

Lecture 04 Database, solubility,



Saturation indices

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Software development/fitting
tools/kinetic:

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Dan Miron



Thermodynamic data

1. Databases

- a. Cement database cemdata18
- b. PC and alkali activated system
- c. GEMS – PHREEQC
- d. «How to» in GEMS

2. Solubility and speciation

3. Saturation indices

4. Hydrates in cement

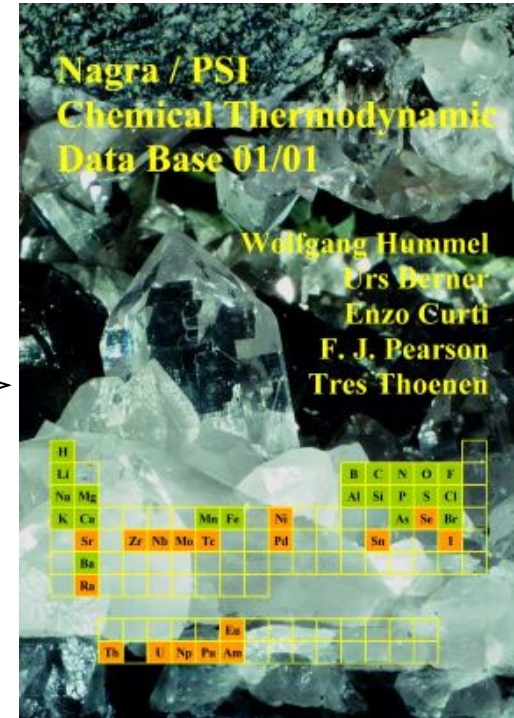
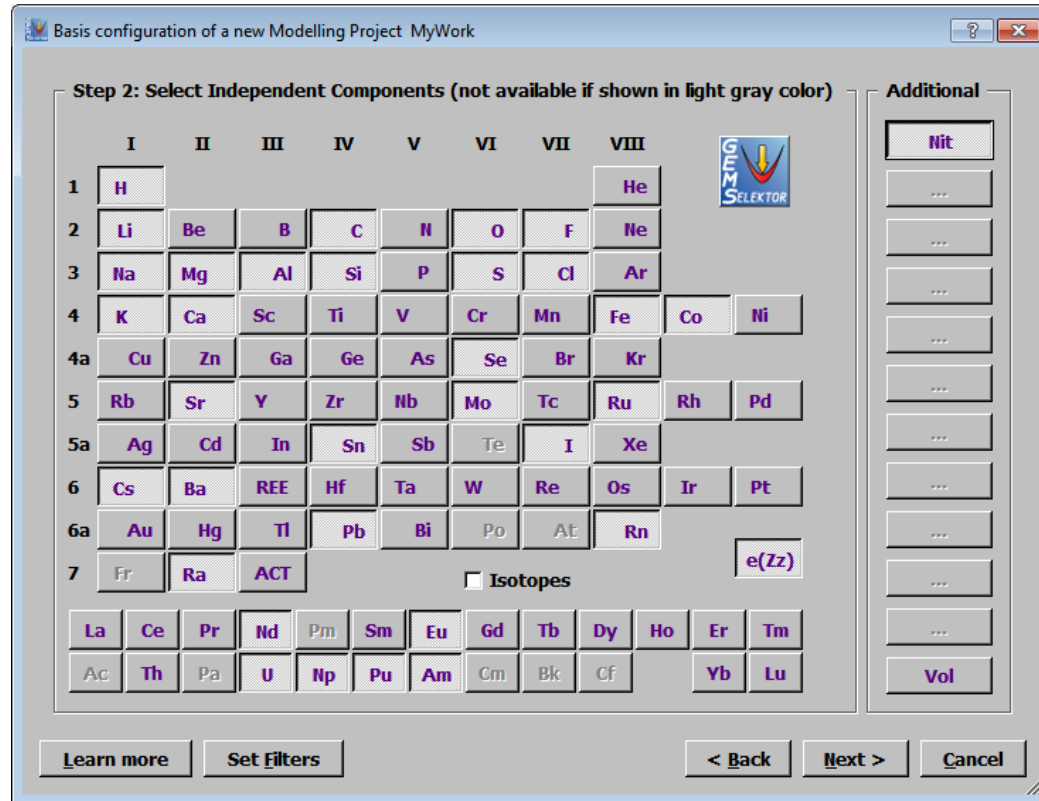
5. Details on how to manage thermodynamic data in GEMS

=> Self study

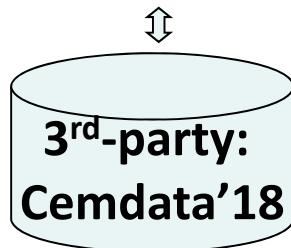
Default ThermoDynamic Databases

New modeling projects can easily be created using default TDBs.

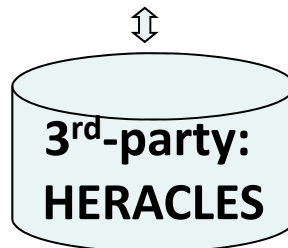
PSI/Nagra 12/07 TDB
[Thoenen ea]



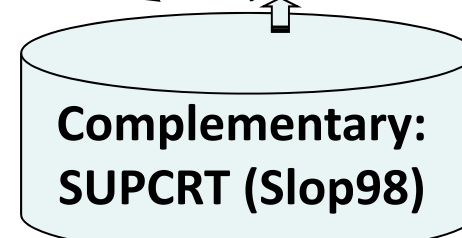
logK at 1 bar 25 C , enhanced with
T,P corrections from SUPCRT



www.empa.ch/cemdata



www.psi.ch/heracles/heracles



www.asu.edu/geopig

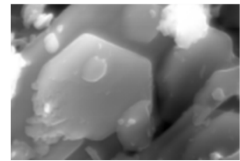
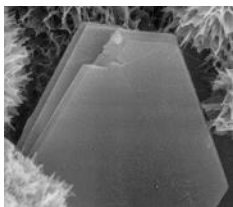


Thermodynamic databases

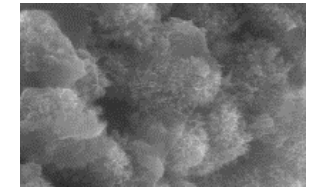
Generic data

general-TDB

- Aqueous phase (Ca²⁺, Ca(OH)⁺, ...)
- Gaseous phase (e.g. CO₂ (g), ...)
- Minerals (calcite, gypsum, portlandite, ...)



Cemdata 18



AFm

SO₄-AFm \rightleftharpoons OH-AFm
 CO₃-AFm
 hemicarb. strätlingite
 Al-AFm \rightleftharpoons Fe-AFm

AFt

SO₄-AFt \rightleftharpoons CO₃-AFt
 thaumasite
 Fe-AFt \rightleftharpoons Al-AFt

hydrogarnet

C₃AH₆
 \rightleftharpoons
 C₃AS_{0.84}H_{4.32}
 \rightleftharpoons
 C₃FS_{0.84}H_{4.32}

C-S-HQ

Ca_{0.67}SiH_{1.5}
 \rightleftharpoons
 C_{0.83}S_{0.67}H_{1.8}
 \rightleftharpoons
 C_{1.3}SH_{2.17}
 \rightleftharpoons
 C_{1.5}S_{0.67}H_{2.5}

Cemdata18 additions:
 Cl₂⁻, NO₃⁻, NO₂⁻-AFm,
 relative humidity, M-S-H,
 zeolites, C-N-A-S-H, ...

Data based on solubility measurements at different temperatures + solid phase characterisation

Database 1

- **Geochemical database** (generally integrated in software)
 - Complex formation: CaOH^+ , CaHCO_3^+ , ...
 - Solubility products: gypsum, calcite,
- **Specific cement database**
 - Babushkin et al. (1985) Thermodynamics of Silicates, Springer
 - Reardon, E.J. (1992) Waste Management 12, 221-239; Atkins et al. (1992) CCR 22, 241-246.
 - **CEM DATA07**: Matschei et al. (2007) CCR, Lothenbach et al. (2008) CCR
 - Blanc et al. (2010) CCR 40, 851-866; 1360-1374
 - **CEM DATA18**: Lothenbach et al. (2019) CCR 115, 472-506:
 - **Friedel's salt**: Balonis ea (2010) CCR 40, 1009-1022
 - **NO_2^- and NO_3^- -AFm**: Balonis ea (2011) Adv Cem Res, 23 (2011) 129-143
 - **CO_3 -hydrotalcite**: Rozov ea (2010, 2011)
 - **C-S-H models**: Kulik (2011) CCR 41, 477-495
 - **Fe-hydrates**: Dilnesa ea (2011, 2012, 2014a, 2014b), CCR
 - **C-A-S-H for alkali activated cements**: Myers (2014) CCR 66, 27-47
 - **Relative humidity**: Baquerizo ea (2015, 2016a, b) CCR
 - **M-S-H**: Nied ea (2016) CCR 79, 323-332
 - **Na- /Ca-zeolites**: Lothenbach ea (2017) J Phys. Chem. Earth 99, 77-94

Cemdata18

Cemdata18 database: Standard thermodynamic properties at 25 °Ca and 1 atm. Update of Cemdata07

The data are fully compatible with the GEMS version of the PSI/Nagra thermodynamic database [6, 7].

	log K_{S0}^*	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm ³ /mol]	Ref
(Al-)ettringite ^{a,b,c}	-44.9	-15205.94	-17535	1900	1939	0.789			707	[3, 4]
C ₆ As ₃ H ₃₀ ^c		-14728.1	-16950.2	1792.4	1452	2.156			708	[8]
C ₆ As ₃ H ₁₃		-10540.6	-11530.3	1960.4	970.7	1.483			411	[8]
C ₆ As ₃ H ₉		-9540.4	-10643.7	646.6	764.3	1.638			361	[8]
tricarboaluminate ^a	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78·10 ⁶		650	[3, 4]
Fe-ettringite ^b	-44.0	-14282.36	-16600	1937	1922	0.855	2.02·10 ⁶		717	[3, 9]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	-3.40·10 ⁶		330	[10]
C ₃ AH ₆ ^d	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25·10 ⁶		150	[11, 12]
C ₃ AS _{0.41} H _{5.18} ^{**d}	-25.35	-5192.9	-5699	399	310	0.566	-4.37·10 ⁶		146	[12]
C ₃ AS _{0.84} H _{4.32} ^{**e}	-26.70	-5365.2	-5847	375	331	0.484	-5.55·10 ⁶		142	[12]
C ₃ FH ₆ ^{f***}	-26.30	-4122.8	-4518	870	330	1.237	-4.74·10 ⁶		155	[12]
C ₃ FS _{0.84} H _{4.32} ^{e,f}	-32.50	-4479.9	-4823	840	371	0.478	-7.03·10 ⁶		149	[12]
C ₃ A _{0.5} F _{0.5} S _{0.84} H _{4.32} ^e	-30.20	-4926.0	-5335	619	367	0.471	-8.10·10 ⁶		146	[12]
C ₃ FS _{1.34} H _{3.32}	-34.20	-4681.1	-4994	820	395	0.383	-8.39·10 ⁶		145	[12]
C ₄ AH ₁₉ ^g	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	369	[11, 13]
C ₄ AH ₁₃		-7325.7	-8262.4	831.5	208.3	3.13			274	[13]
C ₄ AH ₁₁		-6841.4	-7656.6	772.7	0.0119	3.56	1.34·10 ⁻⁷		257	[13]
C ₂ AH _{7.5}	-13.80	-4695.5	-5277.5	450	323	0.728			180	[11]
CAH ₁₀	-7.60	-4623.0	-5288.2	610	151	1.113		3200	193	[11]
C ₄ AsH ₁₆		-8726.8	-9930.5	975.0	636	1.606			351	[13, 14]
C ₄ AsH ₁₄ ^g		-8252.9	-9321.8	960.9	1028.5				332	[13, 14]
C ₄ AsH ₁₂ ^h		-7778.4	-8758.6	791.6	175	2.594			310	[13, 14]
C ₄ AsH _{10.5}		-7414.9	-8311.9	721	172	2.402			282	[13, 14]
C ₄ AsH ₉		-7047.6	-7845.5	703.6	169	2.211			275	[13, 14]
C ₄ Ach ₁₁	-31.47	-7337.46	-8250	657	618	0.982	-2.59·10 ⁶		262	[3, 4]
C ₄ Ach ₉		-6840.3	-7618.6	640.6	192.4	2.042			234	[13]
C ₄ Ac _{0.5} H ₁₂	-29.13	-7335.97	-8270	713	664	1.014	-1.30·10 ⁶	-800	285	[3, 4]
C ₄ Ac _{0.5} H _{10.5}		-6970.3	-7813.3	668.3	0.0095	2.836	1.07·10 ⁻⁷		261	[13]
C ₄ Ac _{0.5} H ₉		-6597.4	-7349.7	622.5	0.0088	2.635	9.94·10 ⁻⁸		249	[13]

Database: Cemdata18

- **PC:**

Focus on **Portland cements and Portland-blends**

- CSHQ (Kulik): Ca/Si 0.67 – 2.2 (portlandite limits to Ca/Si \approx 1.6)
- $(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$ and $(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$ to **estimate** alkali uptake
- Very stable hydrotalcite from Atkins: $\text{Mg}_4\text{Al}_2\text{O}_{10} \cdot 10\text{H}_2\text{O}$

- **AAM18**

Focus on **alkali activated materials**

- CSHT (Kulik) with Na uptake and Al-uptake (in bridging site) (Myers et al. 2014)
Ca/Si **0.67 – 1.5**
- Less stable hydrotalcite, variable Mg/Al (Myers et al. 2015)
 $\text{Mg}_4\text{Al}_2\text{O}_{10} \cdot 10\text{H}_2\text{O}$, $\text{Mg}_6\text{Al}_2\text{O}_{12} \cdot 12\text{H}_2\text{O}$, $\text{Mg}_8\text{Al}_2\text{O}_{14} \cdot 14\text{H}_2\text{O}$

- **Cannot be used at the same time**

- Further CSH models can be activated by introducing additional solid solutions in «Phase»

- Tob-jennite (Kulik and Kersten 2001, Lothenbach and Winnefeld 2006)
- CSHT (Kulik 2011)

