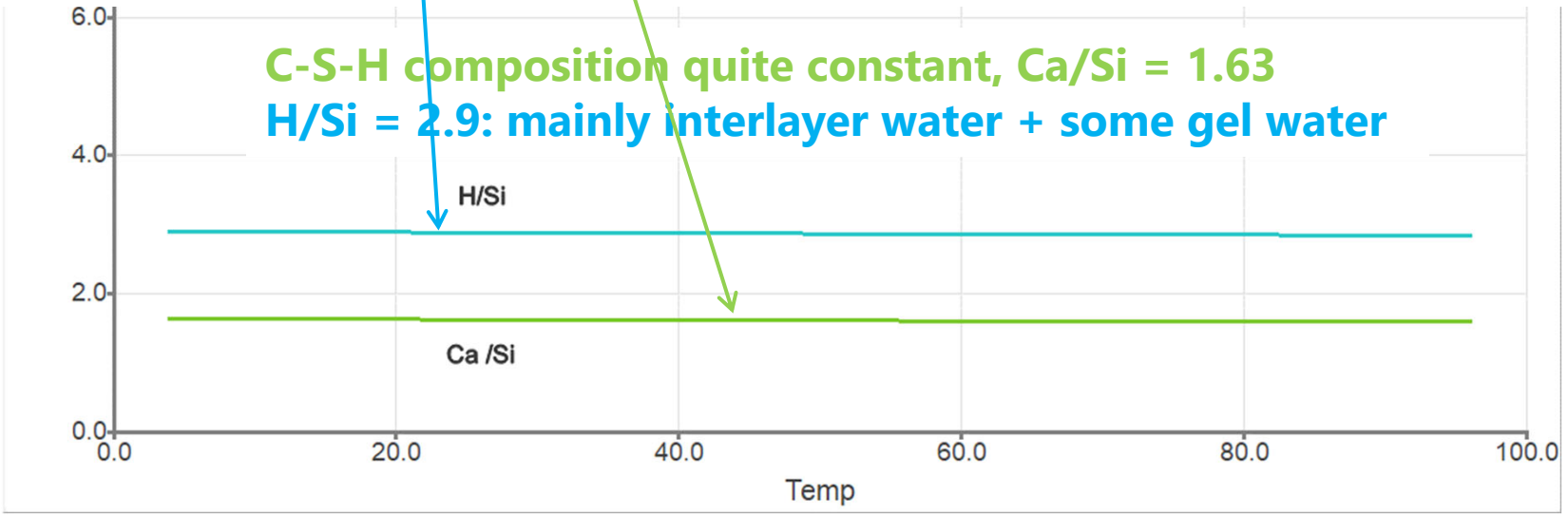
total H/Si decreases



Interlayer + gel water

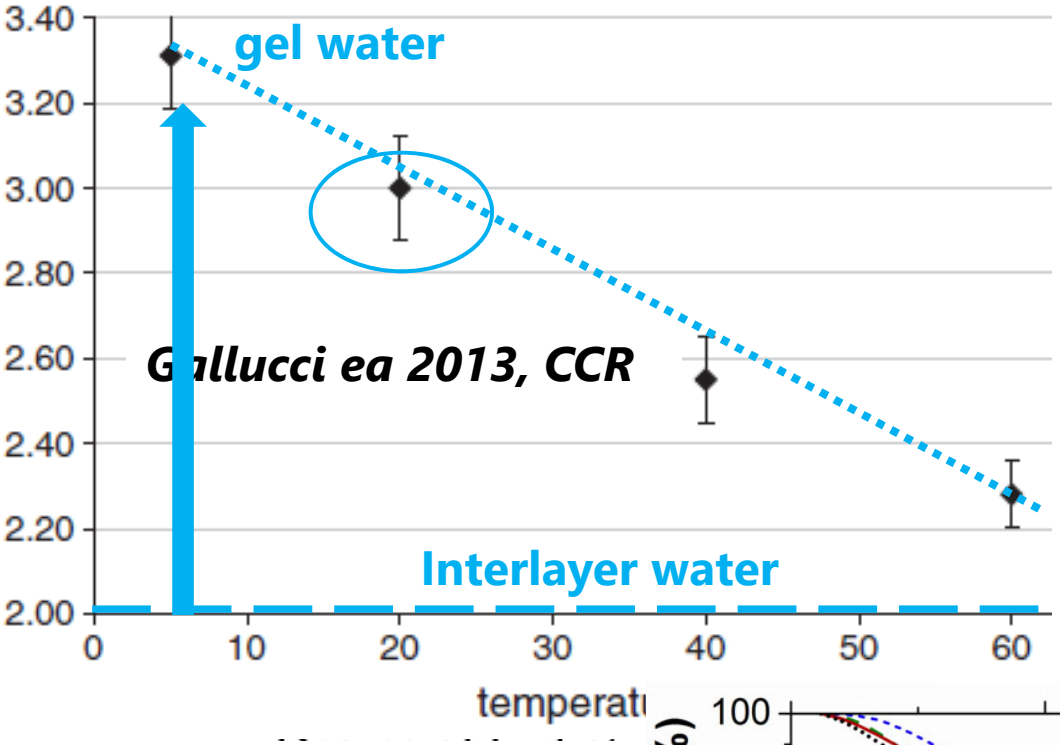
Muller ea 2013
J Phys Chem C

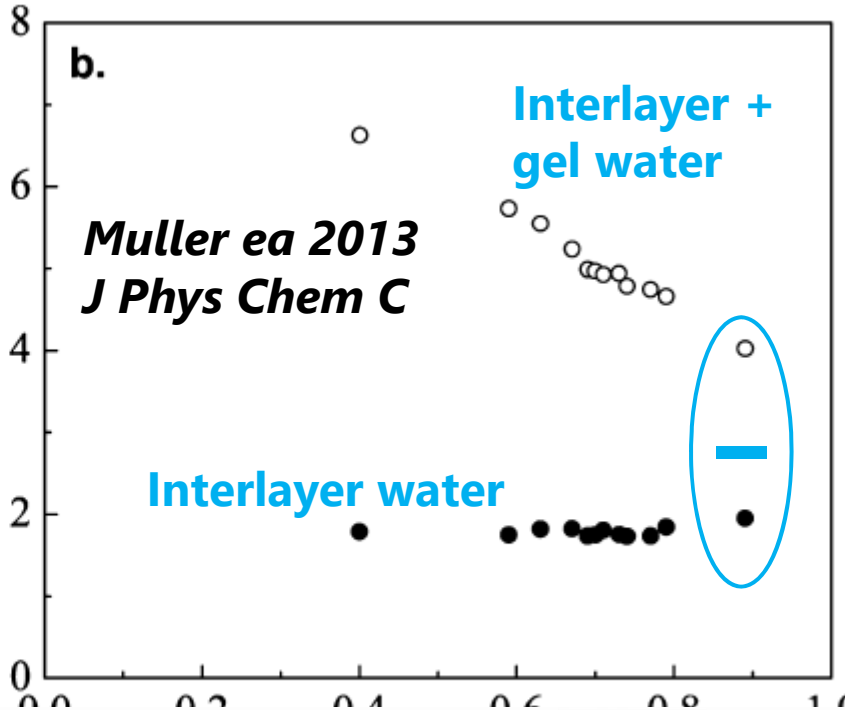
Interlayer water



C-S-H composition quite constant, Ca/Si = 1.63

H/Si = 2.9: mainly interlayer water + some gel water





⇒ **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, …