

Lecture 10

Hydrated Portland cement



Effect of temperature

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Software development/fitting
tools/kinetic:

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Dan Miron

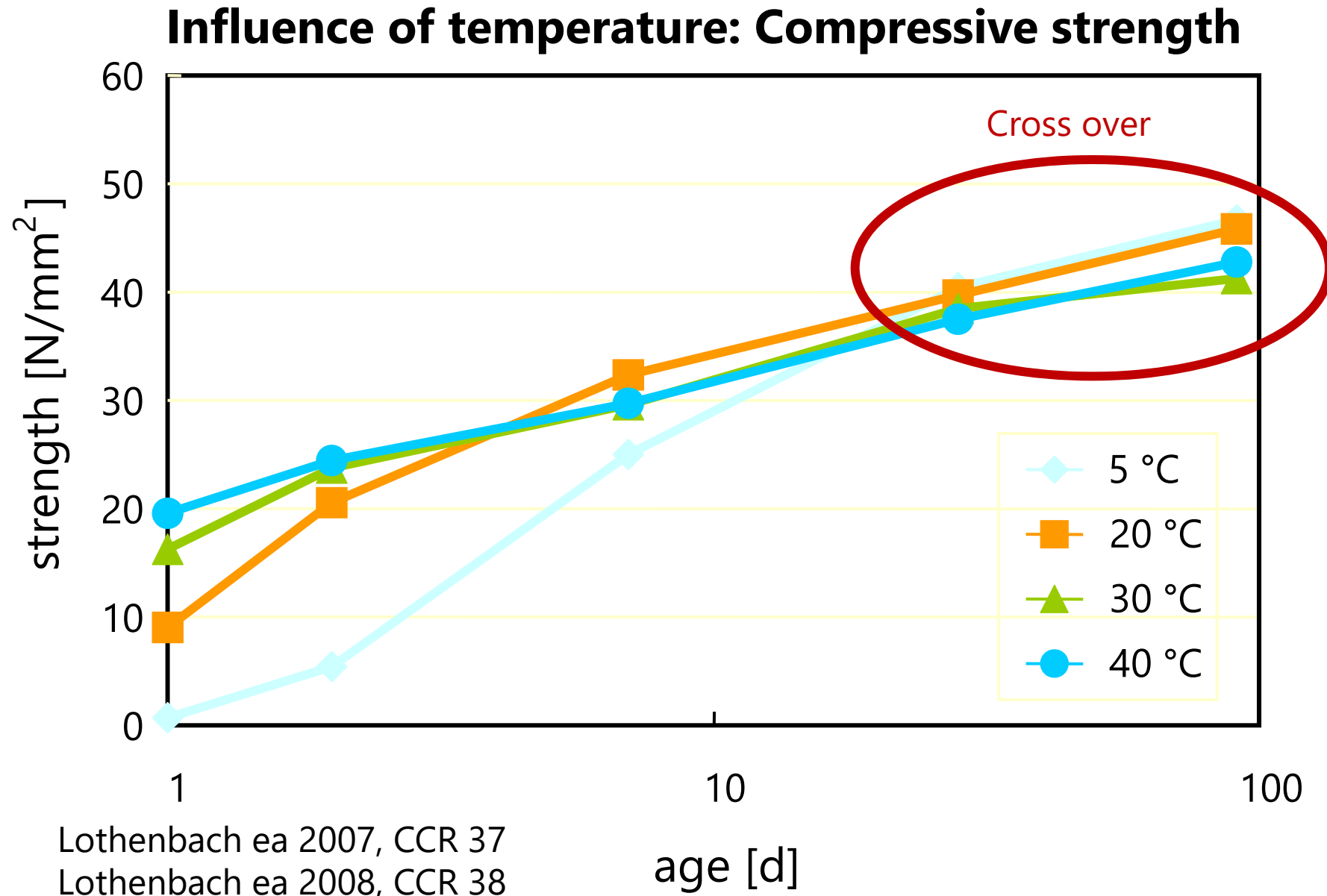


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Hydration of Portland cement at different temperatures

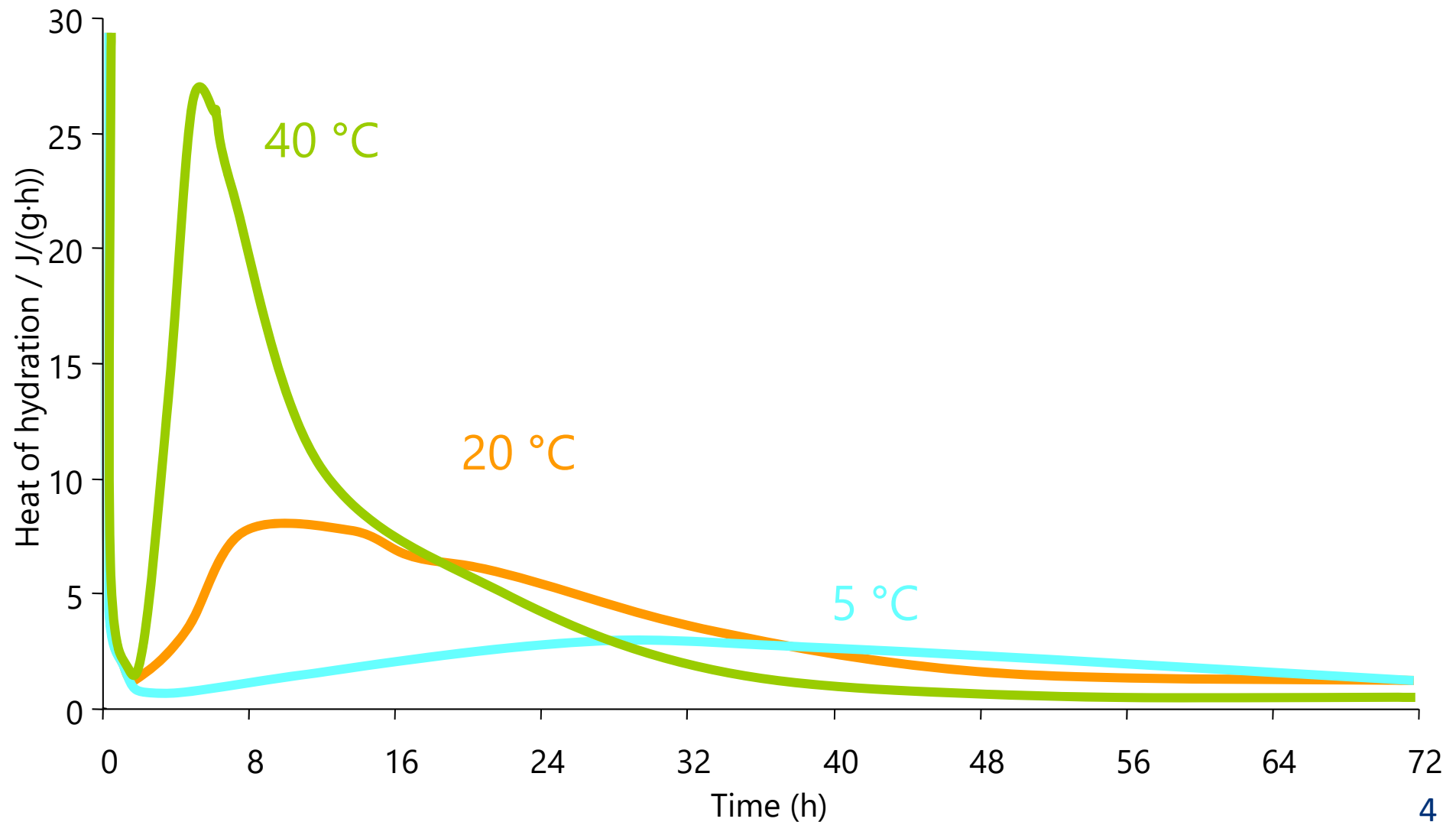
- 1) Experimental evidences
- 2) Temperature calculation in GEMS
(Limestone-blended cement)

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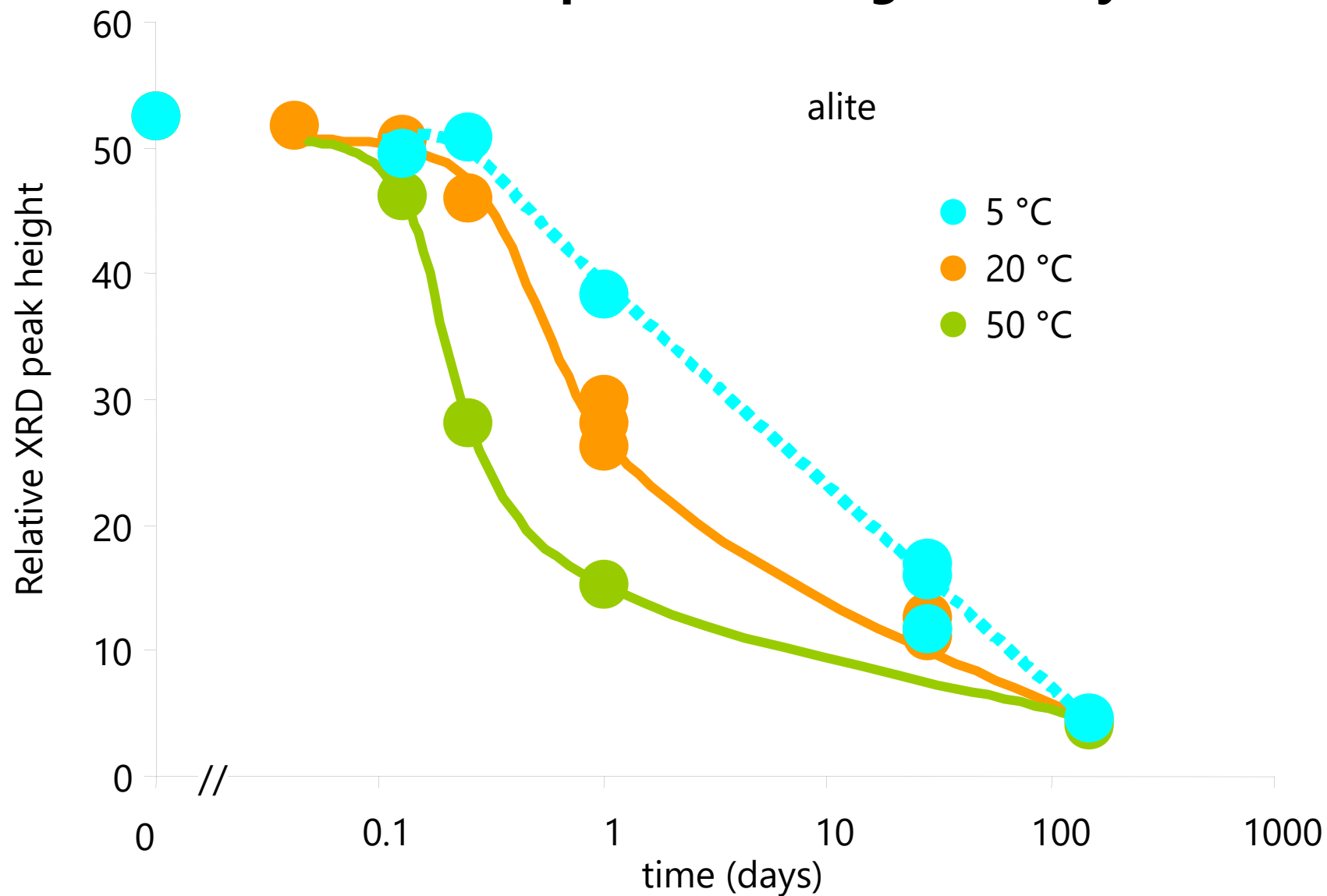
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Influence of temperature: Isothermal calorimetry