All details in Lothenbach et al. (2019) CCR 115, 472-506

Recommended selection for PC and blended cements

Basis configuration of a new Modelling Project PC

Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

- Aqueous electrolyte
- Gas mixture
- Non-ideal fluids
- Plasma
- Crystalline solids
- Dispersed solids
- Liquids, glasses
- Silicate melts
- Sorption, Ion exchange
- Polyelectrolytes
- Liquid hydrocarbons
- Skip solid solutions

Built-in Database	Version
<input checked="" type="checkbox"/> 3rdparty	
<input checked="" type="checkbox"/> cemdata	18.01
<input checked="" type="checkbox"/> .	
<input type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> csh	
<input type="checkbox"/> csh2o	18.01
<input type="checkbox"/> csh3t	18.01
<input type="checkbox"/> cshkn	18.01
<input checked="" type="checkbox"/> cshq	18.01
<input checked="" type="checkbox"/> ht	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
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<input type="checkbox"/> claysor	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

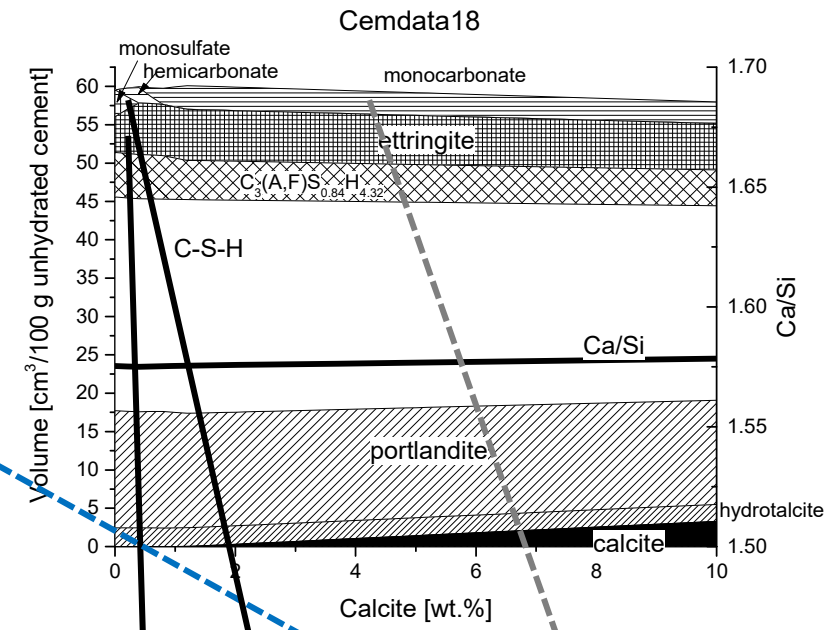
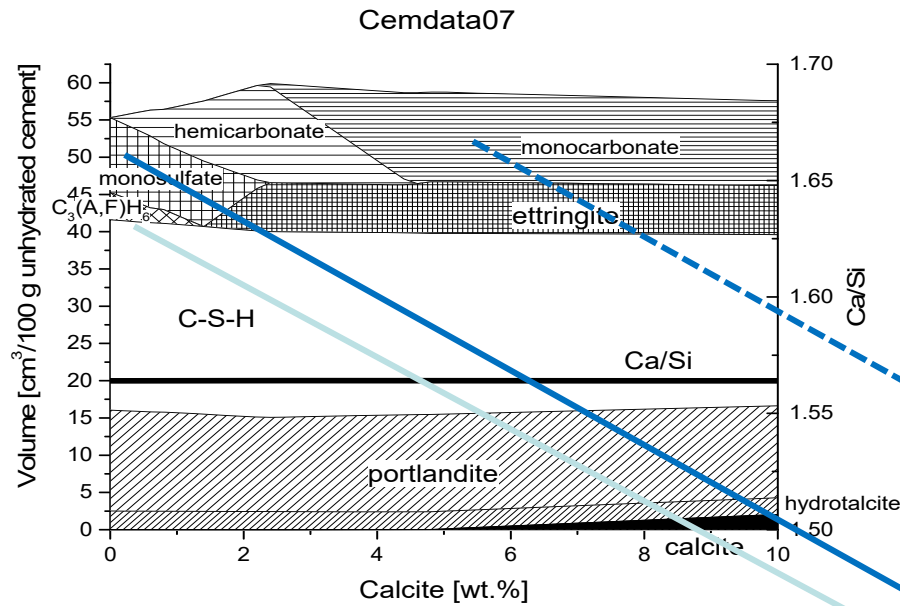
Cement database
«aam» deactivated

1 CSH model selected

General psi-nagra database

Learn more < Back Next > Cancel

What did change with cemdata18 ?

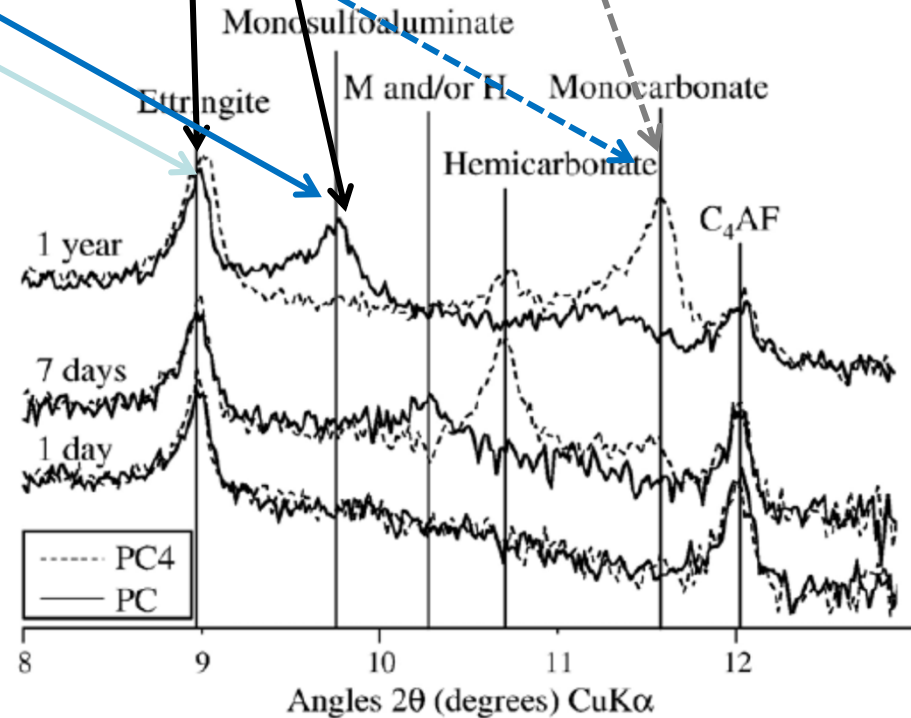


Lothenbach et al. 2008

Cemdata18: $C_3(A,F)S_{0.84}H_{4.32}$

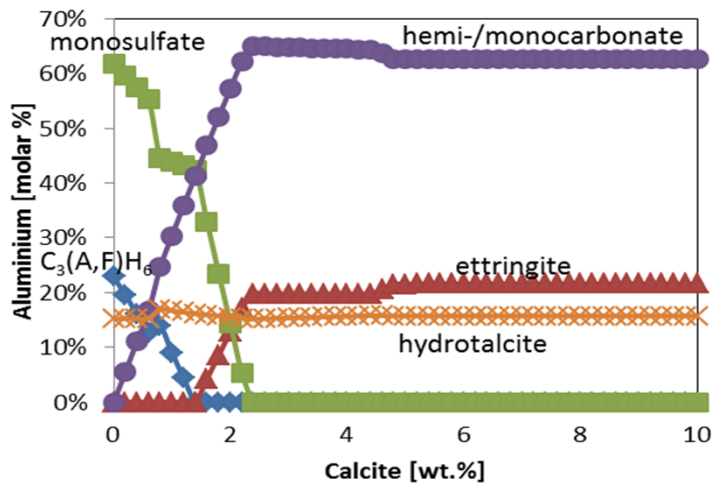
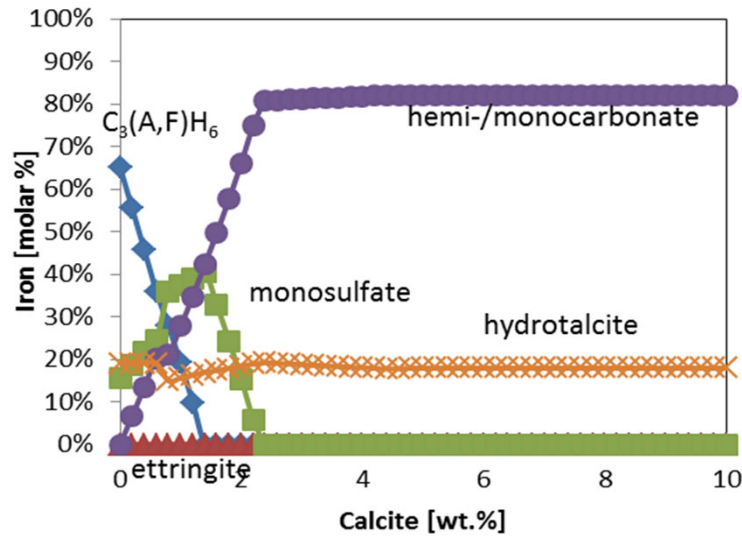
=> Some Al in Si-hydrogarnet

- No calcite: Ettringite, less monosulfate as all Fe and some Al in Si-hydrogarnet
- Calcite: less monocarbonate as some Al in Si-hydrogarnet, less strong volume effect of limestone



Cemdata07

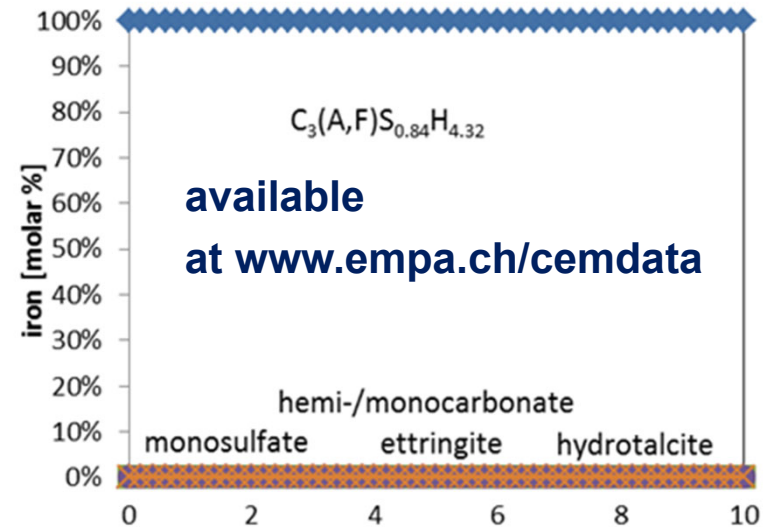
main effect on Al and Fe distribution



No calcite: More ettringite, less monosulfate as all Fe and some Al in Si-hydrogarnet

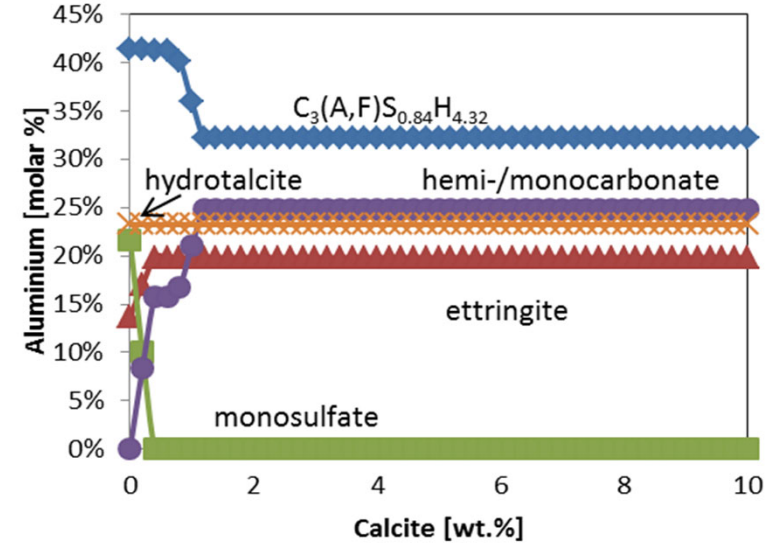
Cemdata18

Fe



available
at www.empa.ch/cemdata

Al



Calcite: less monocarbonate as some Al in Si-hydrogarnet

Cemdata18 for AAM

For alkali activated materials

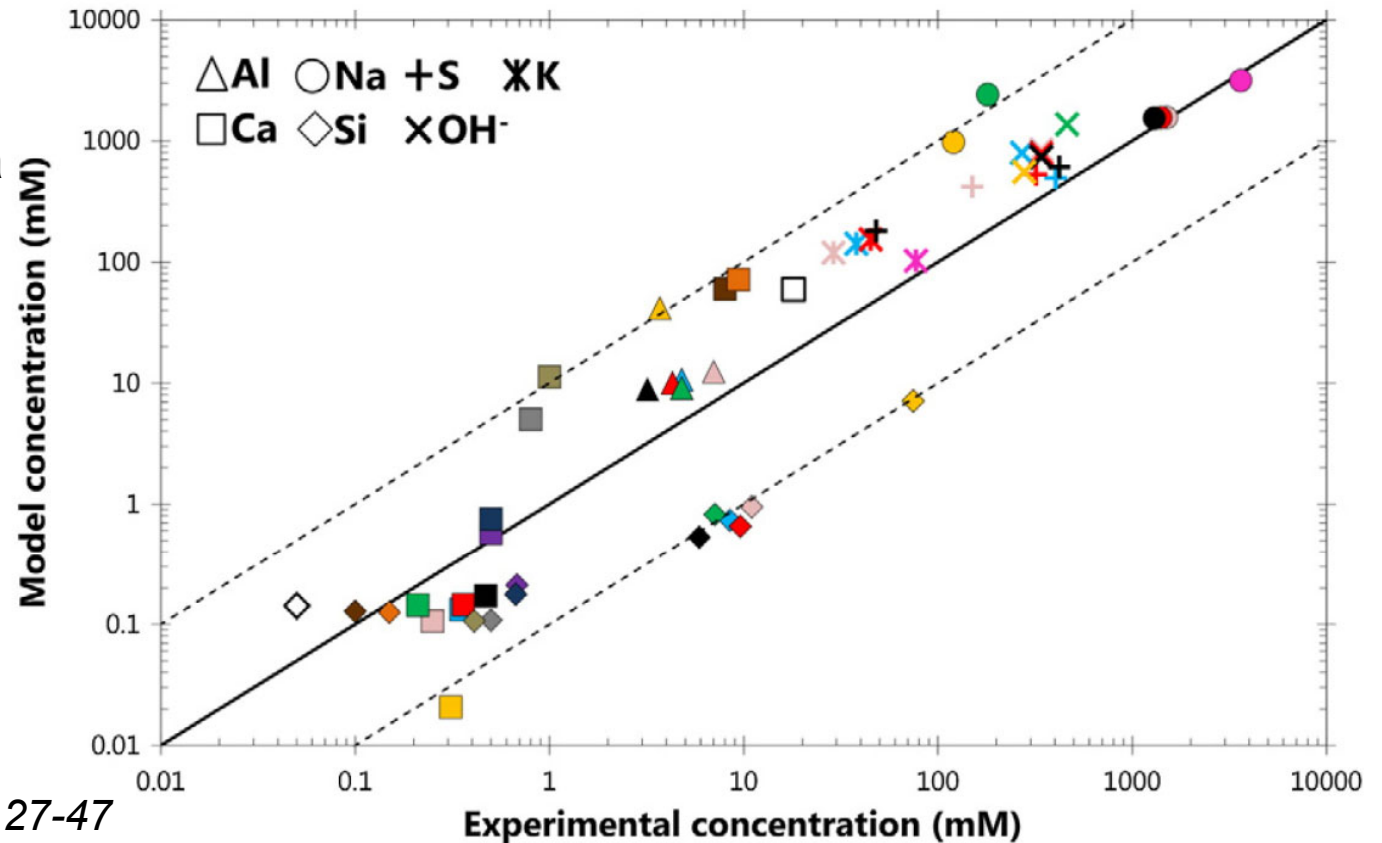
Same data as in Cemdata18 for PC with the following exceptions