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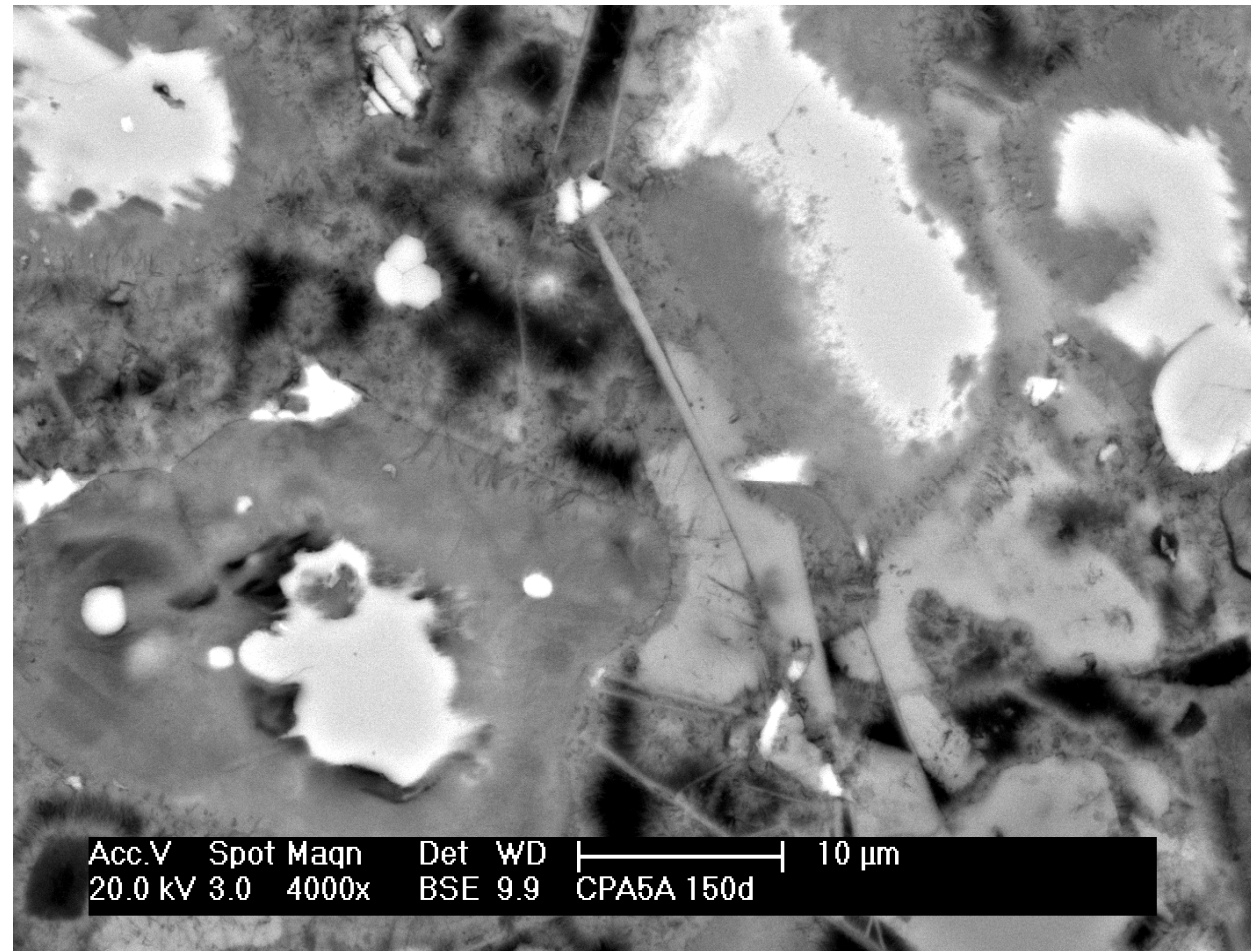
Influence of temperature: Progress of hydration



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Influence of temperature: Microstructure

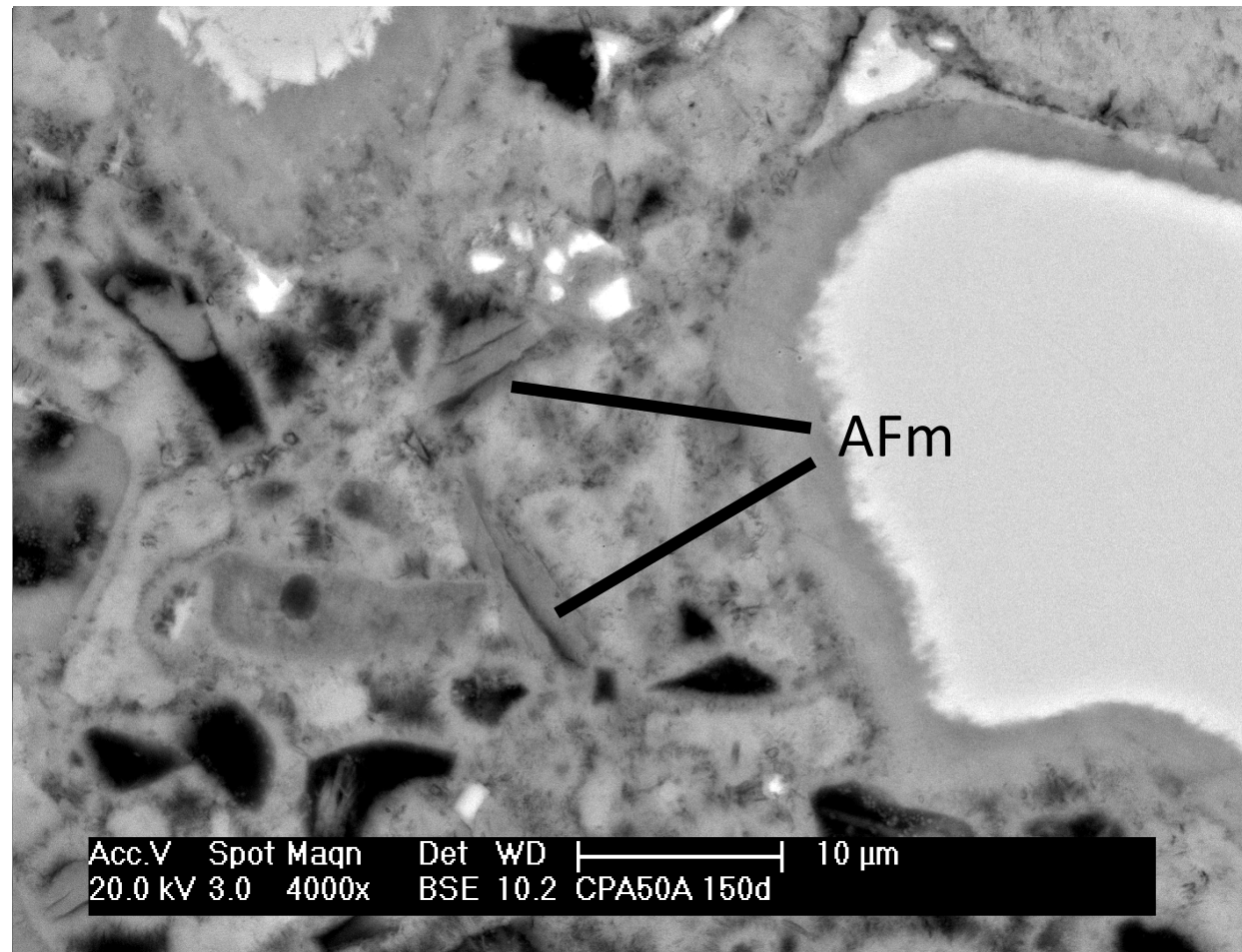
5°C, 150 days



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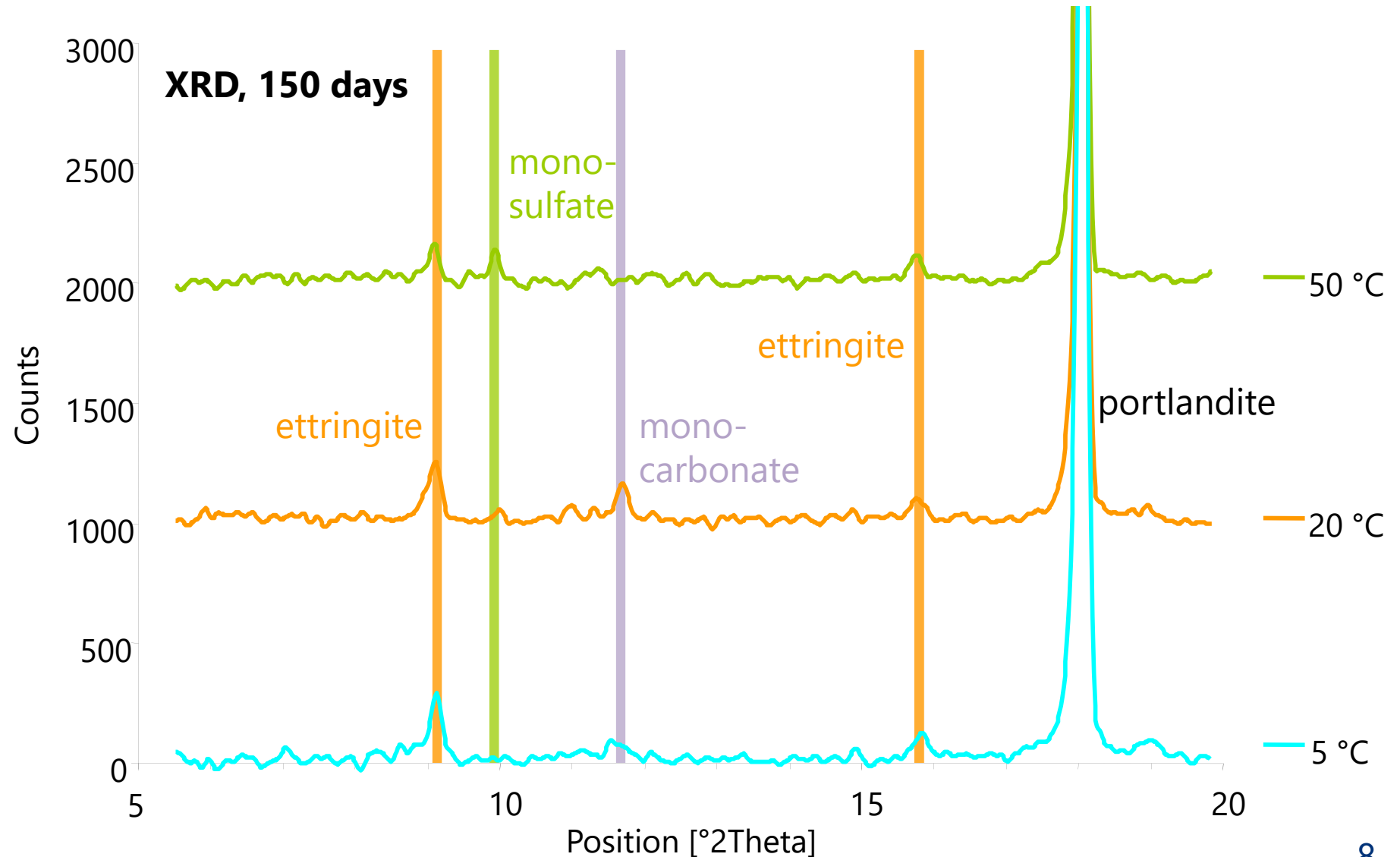
Influence of temperature: Microstructure