CNASH model

(Myers ea 2014):

Ca/Si = 0.67 to 1.5;

uptake of Al and Na



Myers ea (2014) CCR 66, 27-47

■ Gruskovnjak et al., 2006 (1 day)	■ Gruskovnjak et al., 2006 (7 days)
■ Gruskovnjak et al., 2006 (28 days)	■ Gruskovnjak et al., 2006 (180 days)
■ Puertas et al., 2004 (7 days, waterglass)	■ Puertas et al., 2004 (7 days, NaOH)
■ Lloyd et al., 2010 (90 days)	■ Song and Jennings, 1999 (28 days, 1 M NaOH)
■ Song and Jennings, 1999 (28 days, 0.5 M NaOH)	■ Song and Jennings, 1999 (28 days, 0.1 M NaOH)
□ Song and Jennings, 1999 (41 days, water)	■ Song and Jennings, 1999 (44 days, 1 M NaOH)
■ Song and Jennings, 1999 (44 days, 0.5 M NaOH)	■ Song and Jennings, 1999 (44 days, 0.1 M NaOH)

Recommended selection for alkali activated materials

Basis configuration of a new Modelling Project AAS

? X

Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

- Aqueous electrolyte
- Gas mixture
- Non-ideal fluids
- Plasma
- Crystalline solids
- Dispersed solids
- Liquids, glasses
- Silicate melts
- Sorption, Ion exchange
- Polyelectrolytes
- Liquid hydrocarbons
- Skip solid solutions

Built-in Database	Version
<input checked="" type="checkbox"/> 3rdparty	
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<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> csh+ht	18.01
<input type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
<input checked="" type="checkbox"/> ss	18.01
<input type="checkbox"/> claysor	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

Cement database

<<aam>> database

<<pc>> deactivated

General psi-nagra database

Learn more

< Back

Next >

Cancel

GEMS versus PHREEQC

Cemdata18 also available in PHREEQC format (uses log K instead of G_f°):

Details see Lothenbach et al. (2019) CCR 115, 472-506:

```

CEMDATA18.1-16-01-2019-phaseVol.dat - Editor
Datei Bearbeiten Format Ansicht ?
# Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated
# Authors: Barbara Lothenbach, Dmitrii Kulik, Thomas Matschei, Magdalena Balonis, Luis Baquerizo,
# Published in Cement and Concrete Research, 2018, in press
#
# Based on CEMDATA18 version 01 (09.10.2017) and PSI/Nagra 12/07 GEM format
#
# Exported to PHREEQC format using ThermoMatch (https://bitbucket.org/gems4/thermomatch) reactions
#
# Temperature dependence described by three-term analytical model
# Valid range : 0 - 100°C
#
#
# Phreeqc version date: 08.05.2018
# update 03.12.2018 - added missing phases: zeoliteP_Ca, chabazite, M075SH, M15SH, zeoliteX, natro
# update 08.01.2019 - corrected INFCNA formula and reaction
# update 16.01.2019 - fixed a3 parameter from the logK analytical function (wrong converted from A
# phreeqc A[3]*log10(T); for phases aded in update update 03.12.2018)
#
# for questions contact: Barbara Lothenbach (barbara.lothenbach@empa.ch); G. Dan Miron (dan.miron@
SOLUTION_MASTER_SPECIES

#
# elemen      species      alk      gfw_formula element_gfw atomic number
#
Al            AlO2-      0.0      AlO2      26.981541  # 13
C            CO3-2      0.0      CO3       12.0108    # 6
# C(0)       SCN-       0.0      SCN        #
# C(-1)      HCN        0.0      HCN        #
C(+4)       CO3-2      2.0      CO3        #
C(-4)       CH4        0.0      CH4        #
Alkalinity  CO3-2      1.0      Ca0.5(CO3)0.5  50.05     #

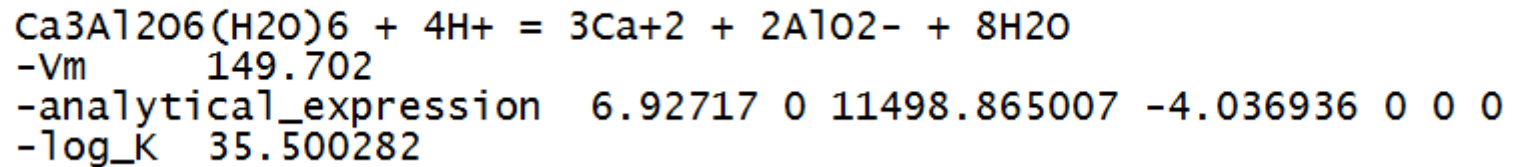
```

Solid solution to be defined by user!

GEMS versus PHREEQC

Cemdata18 also available in PHREEQC format (*uses log K instead of G°*):

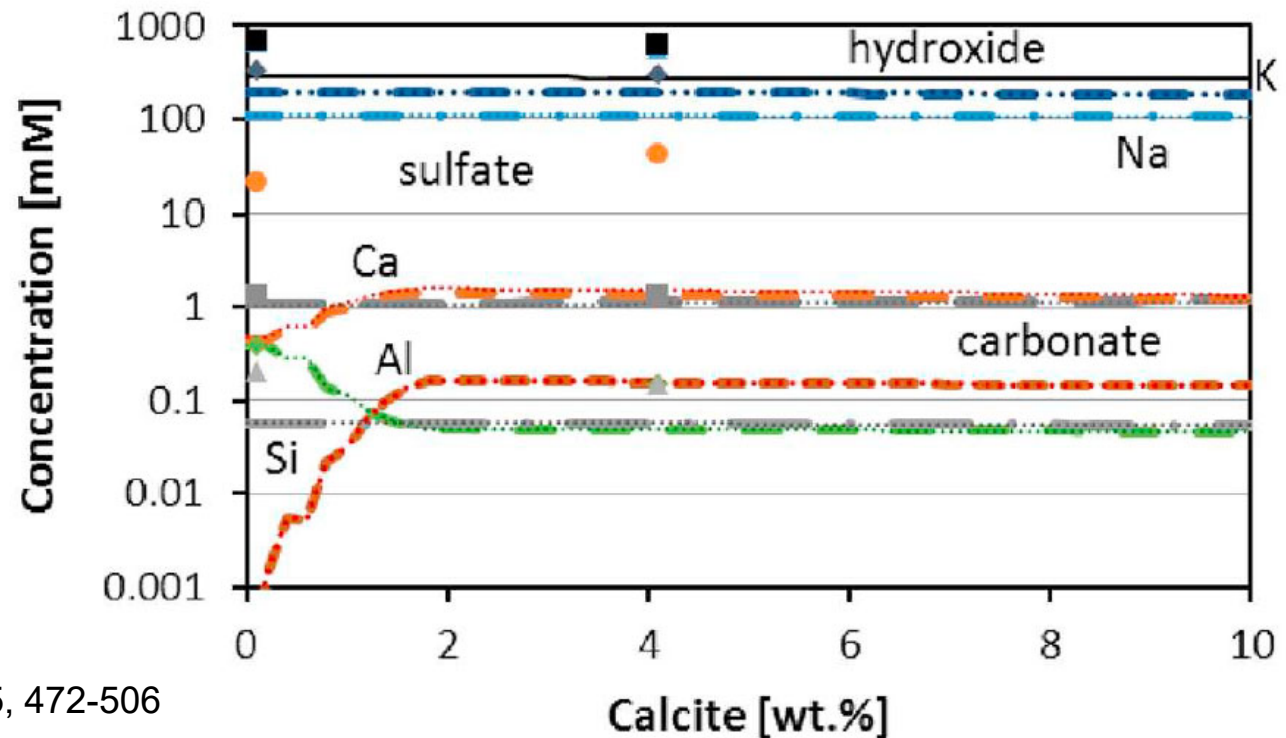
C3AH6



Identical results

GEMS: dashed - - -

PHREEQC: dotted ...
 (ideal solid solution)



Database 3

- Geochemical database and specific cement database have to be consistent!
- Use the specific cement database only with the correct geochemical database!

- Data formats:

- Log K values (PHREEQC, GEMS, MINEQL, ...)
- ΔG_f° (Gibbs free energy of formation) (GEMS, MTDATA, ...)

- convertible: $K = e^{-\frac{\Delta G_r^\circ}{RT}}$

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

Thermodynamic modelling: **Limits**

- **Thermodynamic data**
 - Small differences in data -> other solids stable
small errors can lead to wrong results
 - Gaps in database: Al-K-Na uptake in C-S-H, ...
- **Kinetics: some phases are metastable**
 - C-S-H metastable (jennite, tobermorite, ...)
 - Hydrated cement thermodynamically unstable
 - Slow kinetics
- **Kinetics: some phases do not form at ambient conditions and in the timeframe considered**
 - Quartz, dolomite, goethite, hematite, gibbsite, talc, thaumasite (only at low temp), ...

GEMS structure

calculations



Thermodynamic database
for experienced users

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: S

Modules Record Data Calculate View Print Window Help

SingleSystem

portlandit:*,*,*,*,*,*,*,*

	3	4	5	6	7	8
1	CO2	0	0	1	25	0

Single calculation

Input: System Definition Results: Equilibrium State

Phase/species	L	T
+ a aq_gen	22	a
+ g gas_gen	5	g
+ s Graphite	1	s
+ s Aragonite	1	s
+ s Calcite	1	s
+ s lime	1	s
+ s Portlandite	1	s
+ s Anhydrite	1	s
+ s Gypsum	1	s
+ s hemihydrate	1	s
+ s Sulphur	1	s

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [DComp :: Thermochemical/EOS data fo...

Modules Record Record List Database Files Window Help

DComp

,,*,*,*

	1	2	3	4
1	g	S-2	H2S	en_
2	s	CO	Gr	dn_
3	s	CaCO	Arg	dn_
4	s	CaCO	Cal	dn_
5	s	CaO	Lim	ce_
6	s	CaOH	Portlandite	dn_
7	s	CaSO	Anh	dn_
8	s	CaSO	Gp	dn_
9	a	w_	H+	an_
10	a	w_	H2O@	an_

Page 1 Page 2 29/08/2012, 12:38

Portlandite
Ca (OH) 2

M0	74.0927	Zz	0	ab	--
V0d	3.306		0		
G0d	-897013		---		
H0d	-984675		---		

Thermodynamic database



**Independent components
(chemical elements: Ca)**

**Dependent components:
e.g. Ca^{2+} , Ca(OH)_2 , ...**

2 input options: both equally valid

**Reaction of dependent components (K)
e.g. $\text{Ca}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Ca(OH)}_2$**

**Calculation and plotting of T/P
dependency**

**Solids phases
single phases / solid solutions**

**Predefined compositions:
e.g. air, PC, slag, ...**

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs

Modules Record Record List Database Files Window Help

Comp

	1	2	3	4
IComp	1	g S-2	H2S	en_
	2	s C0	Gr	dn_
	3	s CaCO	Arg	dn_
DComp	4	s CaCO	Cal	dn_
	5	s CaO	Lim	ce_
	6	s CaOH	Portlandite	dn_
ReacDC	7	s CaSO	Anh	dn_
	8	s CaSO	Gp	dn_
	9	a w_	H+	an_
	10	a w_	H2O@	an_
RTparm	11	g C+4	CO2	en_
	12	g C-4	CH4	en_
	13	g H0	H2	en_
Phase	14	s CasOH	hemihydrate	ce_
	15	g O0	O2	en_
Compos	16	a Ca	Ca(CO3)@	cn_
	17	a Ca	Ca(HCO3)+	cn_
	18	a Ca	Ca(SO4)@	cn_
	19	a Ca	Ca+2	an_
	20	a Ca	CaOH+	cn_
	21	a wC+4	CO2@	bn_
	22	a wC+4	CO3-2	bn_
	23	a wC+4	HCO3-	an_

Page 1

Portlandit
Ca (OH) 2

M0

V0d

G0d

H0d

S0d

Cp0d

PrTr

LamST

BetAlp

0 Robie_
1 AUG20_

1) GEMS: independent components

The screenshot displays the GEM-Selektor 3 (GEMS3) software interface. The main window shows a table of independent components (IComp) with columns 1, 2, and 3. The table lists the following components:

1	2	3
1	C e	Carbon_
2	S e	Sulfur_
3	O o	Oxygen_
4	H h	Hydrogen_
5	Ca e	Calcium_
6	Zz z	Electric_charge_

The detailed data entry window for Calcium shows the following properties:

ICname	Calcium NEA (CODATA)		
ICform	Ca		
StdSt	s	IC DC	---
M0i	40.078	S0i	41.59
Cp0i	25.929		
V0i	25.86	IXi	1
Valen	2		
indMT	20	Ri	---
Zi	---		

Contains basic properties of elements (e.g. molar weight, standard state entropy, valence number)

2) GEMS: dependent components (DComp)

The screenshot shows the GEMS software interface. On the left is a sidebar with icons for IComp, DComp (highlighted with a green circle), ReacDC, RTparm, Phase, and Compos. The main window displays a table of dependent components (DComp) with columns 1, 2, 3, and 4. The table lists 20 species, including Portlandite (row 6). On the right, a window titled 'ICComp :: Data for Independent Components' is open, showing thermochemical data for 'Calcium NEA (CODATA)'. The data is presented in a table format with various thermodynamic properties and their units.