50°C, 150 days



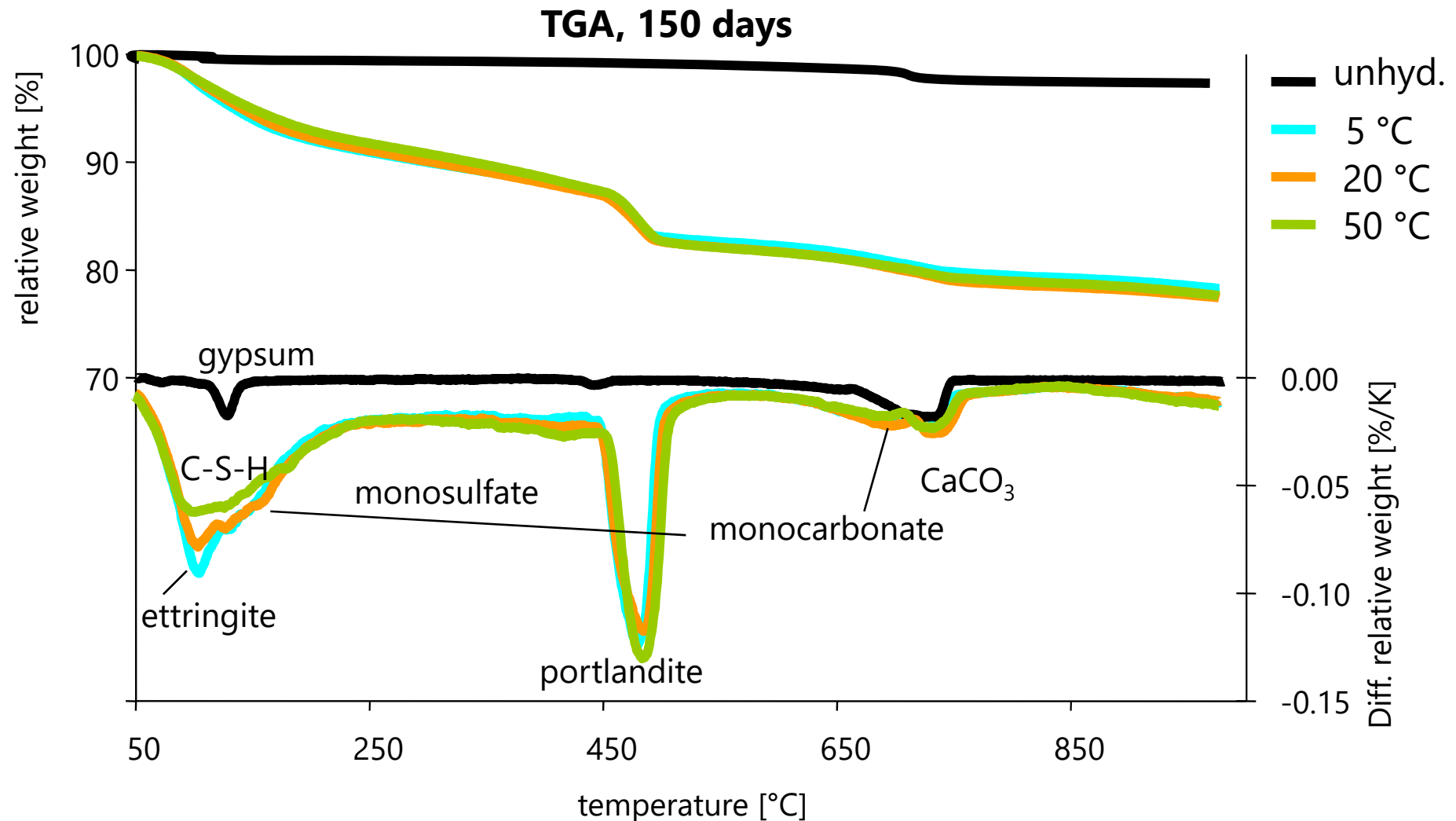
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Influence of temperature: Hydrate assemblage



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Influence of temperature: Hydrate assemblage



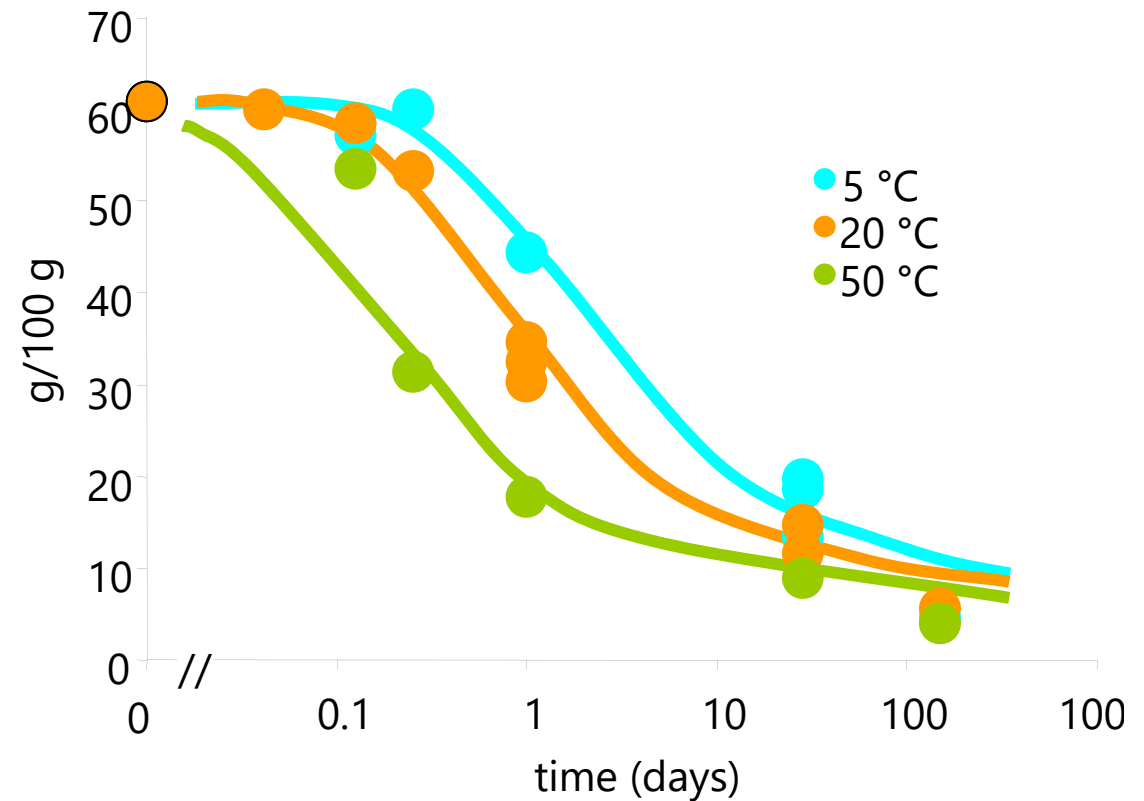
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Modelling: Temperature