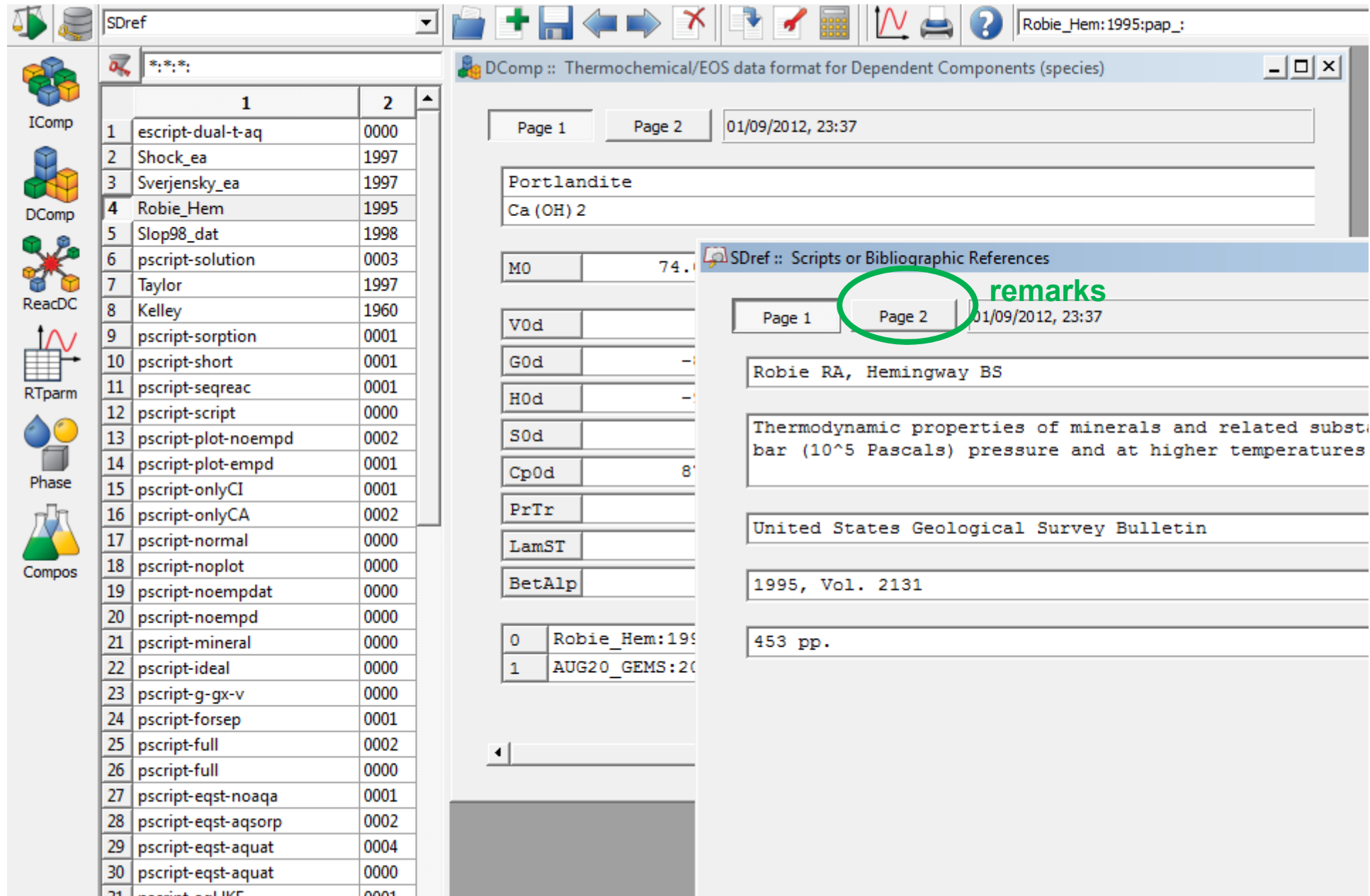
ICname	Mass (g/mol)	charge	For activity coefficients
Portlandite	74.0927	0	ab
Ca(OH) ₂			

Property	Value	Units
V0d	3.306	0
G0d	-897013	---
H0d	-984675	---
S0d	83.4	---
Cp0d	87.5053	0
PrTr	1	25
LamST	---	---
BetAlp	---	---

Reference (F2)	Value
0 Robie_Hem:1995:pap:	All
1 AUG20_GEMS:2001:dat:	G0 from logK = -22.8

**Standard state
thermodynamic data
of solids and
aqueous species**

GEMS: dependent components (DComp)



The screenshot displays the GEMS software interface. On the left, a vertical toolbar contains icons for various components: IComp, DComp, ReacDC, RTparm, Phase, and Compos. The main window is titled 'SDref' and contains a table with two columns, '1' and '2'. The table lists various dependent components and their associated values.

	1	2
1	escript-dual-t-aq	0000
2	Shock_ea	1997
3	Sverjensky_ea	1997
4	Robie_Hem	1995
5	Slop98_dat	1998
6	pscript-solution	0003
7	Taylor	1997
8	Kelley	1960
9	pscript-sorption	0001
10	pscript-short	0001
11	pscript-seqreac	0001
12	pscript-script	0000
13	pscript-plot-noempd	0002
14	pscript-plot-empd	0001
15	pscript-onlyCI	0001
16	pscript-onlyCA	0002
17	pscript-normal	0000
18	pscript-noplot	0000
19	pscript-noempdat	0000
20	pscript-noempd	0000
21	pscript-mineral	0000
22	pscript-ideal	0000
23	pscript-g-gx-v	0000
24	pscript-forsep	0001
25	pscript-full	0002
26	pscript-full	0000
27	pscript-eqst-noaqa	0001
28	pscript-eqst-aqsorp	0002
29	pscript-eqst-aquat	0004
30	pscript-eqst-aquat	0000
31	pscript-eqst-aquat	0001

On the right, a window titled 'DComp :: Thermochemical/EOS data format for Dependent Components (species)' is open. It shows a list of species: Portlandite and Ca (OH) 2. Below this, a table lists various thermodynamic properties (M0, V0d, G0d, H0d, S0d, Cp0d, PrTr, LamST, BetAlp) with their corresponding values.

Overlaid on the DComp window is another window titled 'SDref :: Scripts or Bibliographic References'. This window has a 'Page 2' tab selected, which is circled in green. The word 'remarks' is written in green above the 'Page 2' tab. The content of the 'Page 2' tab includes the following text:

Robie RA, Hemingway BS

Thermodynamic properties of minerals and related substances (10⁵ Pascals) pressure and at higher temperatures

United States Geological Survey Bulletin

1995, Vol. 2131

453 pp.

GEMS: dependent components (DComp)

The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The main window displays a list of dependent components (DComp) with columns for phase, formula, name, and site. A right-click context menu is visible over the list. The 'DComp :: Thermochemical/EOS data format for Dependent Components (species)' window is open, showing thermochemical data for species 6 (CaOH) and 7 (CaSO). The data includes TCint (Temperature range where equations are valid) and aiCpT (Coefficients for the heat capacity equation). The temperature range for species 6 is 0 to 426.85 K. The coefficients for species 6 are: a0 = 186.7, a1 = -0.02191, a2 = 0, a3 = -1600, a4 = 0, a5 = 0, a6 = 0, a7 = 0, a8 = 0, a9 = 0.

Right click: further information/help

Temperature/Pressure effect on heat capacity

Temperature range where equations are valid

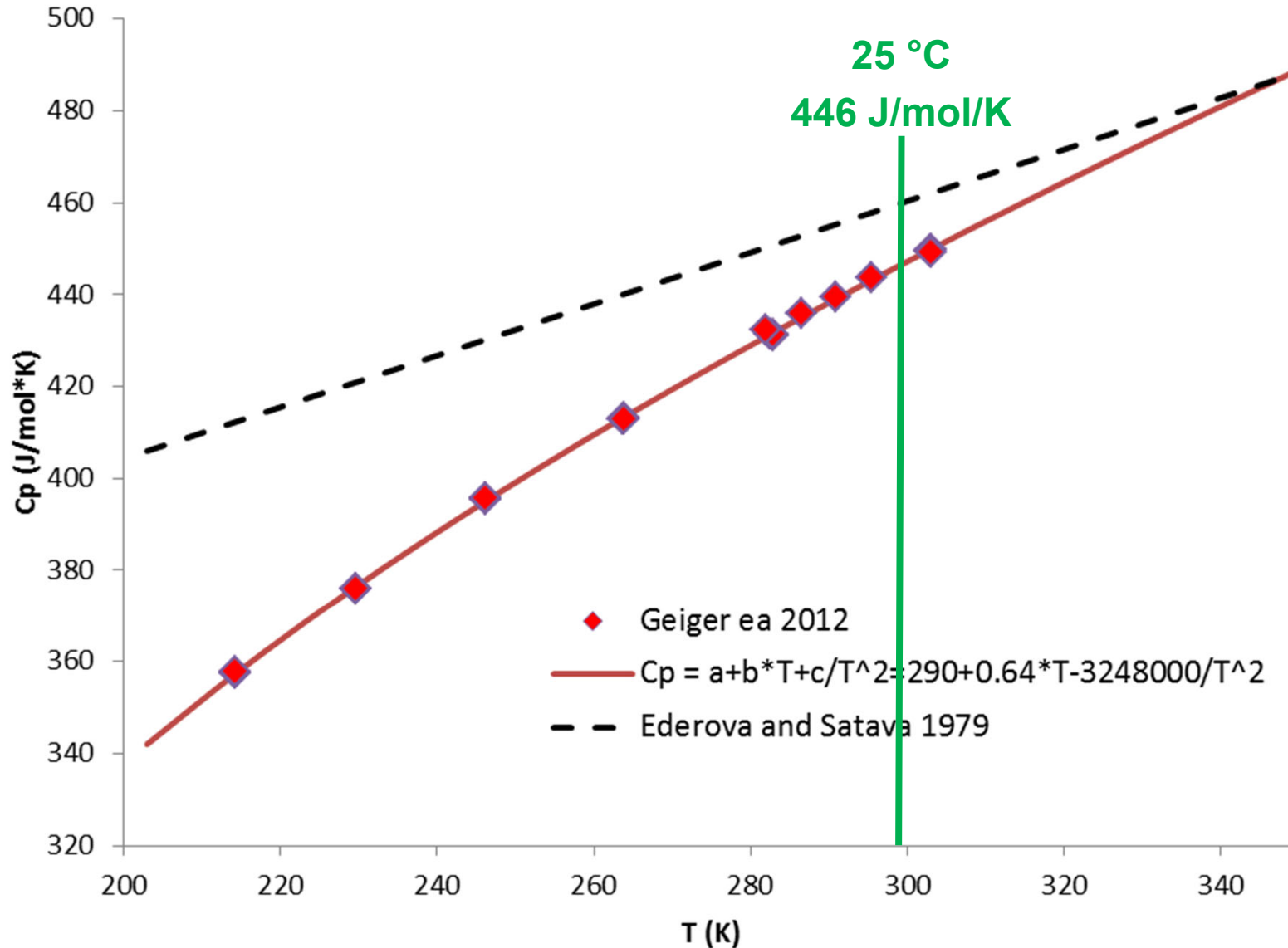
$$Cp^0 = a_0 + a_1T + a_2T^2 + a_3T^{-0.5} + a_4T^2 + a_5T^3 + a_6T^4 + a_7T^{-3} + a_8T^{-1} + a_9T^{0.5}$$

Tabulated values

	log K ₅₀ [*]	a ₀ [J/K/mol]	a ₁	a ₂	a ₃	V° [cm ³ /mol]	Ref
(Al-)ettringite ^{a,b,c}	-44.9	1939	0.789			707	[3, 4]
CH (portlandite)	-5.2	187	-0.022		-1600	33	[6, 7]
SiO _{2,am}	1.476	47	0.034	-1.13·10 ⁶		29	[3, 4]

GEMS: dependent components (DComp)

Heat capacity of C_3AH_6



3) GEMS: reactions (ReacDC)

Modules Record Record List Database Files Window Help

ReacDC

ReacDC :: Reaction-defined data format for Dependent Components (species)

Page 1 Page 2 01/09/2012, 23:37

S-2 name
S|-2|-2 Chemical composition (defined format)

	SC	DC		REsDC			
0		-1	d	a	wS-2	HS-	bnp
1		1	d	a	w_	H+	anp
2		1	n	a	wS-2	S-2	cnp

Reaction component Uncertainty

V0r	0	2.02095	---
logKr	1e-019	-19	---
G0r	108452.8	120422	---
H0r	108452.8	92236	---
S0r	0	68.1992	---
Cp0r	0	-93.927	---
NisoX	---	---	---

Pressure Temperature Mass (g/mol) charge

PrTr	1	25	M0	32.067	-2
------	---	----	----	--------	----

Activity coefficients

BetAl	---	---	ab	4	---
-------	-----	-----	----	---	-----

Reference (F2)

AUG20_GEMS:2001:dat: logK

HS⁻ = H⁺ + S²⁻; log K = -19
{H⁺}{S²⁻}/{HS⁻} = 10⁻¹⁹

Volume (1 J/bar = 10 cm³/mol)
Constant K (-)
Free energy of react (J/mol)
Enthalpy of react (J/mol)
Entropy (J/mol/K) ΔG = ΔH-TS
Heat capacity (J/mol/K)

Standard state
thermodynamic data of
solids and aqueous species:
Reaction data are known

5.) Thermodynamic Phases

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Phase

	1	2	3	4	5
1	s	C	Graphite	c	nagra-psi
2	s	CaCO	Aragonite	c	nagra-psi
3	s	CaCO	Calcite	c	nagra-psi
4	s	CaO	lime	c	cem_
5	s	CaOH	Portlandite	c	cem_np_
6	s	CaSO	Anhydrite	c	nagra-psi
7	s	CaSO	Gypsum	c	nagra-psi
8	s	CaSO	hemihydrate	c	cem_
9	s	S	Sulphur	c	nagra-psi

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 01/09/2012, 23:37

Portlandite Ca(OH)2 cryst.
nagra-psi

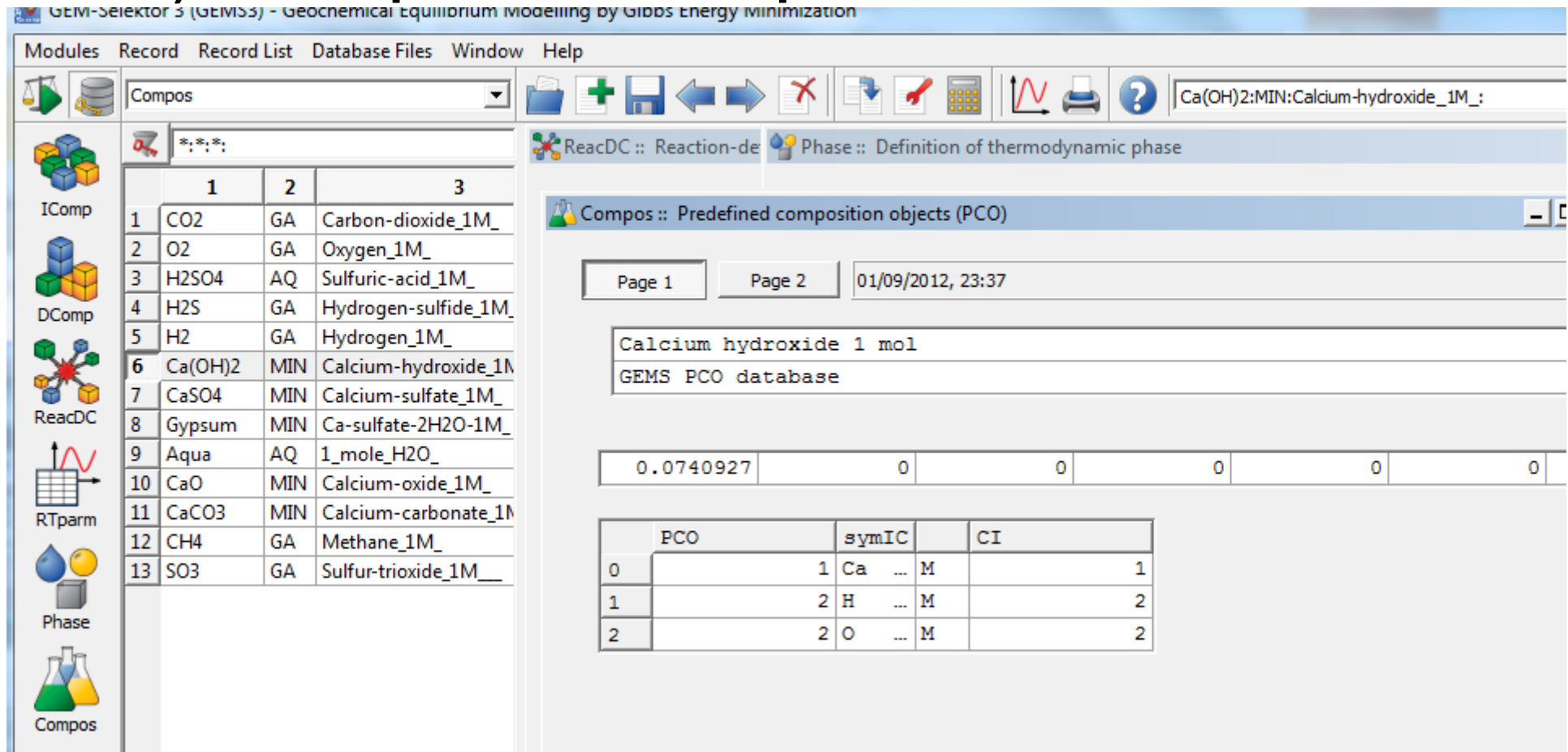
0 0 0 0 0 0

O d s CaOH Portlandite ...

O: single solid d: DComp

- To include a solid in the actual project database, a phase has to be defined
- The thermodynamic properties of this phase are based on the properties in the dependent component entry of the database and possible additional data e.g. mixing parameters for solid solutions

6) GEMS: predefined composition



The screenshot shows the GEM-Selektor 3 (GEMS) software interface. The main window displays the 'Compos' module, which is used for defining predefined composition objects (PCO). The interface includes a menu bar (Modules, Record, Record List, Database Files, Window, Help), a toolbar with various icons, and a central workspace. The workspace shows a table of predefined composition objects (PCO) with columns for PCO, symIC, and CI. The table contains three rows of data:

PCO	symIC	CI
0	1 Ca ... M	1
1	2 H ... M	2
2	2 O ... M	2

***Contains chemical compositions of input
(e.g. PC, slag, Ca(OH)₂, HCl, ...)***

Alternative way of input, no thermodynamic properties needed

Thermodynamic data

1. Databases
2. **Portlandite solubility and speciation**
 - a. effect of temperature
 - b. pH
3. Saturation indices
4. Hydrates in cement
5. Details on how to manage thermodynamic data in GEMS
=> Self study

Thermodynamic data portlandite

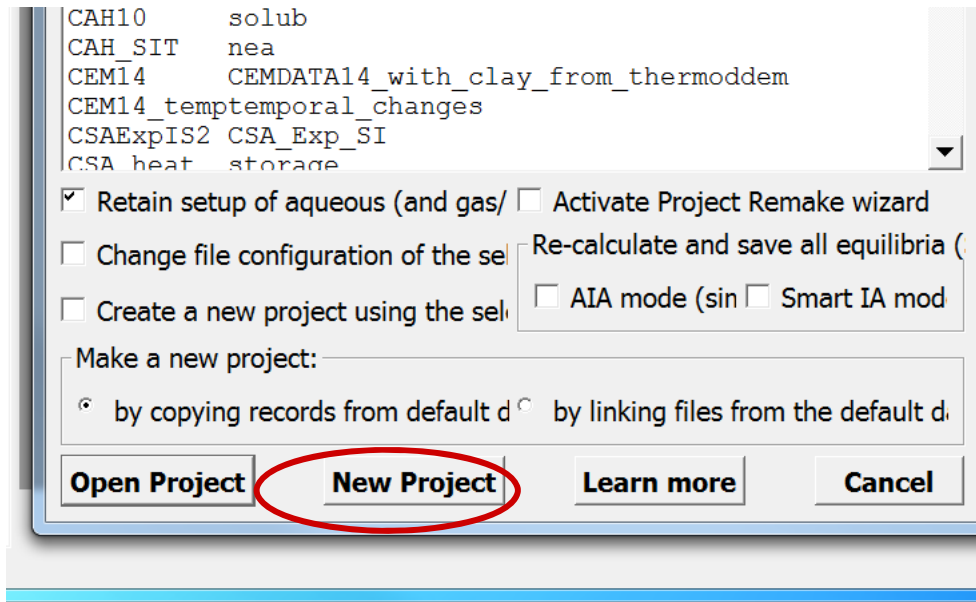
- Ca(OH)₂

$$\begin{aligned}
 - K_{s0,H^+} &= \frac{\{H^+\}^2 \{Ca(OH)_2\}}{\{Ca^{2+}\} \{H_2O^0\}} = \frac{\{H^+\}^2 \cdot 1}{\{Ca^{2+}\} \{H_2O^0\}} = 10^{-22.8} & \Delta &= 1 / K_w^2 \\
 - K_{s0,OH^-} &= \frac{\{Ca(OH)_2\}}{\{Ca^{2+}\} \{OH^-\}^2} = \frac{1}{\{Ca^{2+}\} \{OH^-\}^2} = 10^{5.2} & \Delta &= 1 / (10^{-14})^2
 \end{aligned}$$

$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

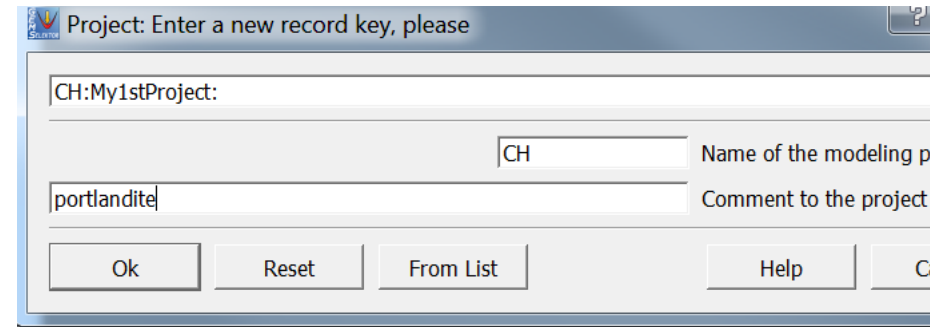
$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

Portlandite			
Ca(OH) ₂			
M0	74.0927	Zz	0 ab --- ---
V0d	3.306		0
G0d	ΔG_f°	-897013	---
H0d	ΔH_f°	-984675	---
S0d		83.4	---
Cp0d		87.5053	0
PrTr		1	25
LamST		---	---
BetAlp		---	---
0	Robie_Hem:1995:pap:	All	
1	AUG20_GEMS:2001:dat:	G0 from logK = -22.8	

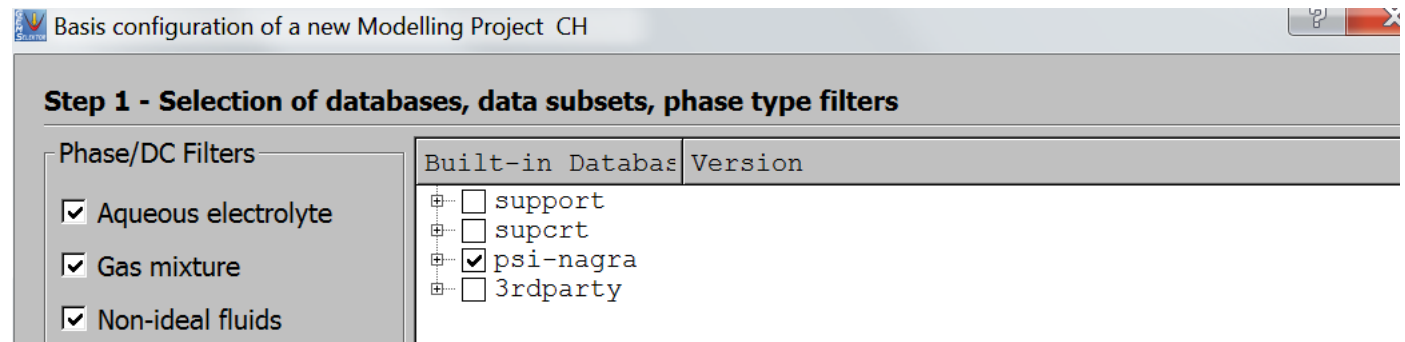


1. Select New project

2. Name it



3. Sufficient to select psi-nagra database only



Portlandite

4. Select elements

Ca, Na, Cl

5. Aqueous electrolyte model: Helgeson for NaCl

Basis configuration of a new Modelling Project gsdfs

Step 2: Select Independent Components (not available if shown in light gray color)

	I	II	III	IV	V	VI	VII	VIII	
1	H								He
2	Li	Be	B	C	N	O	F		Ne
3	Na	Mg	Al	Si	P	S	Cl		Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co Ni
4a	Cu	Zn	Ga	Ge	As	Se	Br		Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh Pd
5a	Ag	Cd	In	Sn	Sb	Te	I		Xe
6	Cs	Ba	REE	Hf	Ta	W	Re	Os	Ir Pt
6a	Au	Hg	Tl	Pb	Bi	Po	At		Rn
7	Fr	Ra	ACT						

Isotop

Setup of aqueous and gas phases in project: CH

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

- Ion-association (IA) with Davies equation, D (default)
- IA with extended Debye-Hueckel equation (Helgeson), common b_gamma and a0, H
- IA with extended Debye-Hueckel equation (Shvarov), common b_gamma and a0, Y
- IA with extended Debye-Hueckel equation (Karpov), common b_gamma, individual a0, 3
- IA with Debye-Hueckel equation, no b_gamma, individual a0, 2
- IA with Debye-Hueckel limiting law (very low ionic strength), 1
- Do not generate; select a user-defined Phase record from database (Q, S, Z), U
- Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq_gen aq EDH_H

Parameters for the aqueous phase model

b_gamma(1,298) value: 0.064

b_gamma(P,T) mode: NaCl

Common a0 value: 3.72

Gamma (neutral species): Calculate as b_gamma

Gamma (water solvent): From osmotic coefficient

Molality conversion: Applied to all species

OK Cancel Check Learn more

Portlandite

2. names

SysEq: Please, enter a new record key:

CH:G:port:0:0:1:25:0:

CH Name of the modeling project

G Thermodynamic potential to minimize {G GV}

port Name of the chemical system definition (CSD)

Name of the chemical system definition (CSD)

0 Volume of the system, dm3 (0 if no volume constraint)

1 Pressure, bar, or 0 for Psat(H2O)g

20 Temperature, C (>= 0) **1. 20°C**

0 Variant number for additional constraints

Ok Reset From List Help Cancel

Input Recipe of Single Thermodynamic System: CH:G:port:0:0:1:20:0:

name solubility of portlandite

Property	Selection	Recipe Input			
		Property	Name	Quantity	Units
Compos (x)	Aqua H2	1	Aqua	1000	g
DComp (xd)	Ca(OH)2 HCl	2	CaO	10	g
IComp (bi)	CaCl2 HCl	3	HCl	1e-09	M
Phase (xp)	CaO KCl	4	NaOH	1e-09	M
Kin.lower (d)		5	O2	0.1	g
Kin.upper (c)					
G0 shift (gE)					
Other Input					