Arrhenius equation

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

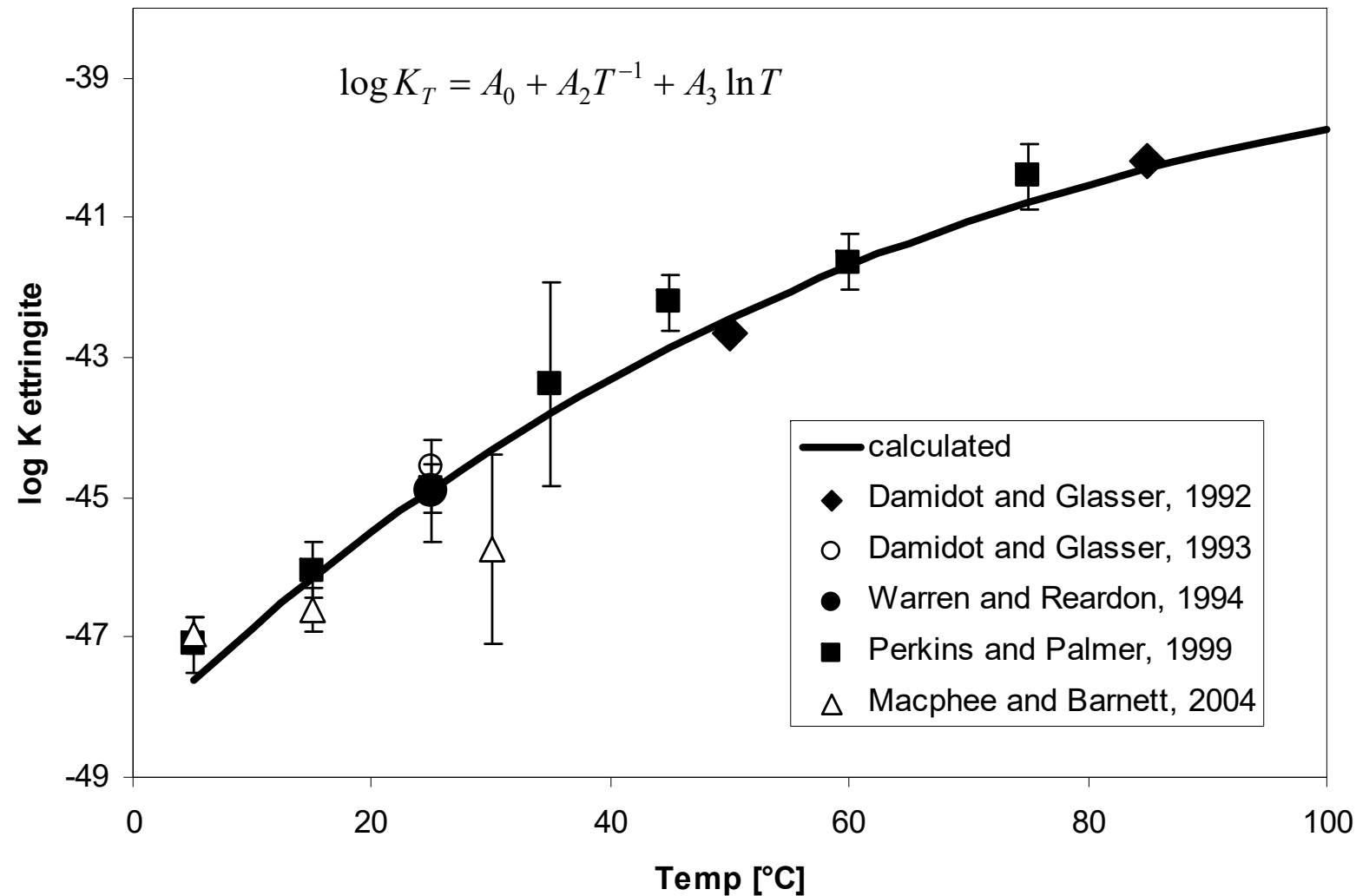
E_a : activation energy



Chemical reactions accelerate with increasing temperature

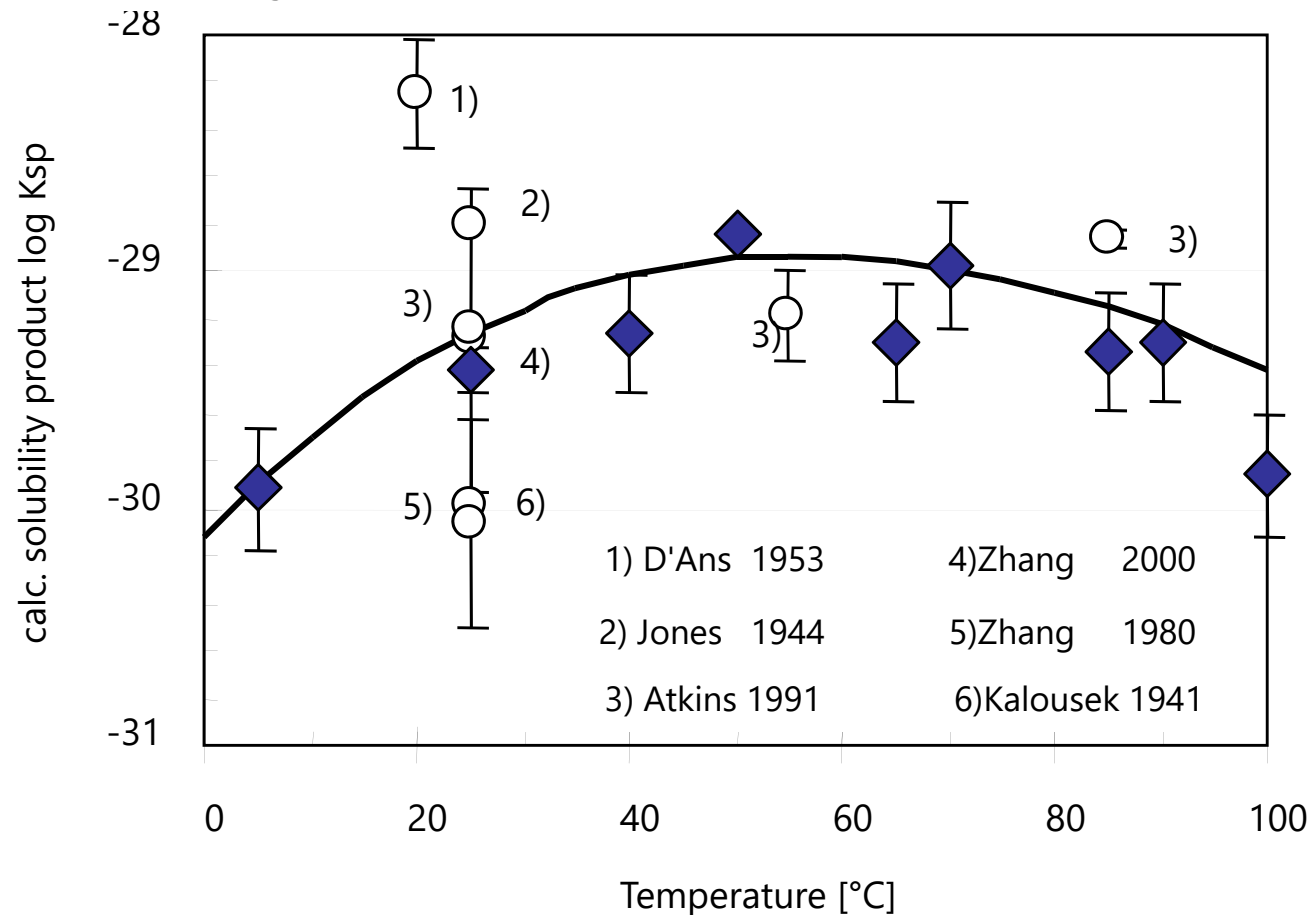
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Solubility of ettringite as f(T)



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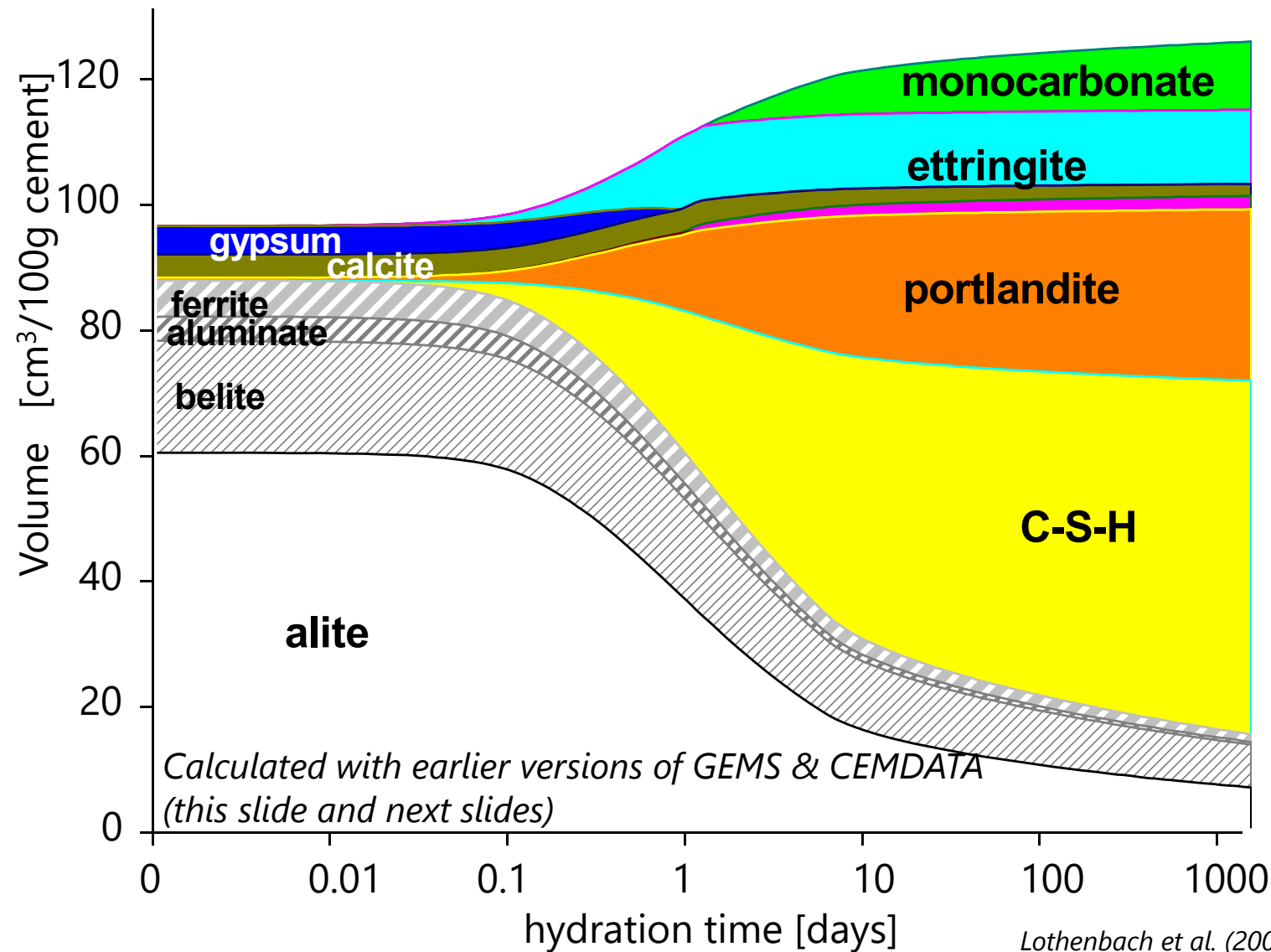
Solubility of monosulfate as f(T)