Input quantities of Compos(itions) contributing to B_ vector

1 L of water
Some CaO
NaOH/HCl for pH
O2

Learn more Print OK Cancel

Portlandite solubility

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic System in Project CH]

Modules Record Data Calculate View Print Window Help

SingleSyster CH:G:port:0:0:1:20:0

Input: System Definition Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coef
a aq_gen	11	a	55.390645	9.503e-10		
Ca+2	S		0.017047484	0.00733756	0.017102427	0.42903552
CaOH+	S		0.0040174978	0.00328104	0.0040304459	0.81406161
Na+	S		9.8363455e-013	8.04087e-13	9.8680473e-013	0.81406161
NaOH@	S		1.6365455e-014	1.65467e-14	1.64182e-014	1.0078099
ClO4-	S		2.4090496e-034	1.96743e-34	2.4168138e-034	0.81406161
Cl-	S		1e-012	8.16686e-13	1.0032229e-012	0.81406161
H2@	S		0	3.16272e-46	0	1.0078099
O2@	S		0.0014195175	0.00143521	0.0014240925	1.0078099
OH-	S		0.038112465	0.031126	0.038235299	0.81406161
H+	T		2.6671239e-013	2.1782e-13	2.6757199e-013	0.81406161
H2O@	W		55.330048	0.999025	0.99890601	1.000119
g gas_gen	2	g	0.0017055997	1.254e-09		
s Portlandite	1	s	0.15725998	-1.165e-07		

pH 12.7, 21 mM Ca tot

System: T = 293.15 K; P = 1.00 bar; V = 1.045 L; Aqueous: built-in EDH(H); pH = 12.662; pe = 8.484; IS = 0.055 m

Portlandite: effect of temperature

1. Create new process

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]

Modules Record Window Help

Process

Controls

0 1
1 1
2
cTm

ipH

0
0
0
0

SysEq: Please, select a parent System for a new Process

Please, select one record key. Filter: CH:*.~*.~*.~*.~*.~*:

CH	G	port	0	0	1	20	0
----	---	------	---	---	---	----	---

Ok Set Filter Help Cancel

P: sequential change of temperature

Process: Please, set a new record key
? X

CH:G:port:0:0:1:20:0:temp:P:

CH	Name of the modeling project
G	Thermodynamic
port	Name of the pare
0	CSD (recipe) varia
0	Volume of the sys
1	Pressure, bar, or
20	Temperature, C
0	Variant number fo
temp	Name of this proc
P	Process simulation

Ok
Reset
From List

GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:temp:P:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of re geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) c

The Process record can be configured in several modes to perform specific simulation scenari control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be easily produ

Any process simulator belongs to one of three types:

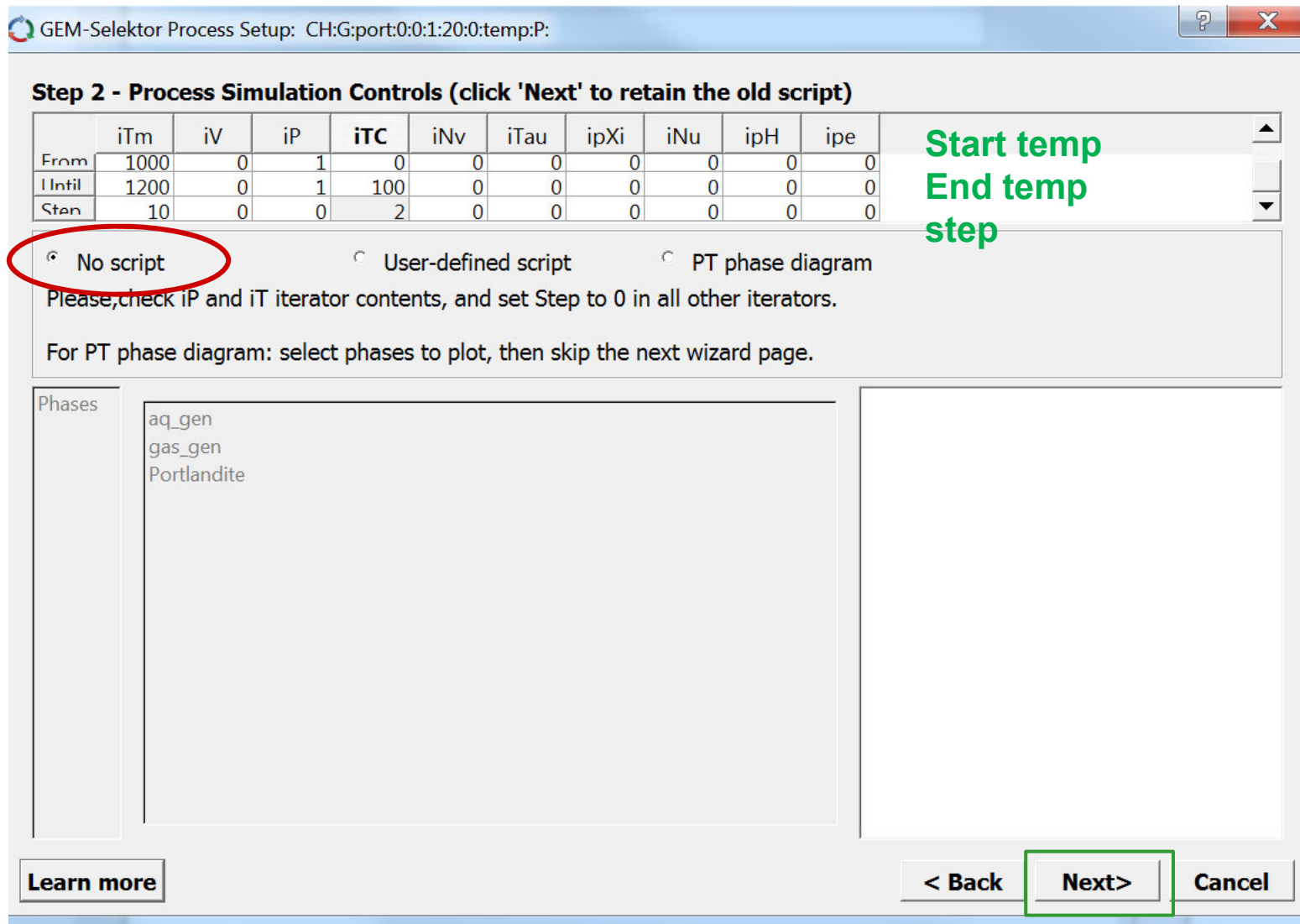
1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from previous step
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; mode

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

P: sequential change of temperature

Here: no additional input script needed



GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:temp:P:

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	0	0	0	0	0	0	0
Until	1200	0	1	100	0	0	0	0	0	0
Step	10	0	0	2	0	0	0	0	0	0

Start temp
End temp
step

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
- gas_gen
- Portlandite

[Learn more](#) < Back **Next>** Cancel

P: sequential change of temperature

GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:temp:P: ? X

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

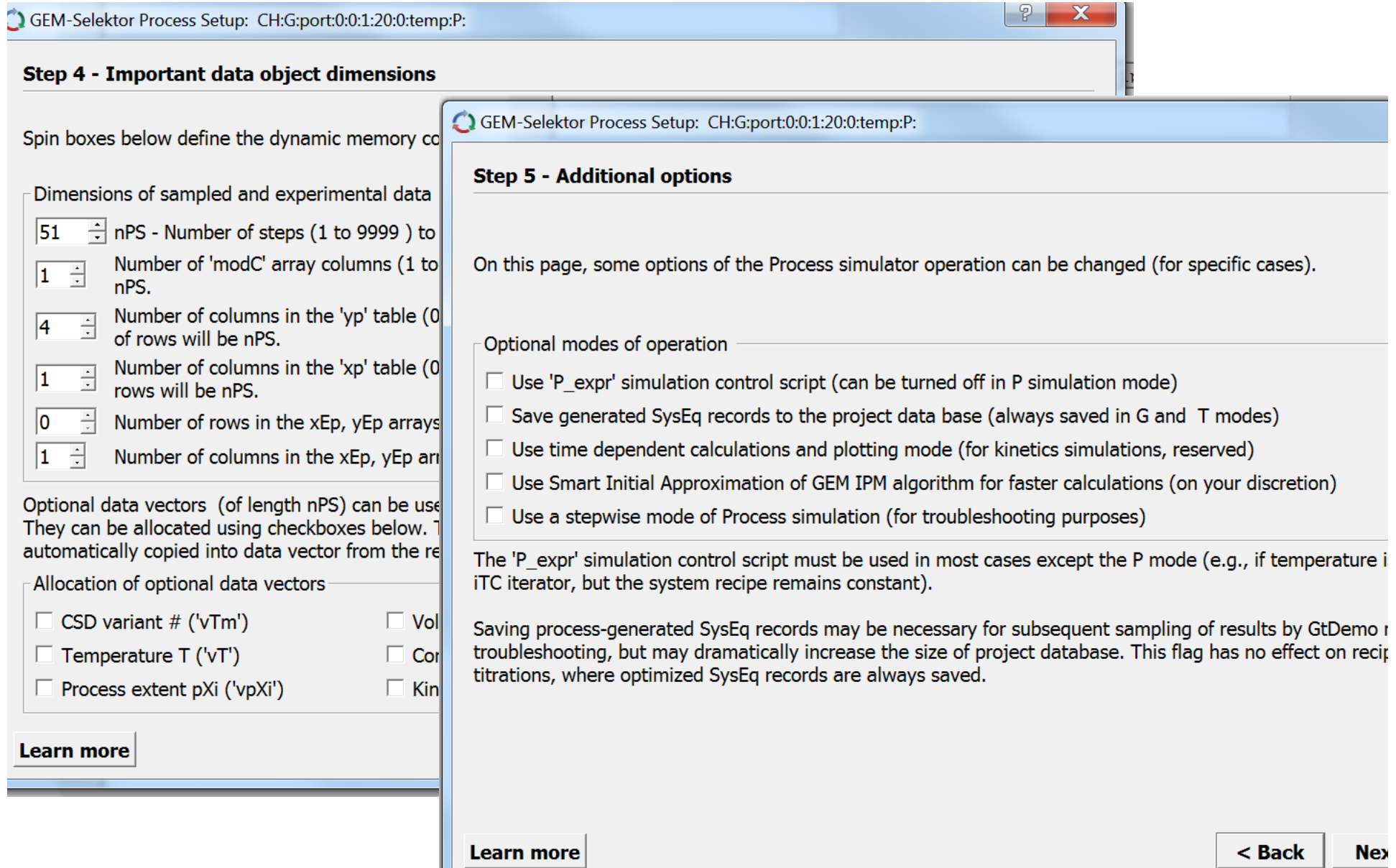
Property	Item Selection	Sampling Script
lgm_t	Ca+2	xp[J] =: TC[0];
icM	CaOH+	yp[J][0] =: m_t[Ca];
Xa	Na+	yp[J][1] =: my[Ca+2];
Xwa	NaOH@	yp[J][2] =: my[CaOH+];
phVol	ClO4-	yp[J][3] =: my[OH-];
phM	Cl-	
Fa	H2@	
bXa(aq_)	O2@	
bXa(gas_)	OH-	
bXs	H+	
L1	H2O@	
Yof	H2	
Aalp	O2	
Sigw	Portlandite	
x		
Wxx		
my		
v		

Molality concentrations of Dependent Components (in mol per kg H₂O)

Select TC as x-axis (by right click)
Select total Ca plus Ca²⁺ and CaOH⁺
all in mol/kg H₂O

Learn more < Back **Next>** Cancel

P: sequential change of temperature



Step 4 - Important data object dimensions

Spin boxes below define the dynamic memory consumption of the process simulation.

Dimensions of sampled and experimental data

- 51 nPS - Number of steps (1 to 9999) to be simulated.
- 1 Number of 'modC' array columns (1 to nPS).
- 4 Number of columns in the 'yp' table (0 to nPS). The number of rows will be nPS.
- 1 Number of columns in the 'xp' table (0 to nPS). The number of rows will be nPS.
- 0 Number of rows in the xEp, yEp arrays.
- 1 Number of columns in the xEp, yEp arrays.

Optional data vectors (of length nPS) can be used for post-simulation analysis. They can be allocated using checkboxes below. The data is automatically copied into data vector from the recipe.

Allocation of optional data vectors

- CSD variant # ('vTm')
- Temperature T ('vT')
- Process extent pXi ('vpXi')
- Volume ('v')
- Corrosion ('vCor')
- Kinetics ('vKin')

[Learn more](#)

Step 5 - Additional options

On this page, some options of the Process simulator operation can be changed (for specific cases).

Optional modes of operation

- Use 'P_expr' simulation control script (can be turned off in P simulation mode)
- Save generated SysEq records to the project data base (always saved in G and T modes)
- Use time dependent calculations and plotting mode (for kinetics simulations, reserved)
- Use Smart Initial Approximation of GEM IPM algorithm for faster calculations (on your discretion)
- Use a stepwise mode of Process simulation (for troubleshooting purposes)

The 'P_expr' simulation control script must be used in most cases except the P mode (e.g., if temperature is varied in the ITC iterator, but the system recipe remains constant).

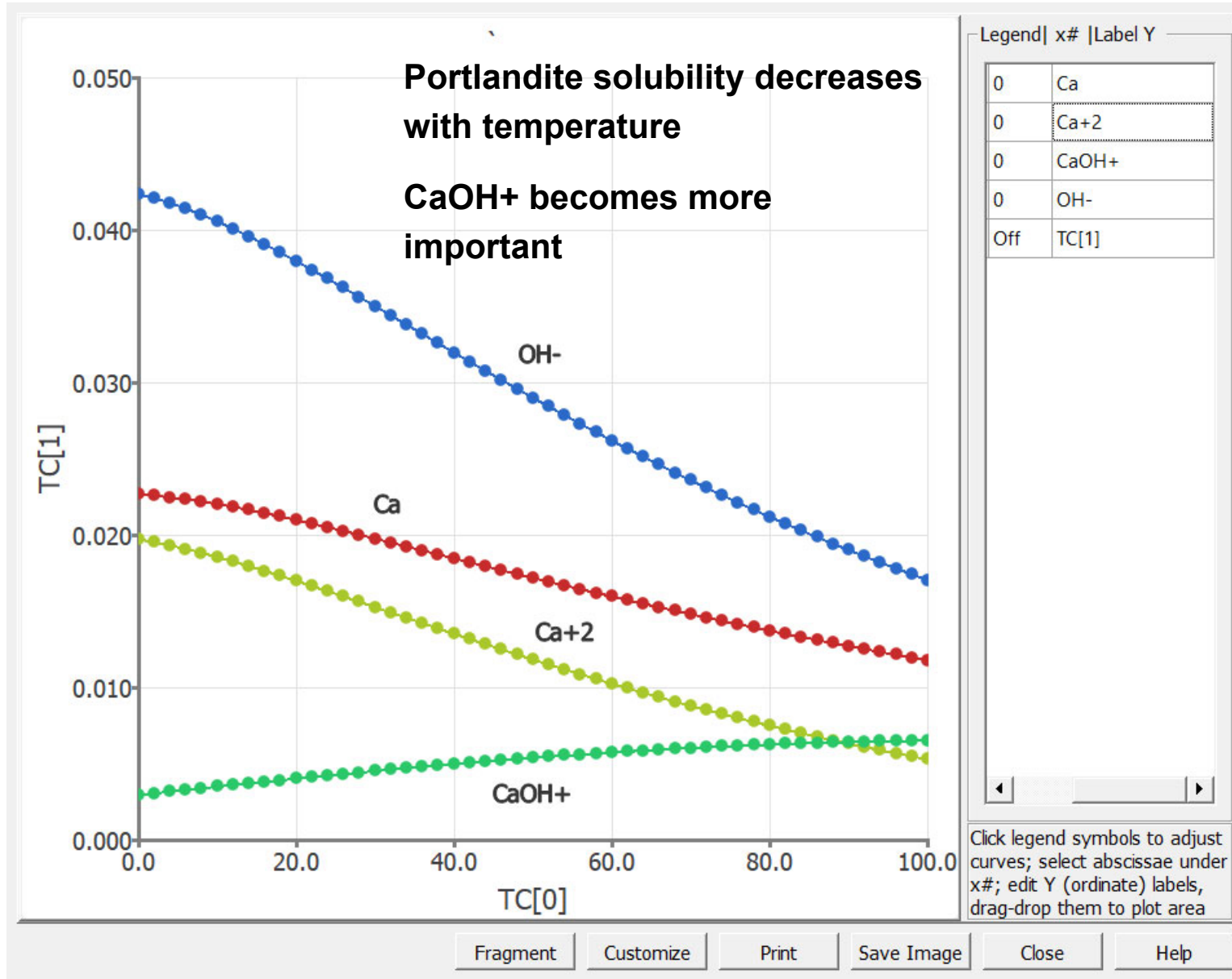
Saving process-generated SysEq records may be necessary for subsequent sampling of results by GtDemo for troubleshooting, but may dramatically increase the size of project database. This flag has no effect on recipe iterations, where optimized SysEq records are always saved.

[Learn more](#)

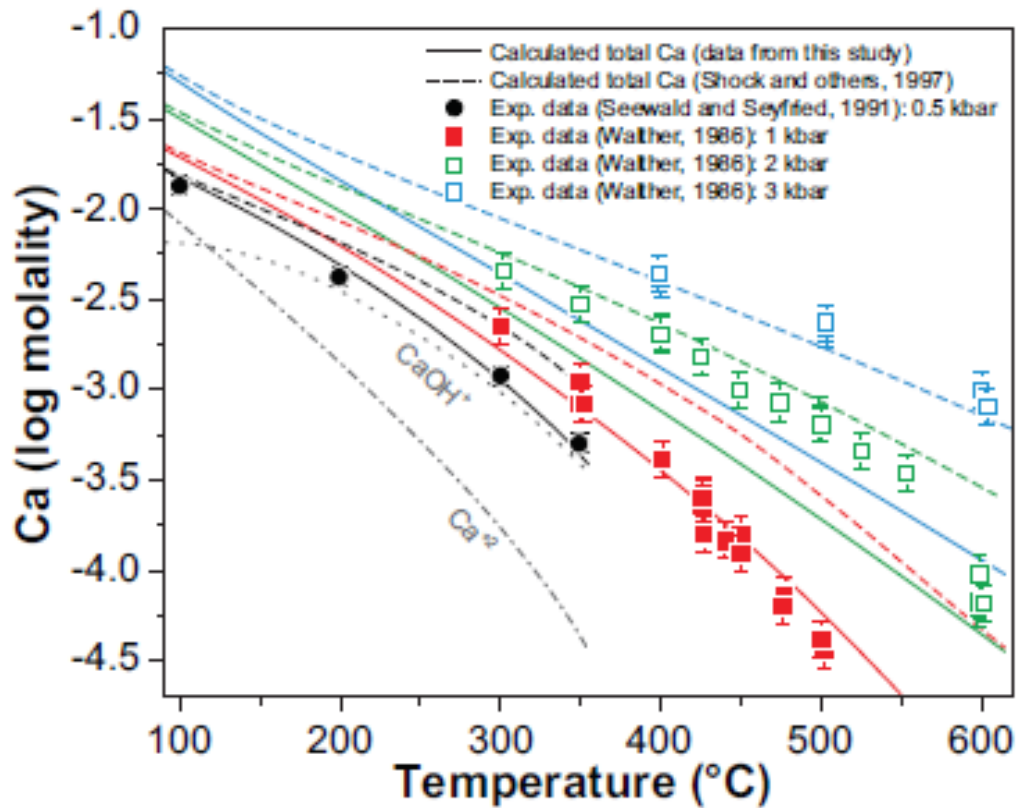
[< Back](#) [Next >](#)

Portlandite

P: sequential change of temperature



Portlandite



Portlandite solubility decreases with temperature

Agrees well with experimental trends

High pressures (kbar!) increases solubility
=> see group work

Fig. 16. Comparison between calculated and experimentally determined portlandite solubility in water (Walther, 1986; Seewald and Seyfried, 1991), expressed as total dissolved Ca as function of temperature at pressures of 0.5, 1.0, 2.0 and 3.0 kbar. Solid symbols represent experimental data points which were used to refine the properties of the CaOH^+ complex, while open symbols represent experimental data points which were not used.

Miron et al. (2017) *American Journal of Science*, 317(7), 755-806

Portlandite: effect of pH

1. Create new process

Process: Please, set a new record key

CH:G:port:0:0:1:20:0:pH:G:

CH Name of the modeling project

G Thermodynamic potential to minimize {G}

port 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

pH Name of this process simulation task

G Process simulation mode code { P, S, L, G, T, R }

Ok Reset From List Help Cancel

GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:pH:T:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and pl geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, w

The Process record can be configured in several modes to perform specific simula control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be

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 pr
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g

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 sc
- R Sequential reactor scheme, uses equilibrium bulk compositions of phases
- L Lippmann diagram (transposed) for a binary solid solution

[Learn more](#)

G: Batch inverse titration (Variation of pH)

Select HCl and NaOH

GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:pH:T: ...

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	20	0	0	0	0	0	0
Until	1200	0	1	20	0	0	0	0	0	0
Step	10	0	0	0	0	0	0	0	0	0

Property-vs-pH diagram
 Constant-pH isotherm diagram

To plot the pH diagram: please, select acid and base from the 'AcidBase' list, and go to the next wizard page.

To plot constant-pH isotherms: in addition, select the trace element addition in the 'AcidBase' list, set the 'ipe' iterator accordingly; select aqueous species in the 'Molality' list for the abscissa; finally select one or more sorbed species from the 'Sorbed' list, then skip the next wizard page.

AcidBase

Molality

Sorbed

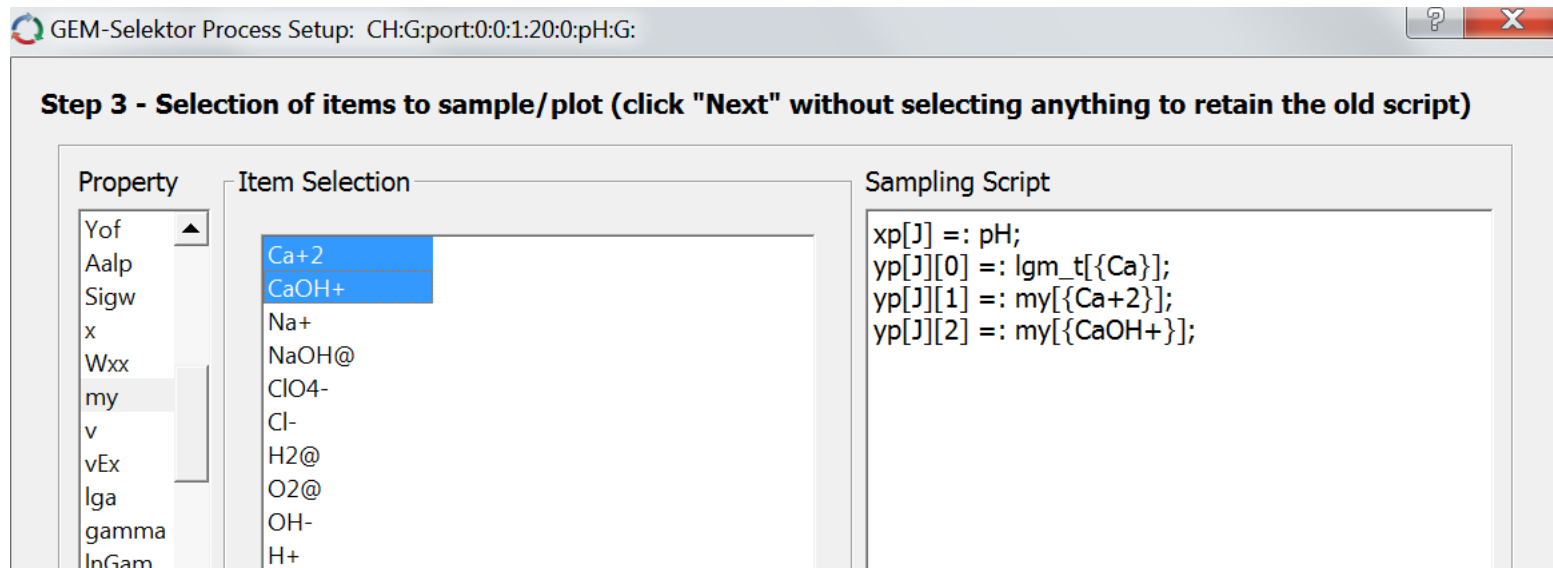
- Aqua
- Ca(OH)₂
- CaCl₂
- CaO
- H₂
- HCl**
- HClO₄
- KCl
- KOH
- NaCl
- NaClO₄
- NaOH**

```

$ pH sequence of inverse titrations
if ( Next=1) begin
  cNu =: cpH-pH; end
if (Next=2) begin
  xa_[{NaOH}] =: ((cEh < 0)? 1e-9:
cEh);
  xa_[{HCl}] =: ((0-cEh < 0)? 1e-9: 0-
cEh);
  modC[J] =: cEh;
end
$ modC[J]: acid or base addition
                    
```

[Learn more](#)
 [< Back](#)
 [Next >](#)
 [Cancel](#)

Output
pH as x-axis
log(Ca tot), Ca²⁺ and CaOH⁺



my[{Ca+2}] = Ca²⁺ concentration (in mol/kg H₂O)

m_t[{Ca}] = total concentration (in mol/kg H₂O) = Ca²⁺ + CaOH⁺ + ...

lgm_t[{Ca}] = log(10) of total concentration (in mol/kg H₂O) = Ca²⁺ + CaOH⁺ + ...)

lg(my[{Ca+2}]) = log(10) of Ca²⁺ concentration (in mol/kg H₂O)

(lg(...)) has to be adapted afterwards)

Adapt input: Temperature, pH interval, max. amount of acid and base

CH:G:portlandite:0:0:1:20:0:pH:G:

Controls Sampling Results Config 26/03/2020, 16:52

effect of pH on Portlandite

temperature

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	0	1	20	0	-0.3	0	12.35	0
1	1033	0	0	1	20	0	2	0.01	14	0
2	1	0	0	0	0	0	1e-011	0	0.05	0
cTm	1032	0	0	1	20	0	-0.3	-0.00381...	13.95	0

accuracy

Start
End
step

```

$ pH sequence of inverse titrations
if ( Next=1) begin      A
  cNu := cpH-pH; end
if (Next=2) begin      B
  xa_[{NaOH}] := ((cEh < 0)? 1e-9: cEh);
  xa_[{HCl}] := ((0-cEh < 0)? 1e-9: 0-cEh);
  modC[J] := cEh;
end
$ modC[J]: acid or base addition  C
    
```

	modC
0	0
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0

A \$ If Next=1 begin, it will check whether cNu is less than or equal to cpH-pH. If not, end and start Next=2.\$

B \$ If Next=2 begin, it will check to add NaOH or HCl. For NaOH, if cEh<0, then add 1e-9 unit NaOH and 0-cEh unit HCl; if cEh>0, then add 1e-9 unit HCl and cEh unit NaOH.\$