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

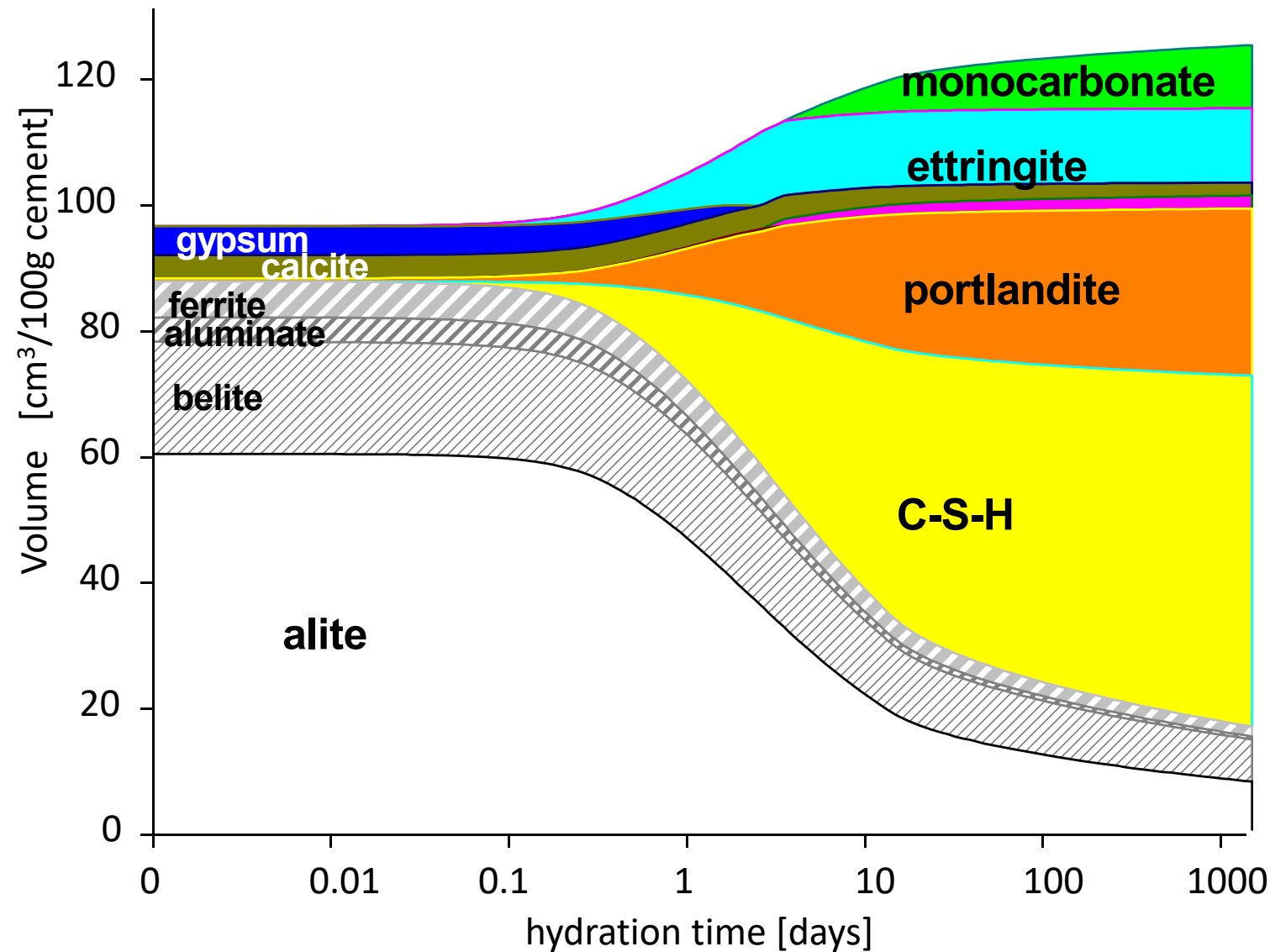
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Hydration: 20°C



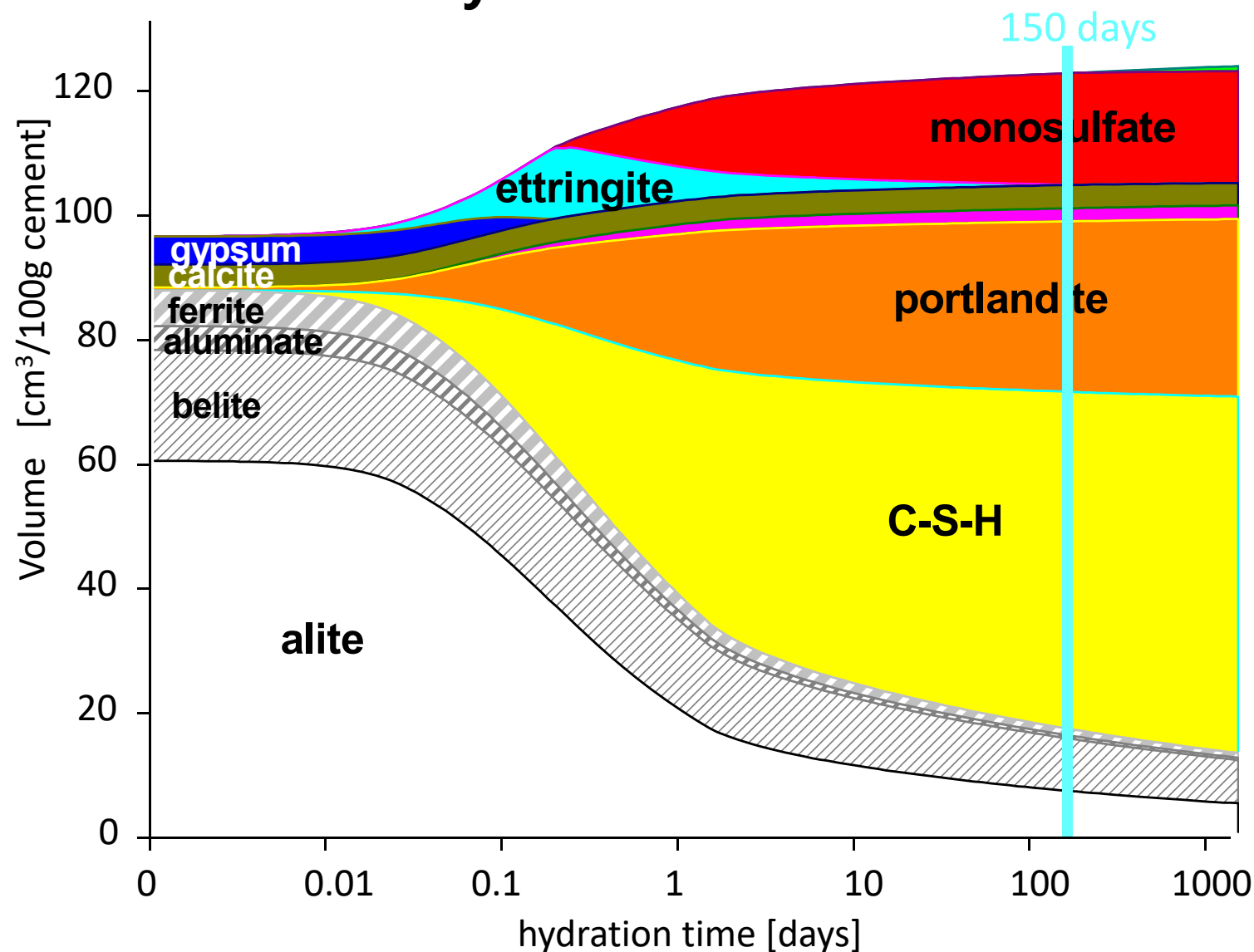
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Hydration: 5°C



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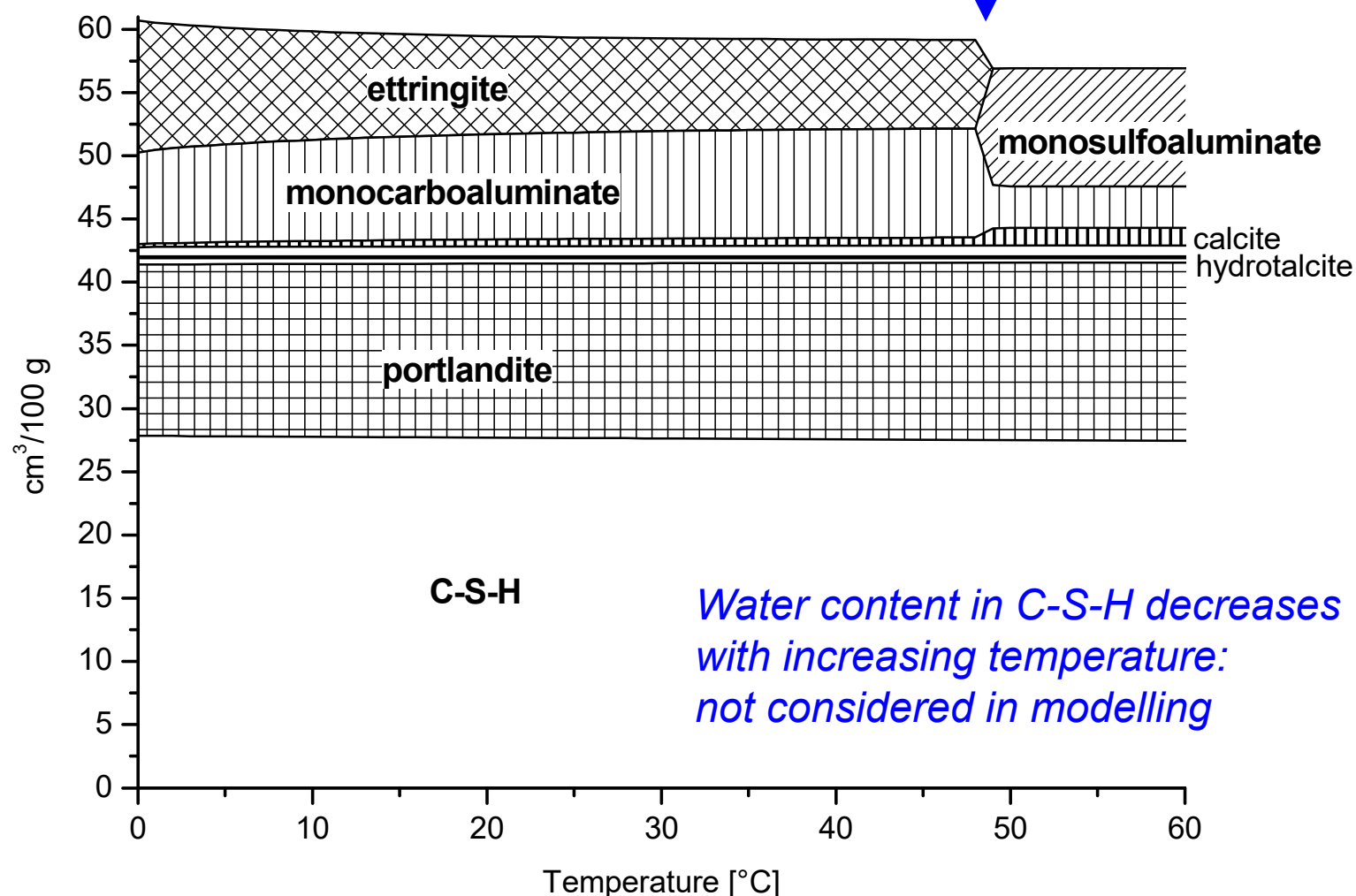
Hydration: 50°C



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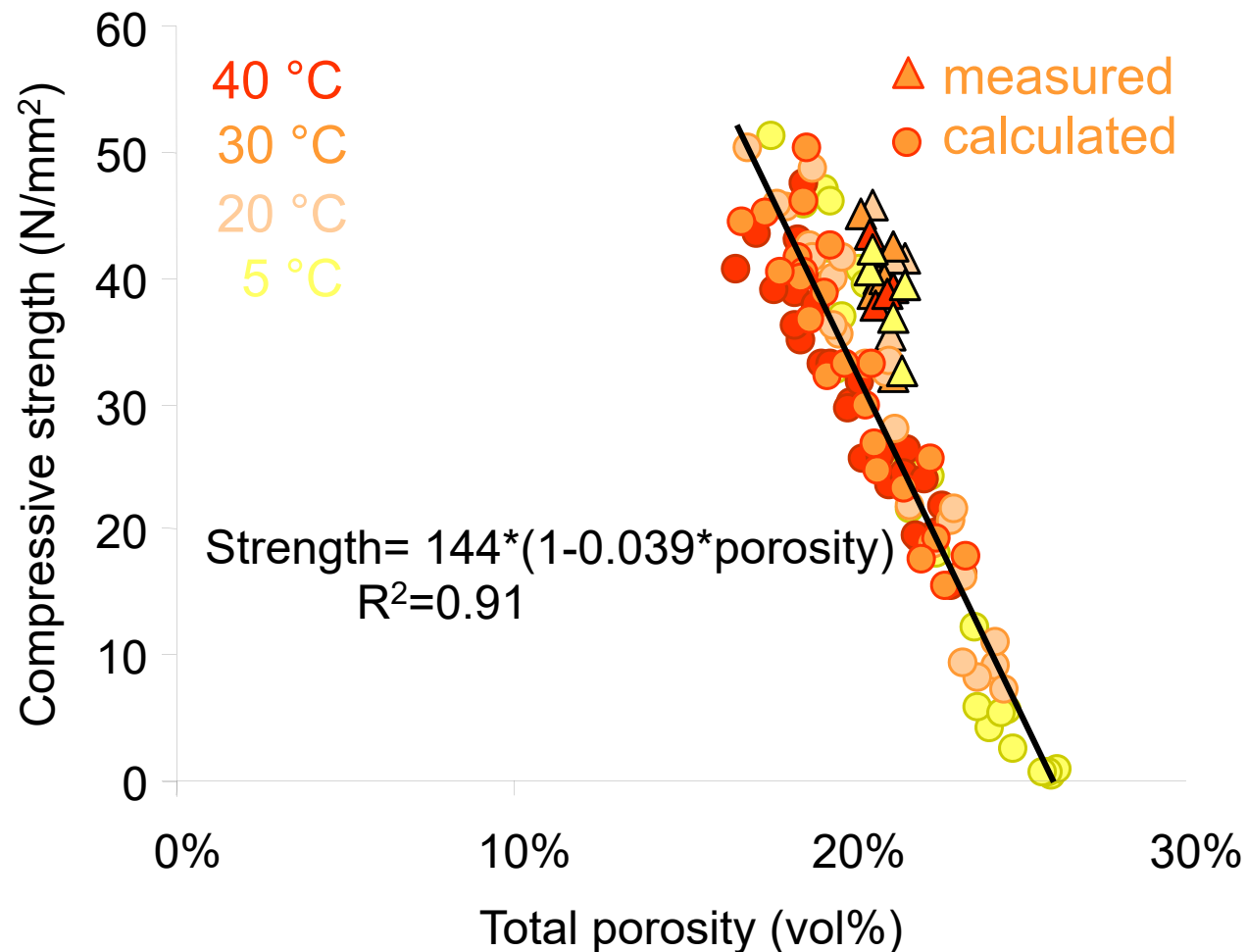
Hydrated OPC: $f(T)$

Calculated with a previous version of CEMDATA



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Hydrated OPC: strength vs. calculated porosity (GEMS)



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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

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

Some O₂ to ensure oxidizing conditions

19

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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

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

The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The main window is titled "GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]". The "Process" module is selected in the left sidebar. A red circle highlights the "Process" icon in the sidebar. Another red circle highlights the "Create a new record from scratch" button in the top toolbar. A dialog box titled "Process: Please, set a new record key" is open, showing the following fields:

- Record key: PC:G:PC2:0:0:1:20:0:PC_temp:P:
- PC: Name of the modeling project
- G: Thermodynamic potential to minimize {G}
- PC2: Name of the parent chemical system definition (CSD)
- 0: CSD (recipe) variant number <integer>
- 0: Volume of the system, dm3
- 1: Pressure, bar, or 0 for Psat(H2O)g
- 20: Temperature, C
- 0: Variant number for additional constraints
- PC_temp: Name of this process simulation task
- P: Process simulation mode code { P, S, L, G, T, R }

A red circle highlights the "PC_temp" field, and a green circle highlights the "P" field. To the right of the dialog box, there is a table with the following data:

iNv	iTau	ipXi	iNu
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

name
temperature and pressure variation

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Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, irreversible geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) can be simulated.

The Process record can be configured in several modes to perform specific simulation scenarios by execution of process control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be easily produced using this wizard.

Any process simulator belongs to one of three types:

1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from previous step (mode R);
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; modes G, T).

Please, choose a process simulation mode: —

- ☒ P Sequential temperature and/or pressure change at fixed bulk composition
- ☐ S Direct sequential change of bulk composition and/or constraints (default)
- ☐ G Batch inverse titration sequence for incremented pH values etc.
- ☐ T One arbitrary inverse titration calculation as defined in Process control script
- ☐ R Sequential reactor scheme, uses equilibrium bulk compositions of phases
- ☐ L Lippmann diagram (transposed) for a binary solid solution

**Temperature and
pressure variation**

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< Back

Next >

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Step 2 - Process Simulation Controls (click 'Next' to retain the old script)

	iTm	iV	iP	ITC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	4	0	0	0	0	0	0
Unt	1200	0	1	96	0	0	0	0	0	0
Step	1	0		2	0	0	0	0	0	0

☒ No script
 ☐ User-defined script
 ☐ PT phase diagram

Please, check iP and iT iterator contents, and set Step to 0 in all other iterators.

For PT phase diagram: select phases to plot, then skip the next wizard page.

Phases

aq_gen	C3AH6	Iron
gas_gen	C4AH13	Fe-carbonate
CSHO	CAH10	Siderite


**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

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 GEM-Selektor Process Setup: PC:G:PC2:0:0:1:20:0:PC_temp:P:
 ✕

Step 4 - Important data object dimensions

Spin boxes below define the dynamic memory configuration of the process simulator.

Dimensions of sampled and experimental data

47

nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' vector.

1

Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be nPS.

14

Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.

1

Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.

0

Number of rows in the xEp, yEp arrays for experimental data (optional)

0

Number of columns in the xEp, yEp arrays for experimental data (optional)

Optional data vectors (of length nPS) can be used for accumulating current process control values for all steps performed. They can be allocated using checkboxes below. The assignment operator (with J index) in the script will override any values automatically copied into data vector from the respective process iterator.

Allocation of optional data vectors

☐ CSD variant # ('vTm')
 ☐ Volume V, l ('vV')
 ☐ Pressure P, bar ('vP')

☐ Temperature T ('vT')
 ☐ Constraints # ('vNV')
 ☐ Process extent Nu ('vNu')

☐ Process extent pXi ('vpXi')
 ☐ Kinetic parameters ('vKin')
 ☐ Time Tau ('vTau')

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< Back
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Controls	Sampling	Results	Config	04/06/2023, 15:28
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NeIt	9999	47	Next	0	I	0	J	46	Jp	46
------	------	----	------	---	---	---	---	----	----	----

pSTkey PC:G:PC2:0:0:1:20:0:

cTm	1000	cNV	0
-----	------	-----	---

cTau	0	cpXi	0	cXi	1	cNu	0
------	---	------	---	-----	---	-----	---

cpH	0	cpe	0	cEh	0	cT	369.15
-----	---	-----	---	-----	---	----	--------

cT: Temperature in K

```

xp[J] =: cTC;
$ y-axis in g per 100 g unhydrated cement
yp[J][0] =: phVol[{CSHQ}];
yp[J][1] =: phVol[{Portlandite}];
yp[J][2] =: phVol[{C3(AF)S0.84H}];
yp[J][3] =: phVol[{ettringite}]+phVol[{SO4 CO3 AFt}]+phVol[{CO3_SO4_AFt}];
yp[J][4] =: phVol[{C4AsH16}];
yp[J][5] =: phVol[{C4AsH14}];
yp[J][6] =: phVol[{C4AsH12}]+phVol[{SO4_OH_AFm}]+phVol[{OH_SO4_AFm}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: phVol[{C4Ac0.5H12}];
yp[J][10] =: phVol[{C4AcH11}];
yp[J][11] =: phVol[{Calcite}];
yp[J][12] =: phVol[{OH-hydrotalcite}];
yp[J][13] =: phVol[{aq_gen}];
  
```

cTC: Temperature in °C

We differentiate between the water contents of monosulfate

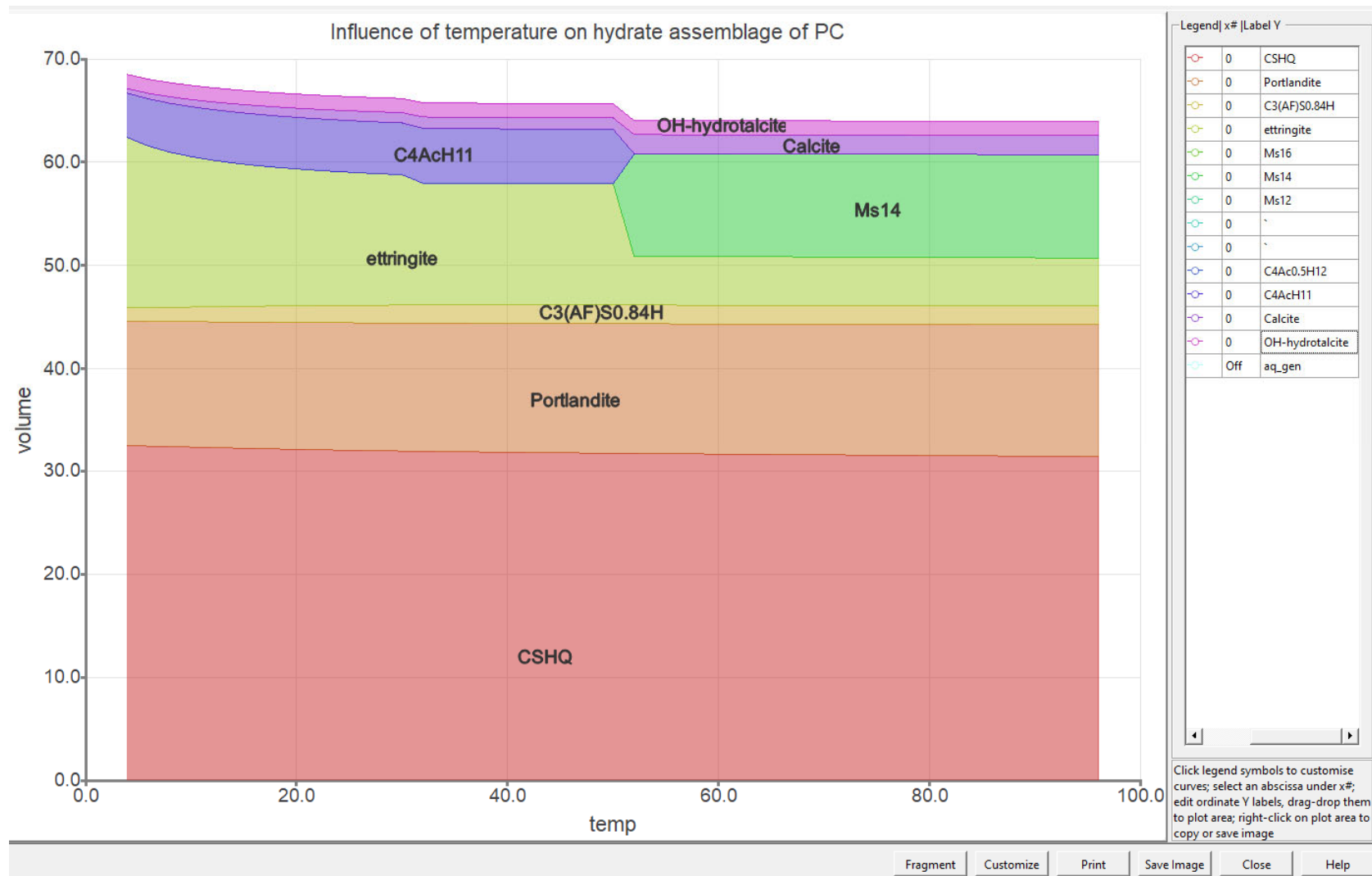
The rest of the output we leave like it is

pX_Nam	temp
--------	------

pLnam	C3 (AF) S0.84H	ettringite	Msl6	Msl4	Msl2	---
-------	----------------	------------	------	------	------	-----

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- Calculate and make a nice cumulative plot



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

Step 2 - Process Simulation Controls (click 'Next' to retain the old script)

	iTm	iV	iP	ITC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	4	0	0	0	0	0	0
Unt	1200	0	1	96	0	0	0	0	0	0
Step	1	0		2	0	0	0	0	0	0

☒ No script
 ☐ User-defined script
 ☐ PT phase diagram

Please, check iP and iT iterator contents, and set Step to 0 in all other iterators.

For PT phase diagram: select phases to plot, then skip the next wizard page.

Phases

aq_gen	C3AH6	Iron
gas_gen	C4AH13	Fe-carbonate
CSHO	CAH10	Siderite

**Numbering
of the single
calculations**

**Start temperature
Stop temperature
Step size**

**No script
needed**

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GEM-Selektor Process Setup: PC:G:PC2:0:0:1:20:0:PC_temp_CSH:P:

Step 3 - Selection of items to sample/plot (click "Next" without selecting anything to retain the old script)

Property

Scalars

- u
- ue
- b
- Cb
- m_t
- lgm_t
- icM
- Xa
- Xwa
- phVol
- phM
- Fa
- bXa(aq_gen)
- bXa(gas_gen)
- bXa(C3(AF)SC)
- bXa(CSHQ)
- bXa(straetlin)
- bXa(ettringite)
- bXa(SO4_OH)
- bXa(OH_SO4)
- bXa(SO4_CO)

Item Selection

Mbx	_nnr[0]	F_RT	Fi_[3]	iTC[
pmXs	_nnr[1]	Xw	T	iTC[
GX	L[0]	Masses[0]	P	iTC[
IS	L[1]	Masses[1]	RTf[0]	cTC
pH	L[2]	Masses[2]	RTf[1]	cT
pe	L[3]	Masses[3]	RoW[0][0]	iNv[
Eh	L[4]	Masses[4]	EpsW[0][0]	iNv[
TC[0]	L[5]	Masses[5]	VisW[0]	iNv[
TC[1]	Fi[0]	Volums[0]	iTm[0]	cNv
TK[0]	Fi[1]	Volums[1]	iTm[1]	iTau
TK[1]	Fi[2]	N_	iTm[2]	iTau
PG[0]	Fi[0]	L_[0]	cTm	iTau
PG[1]	Fi[1]	L_[1]	iV[0]	cTai
Vx[0]	Fi[2]	L_[2]	iV[1]	ipXi
Vx[1]	denW[0][0]	L_[3]	iV[2]	ipXi
It	denW[1][0]	L_[4]	cV	ipXi
ItEfd	epsW[0][0]	L_[5]	iP[0]	cpX
Itlpm	epsW[1][0]	Fi[0]	iP[1]	cXi
Psi_DK[0]	InP	Fi[1]	iP[2]	iNu
Psi_DK[1]	RT	Fi[2]	cP	iNu

Sampling Script

```

xp[J] = J;
yp[J][0] =: pH;
yp[J][1] =: bXa[{CSHQ}][{Ca}];
yp[J][2] =: bXa[{CSHQ}][{Si}];
yp[J][3] =: my[{OH-}];

```

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

**bXa[{CSHQ}][{Ca}]:
mol Ca in C-S-H
solid solution**

**my[{OH-}]:
OH⁻ concentration
(in mol/kg H₂O)**

List of static data objects (see tooltip on each object name)

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Controls	Sampling	Results	Config	04/06/2023, 15:58
----------	----------	---------	--------	-------------------

NeIt	9999	47	Next	0	I	0	J	46	Jp	46
------	------	----	------	---	---	---	---	----	----	----

pSTkey	PC:G:PC2:0:0:1:20:0:	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 C-S-H
yp[J][1] =: bXa[{CSHQ}][{Ca}]/bXa[{CSHQ}][{Si}];
$ plotting H/Si in C-S-H: H/2 = H2O
yp[J][2] =: bXa[{CSHQ}][{H}]/2/bXa[{CSHQ}][{Si}];
$ log OH- conc
yp[J][3] =: 14+lg(my[{OH-}]);
  
```


pX_Nam	Temp
--------	------

pLnam	pH	Ca /Si	H/Si	14-pOH
-------	----	--------	------	--------

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

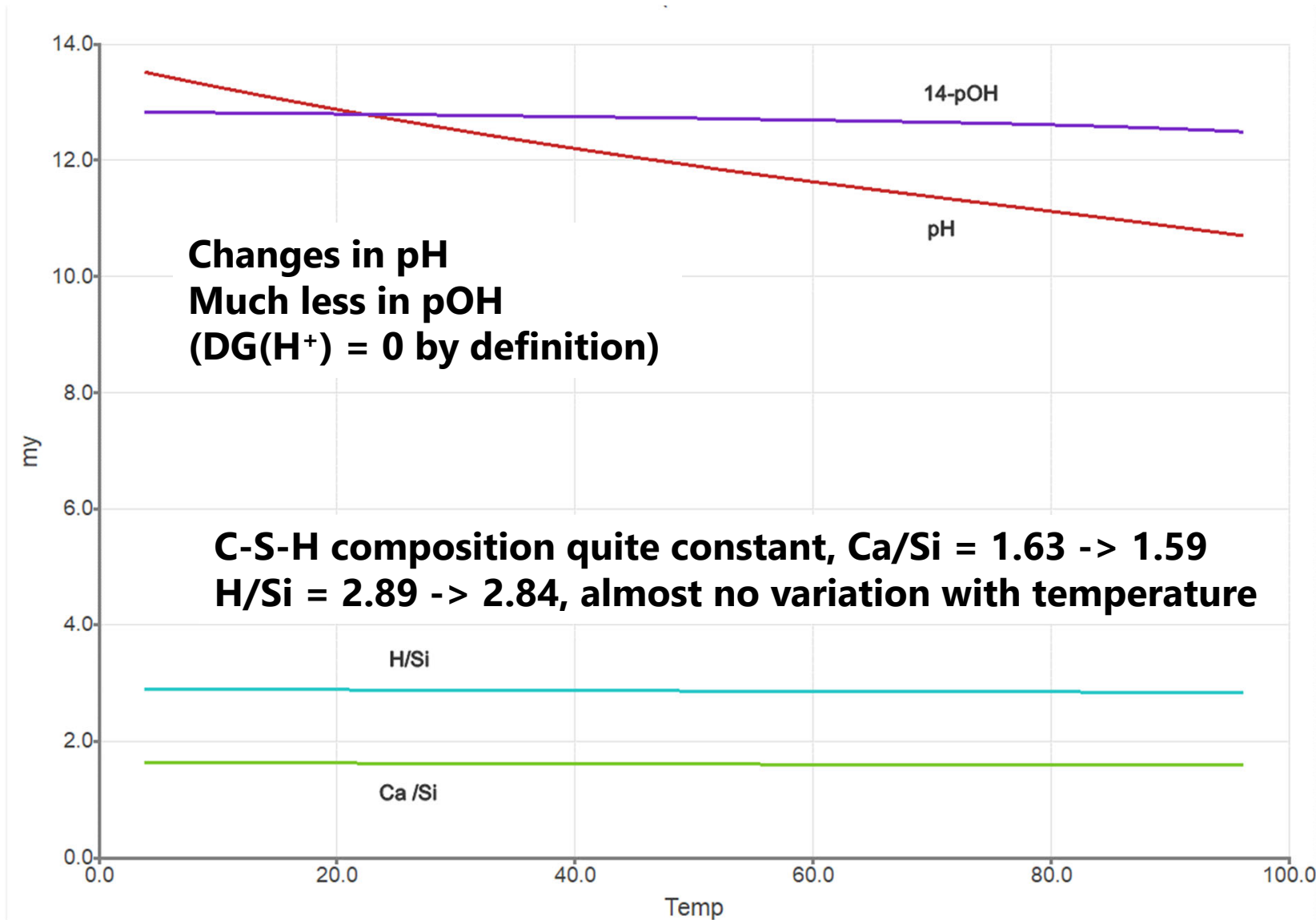
$bXa[CSHQ][H]/2/bXa[CSHQ][Si]$:

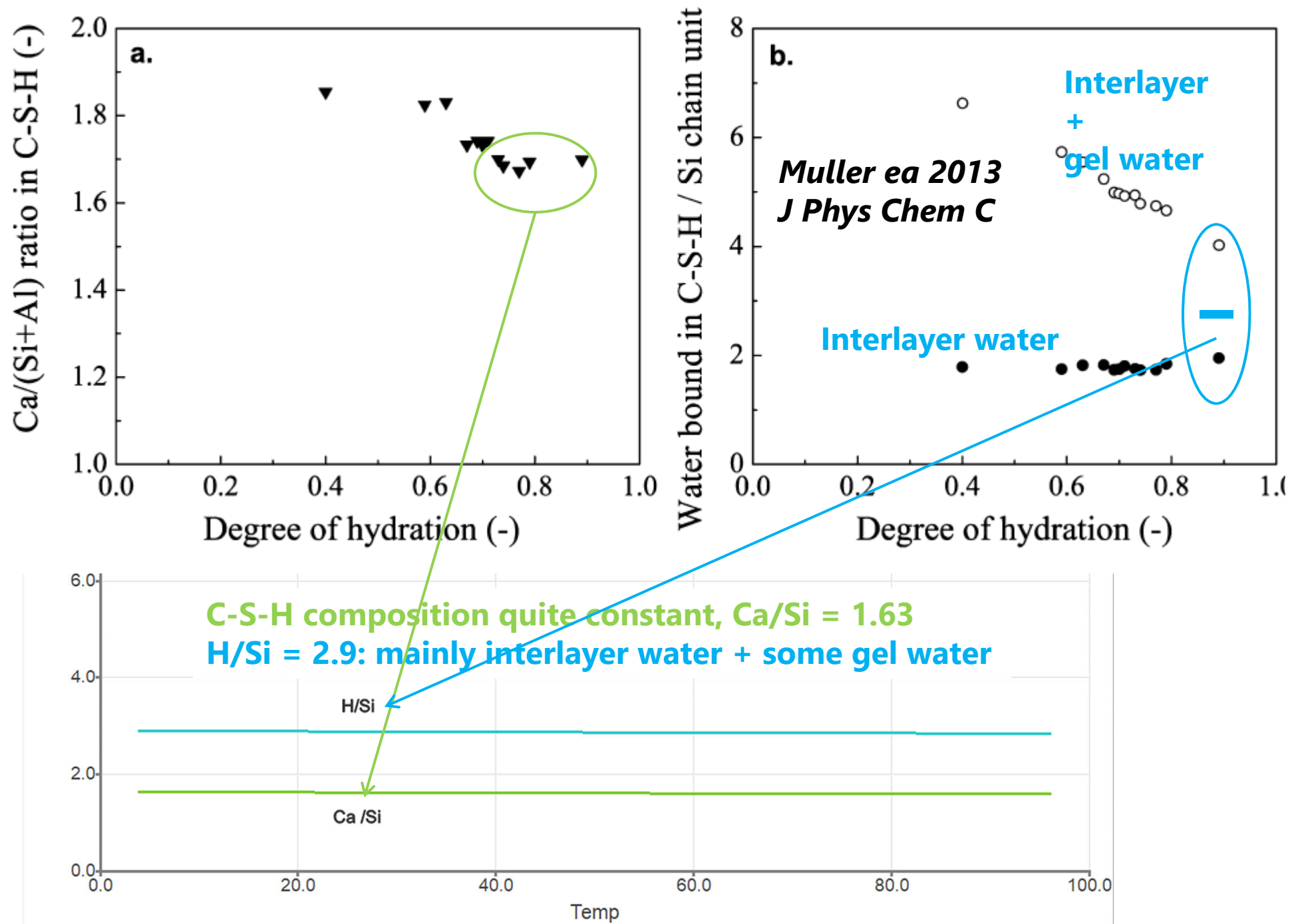
molar H/Si in C-S-H solid solution (H/2 = H₂O)

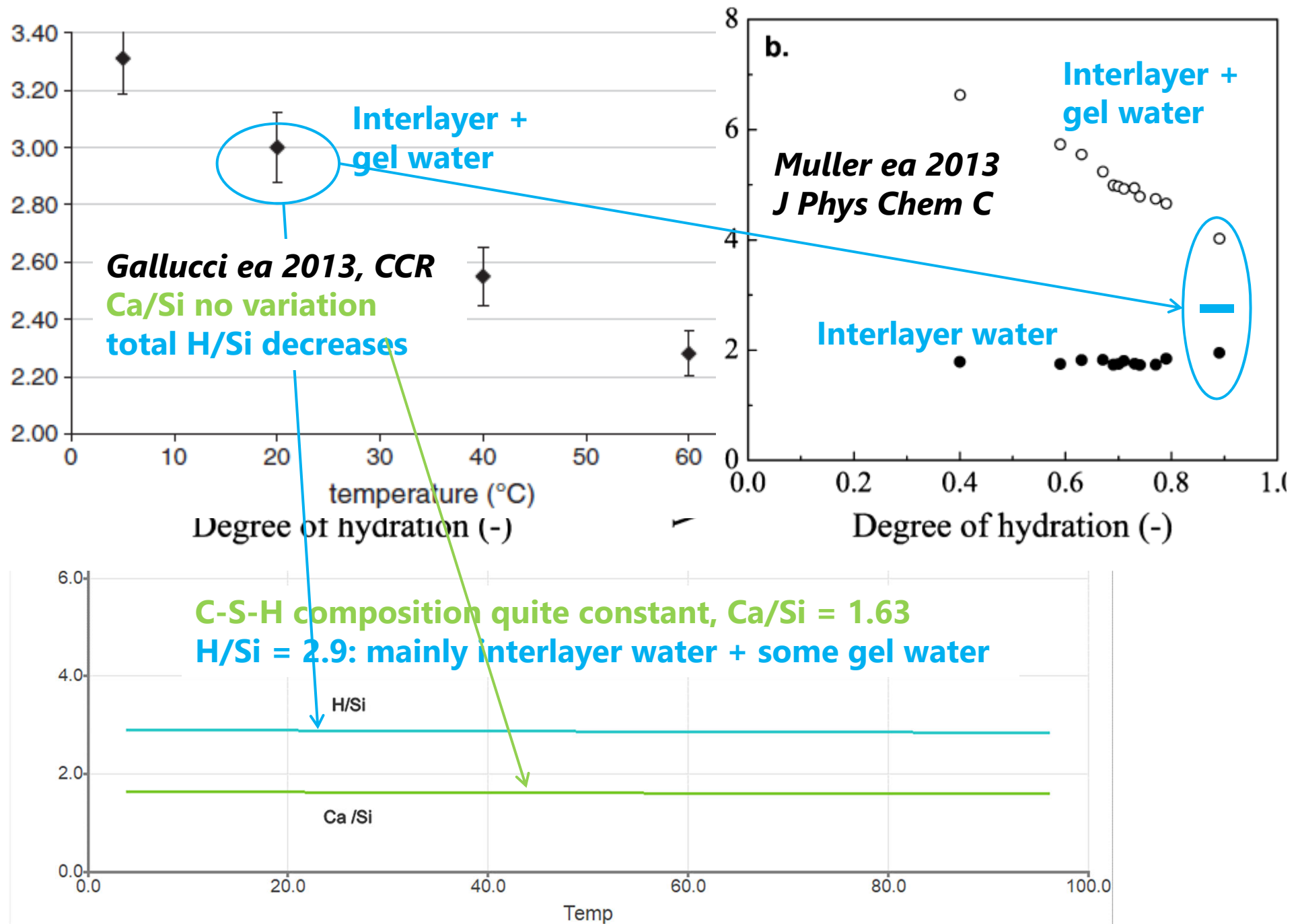
14+lg(my[OH⁻]) equals pH at 25 °C

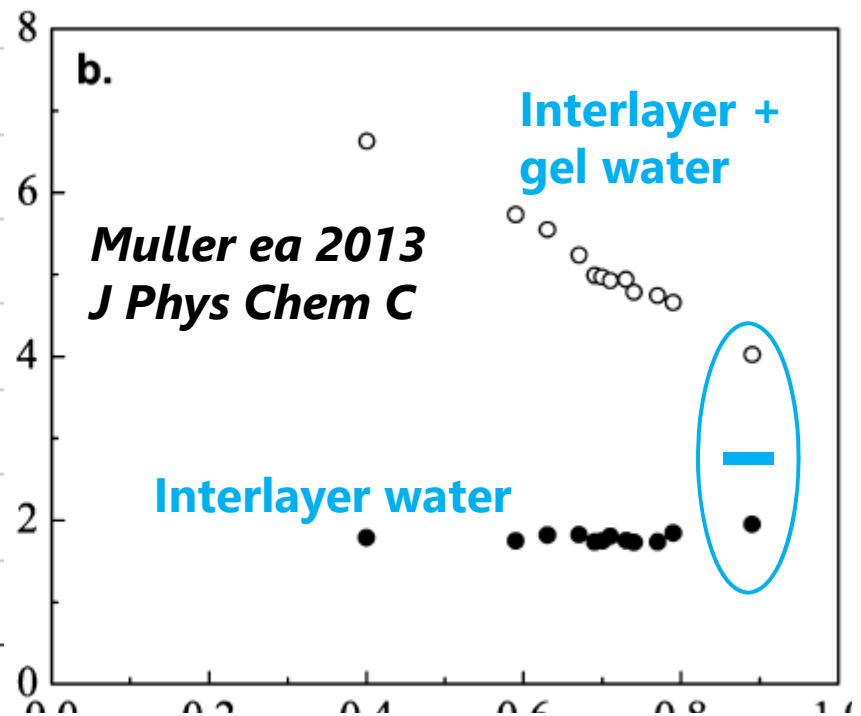
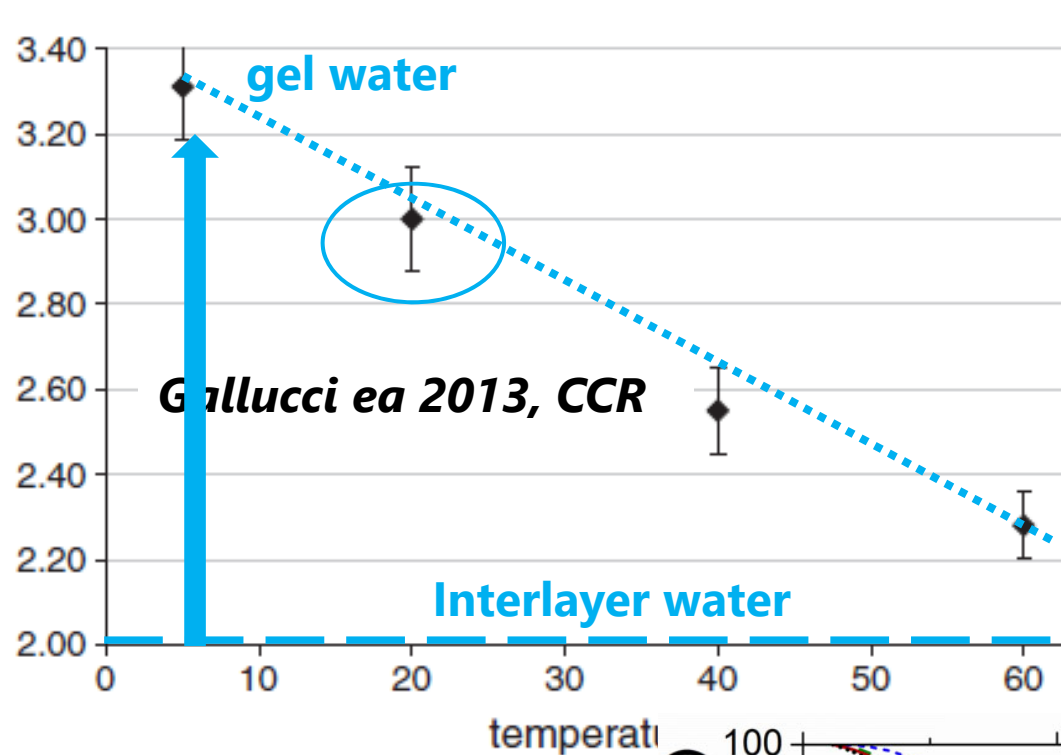
=> to illustrate temperature effect on pH:

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⇒ 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, ...