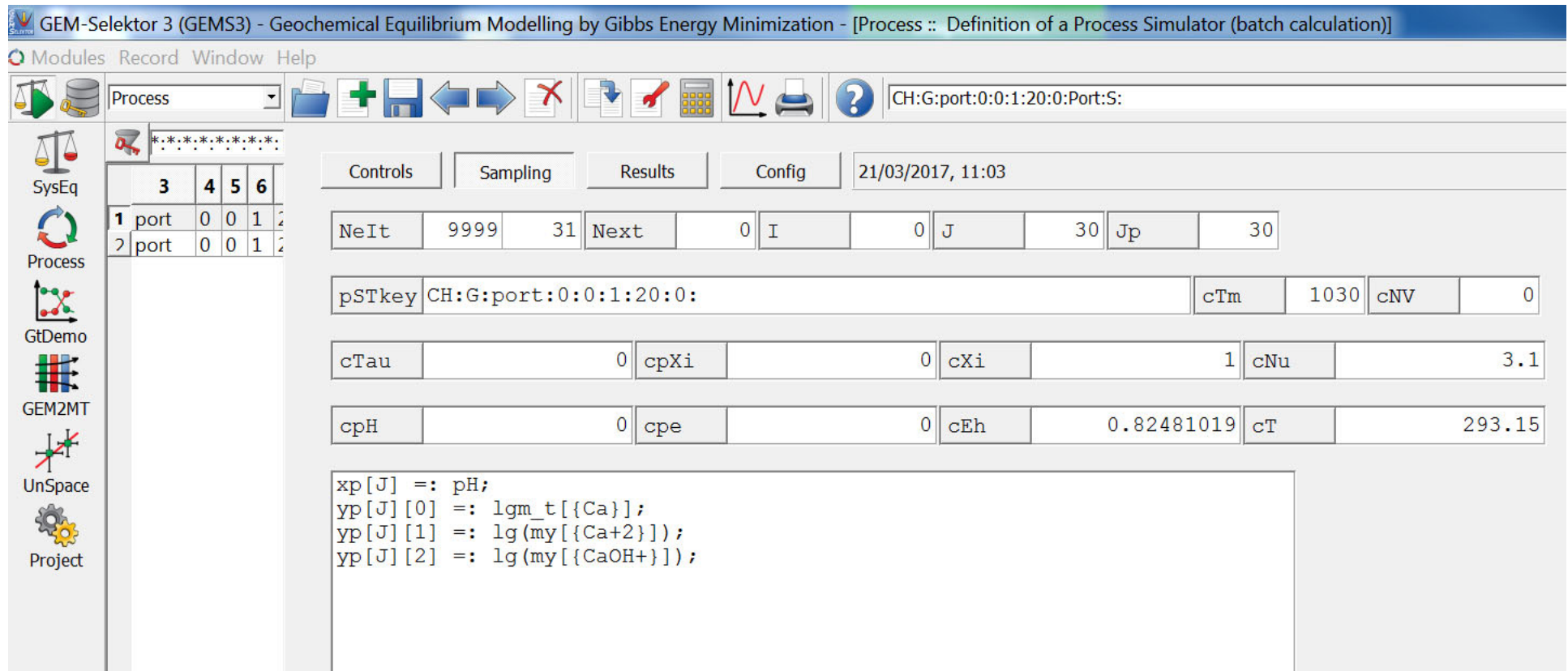
C (unit for the added acid or base listed in modC[J] is M (defined in single calculation (SysEq))

Collection of data

pH, total concentrations

concentrations of species

(use lg() = log₁₀ for better readability)



The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The title bar reads "GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]". The menu bar includes "Modules", "Record", "Window", and "Help". The toolbar contains various icons for file operations and simulation control. The main window is titled "Process" and shows a configuration for a process simulator. The process name is "CH:G:port:0:0:1:20:0:Port:S:". The interface is divided into several sections: "Controls", "Sampling", "Results", and "Config". The "Config" section is active, showing various parameters for the simulation. The "Results" section shows the output of the simulation, including pH and concentrations of species.

3	4	5	6
1 port	0	0	1
2 port	0	0	1

NeIt	9999	31	Next	0	I	0	J	30	Jp	30
------	------	----	------	---	---	---	---	----	----	----

pSTkey	CH:G:port:0:0:1:20:0:	cTm	1030	cNV	0
--------	-----------------------	-----	------	-----	---

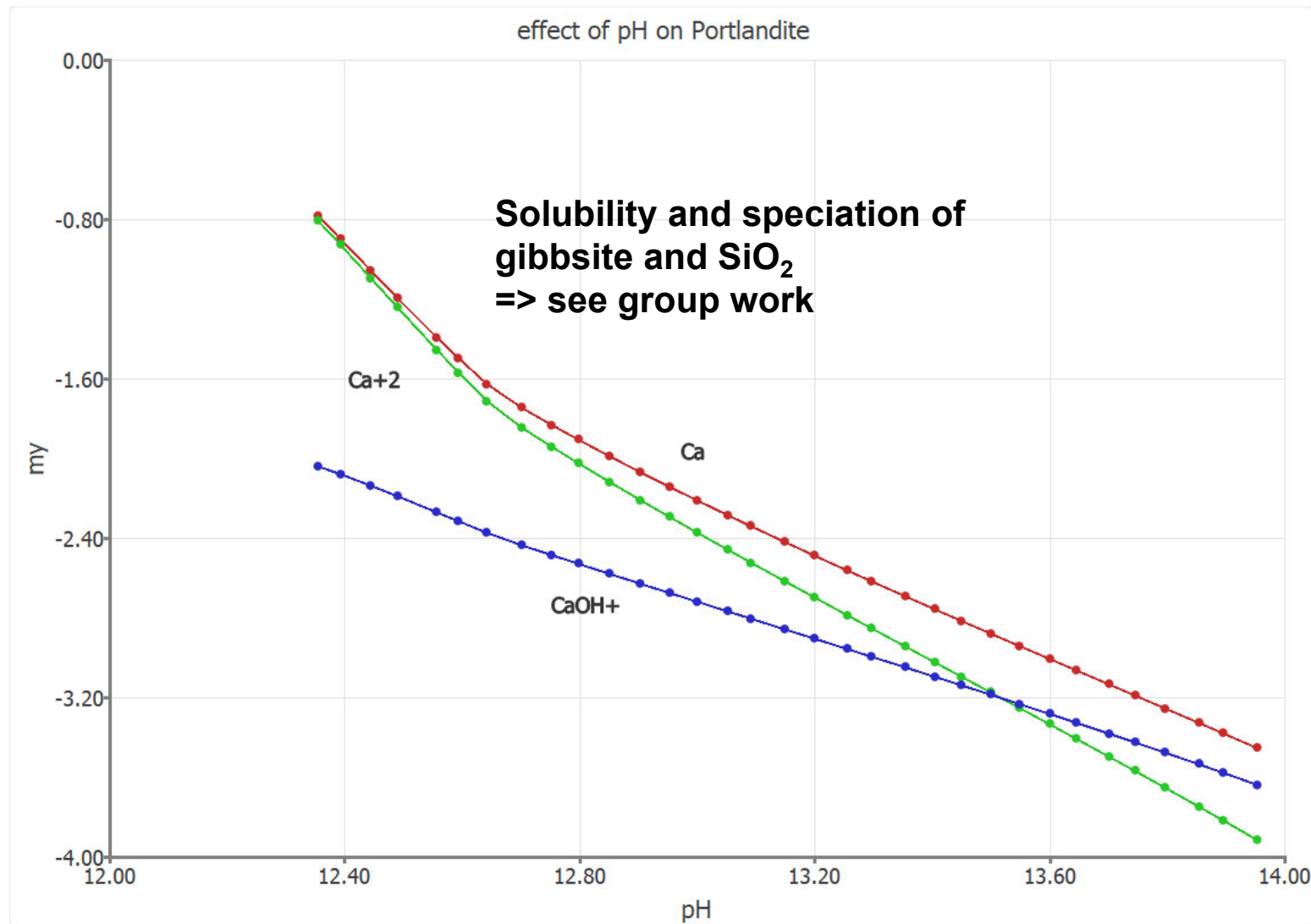
cTau	0	cpXi	0	cXi	1	cNu	3.1
------	---	------	---	-----	---	-----	-----

cpH	0	cpe	0	cEh	0.82481019	cT	293.15
-----	---	-----	---	-----	------------	----	--------

```

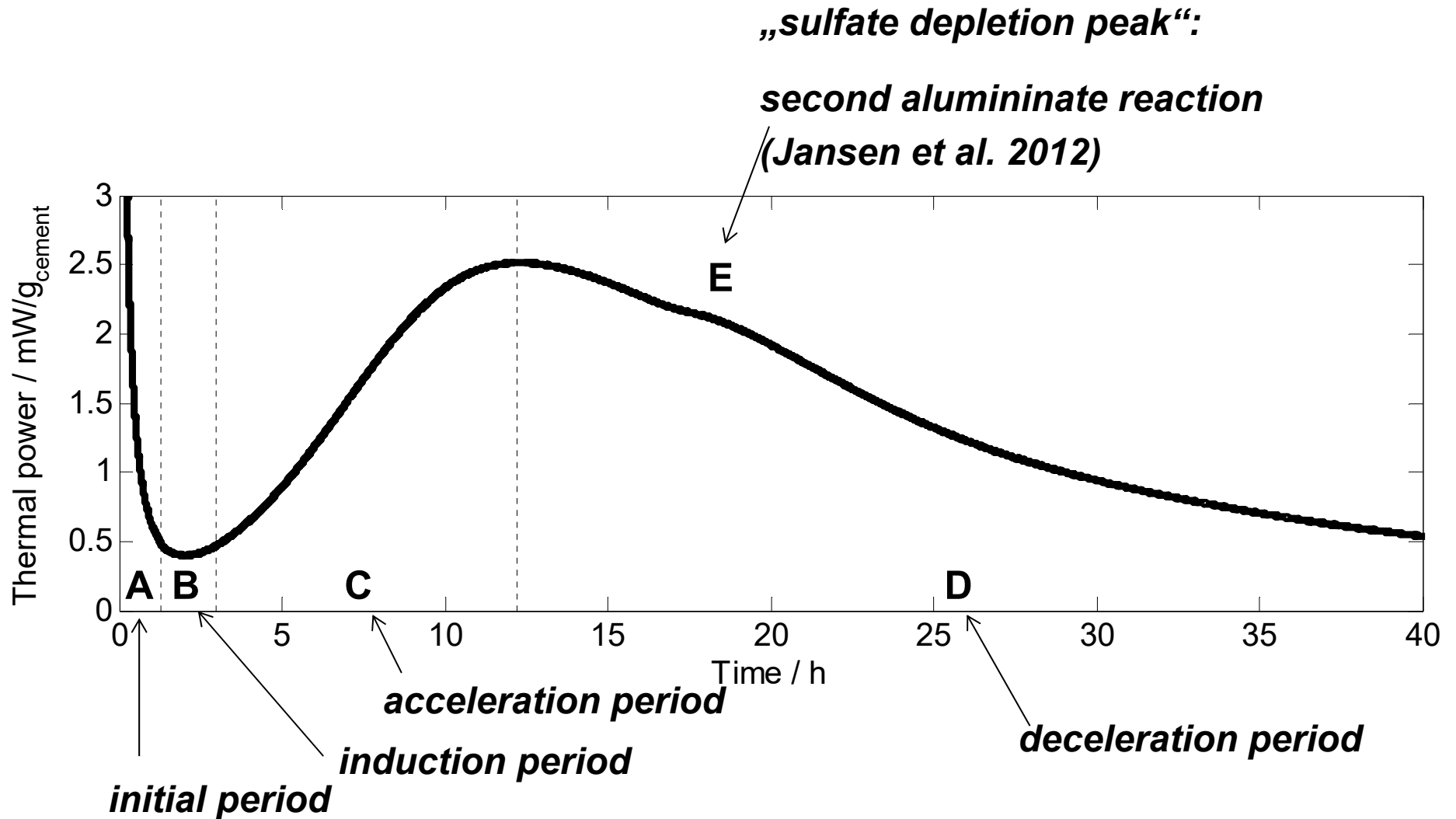
xp[J] =: pH;
yp[J][0] =: lgm_t[{Ca}];
yp[J][1] =: lg(my[{Ca+2}]);
yp[J][2] =: lg(my[{CaOH+}]);
    
```

- Lower Ca concentrations at high pH
 - $K_{s0} = \{Ca^{2+}\} \cdot \{OH^{-}\}^2 : pH \uparrow = OH^{-} \uparrow \Rightarrow Ca^{2+} \downarrow$
 - pH increase: more $CaOH^{+}$



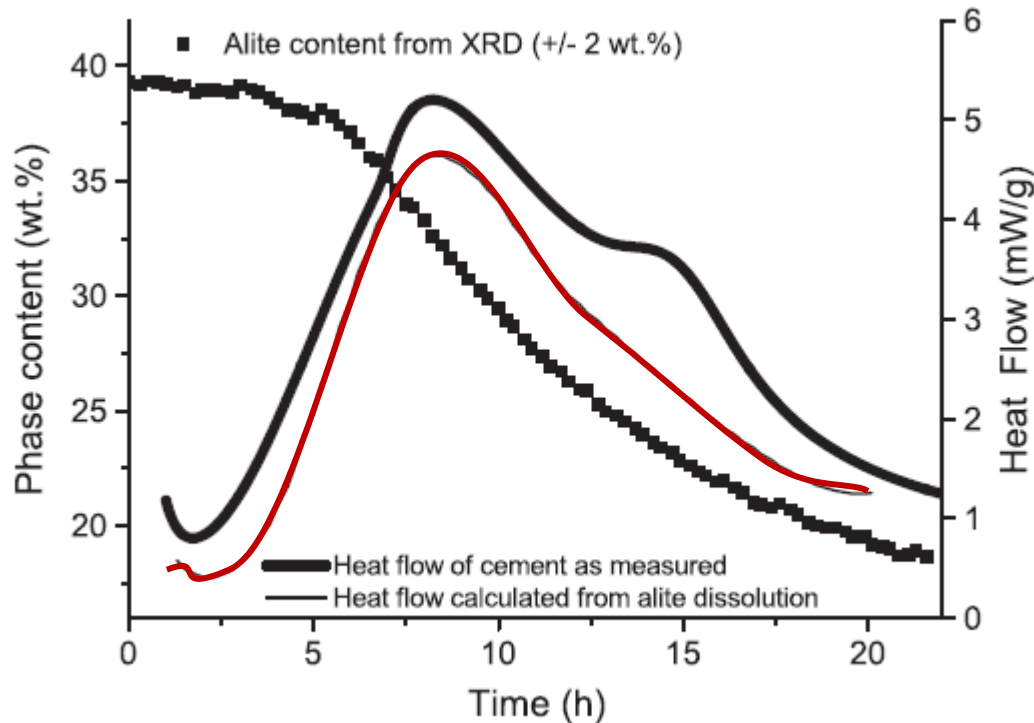
Cement hydration: calorimetry ↔ enthalpy

Isothermal calorimetry



Heat of hydration (I)

Main early reaction: **C₃S(alite) + water → C-S-H + portlandite**



	ΔH_f [kJ/Mol]	Mol weight [g/Mol]
Alite	-2929	228.2
H ₂ O	-286	18
CSH	-2890	201.9
Portlandite	-986	73.97

Enthalpy of alite reaction
 $= -(-2929 - 3.9 \cdot 286) + (-2890 - 1.3 \cdot 986)$
 $= -127 \text{ kJ/mol}$
 $\Rightarrow -558 \text{ J/g Alite}$

Table 3
 Enthalpies of reaction for the assumed reactions.

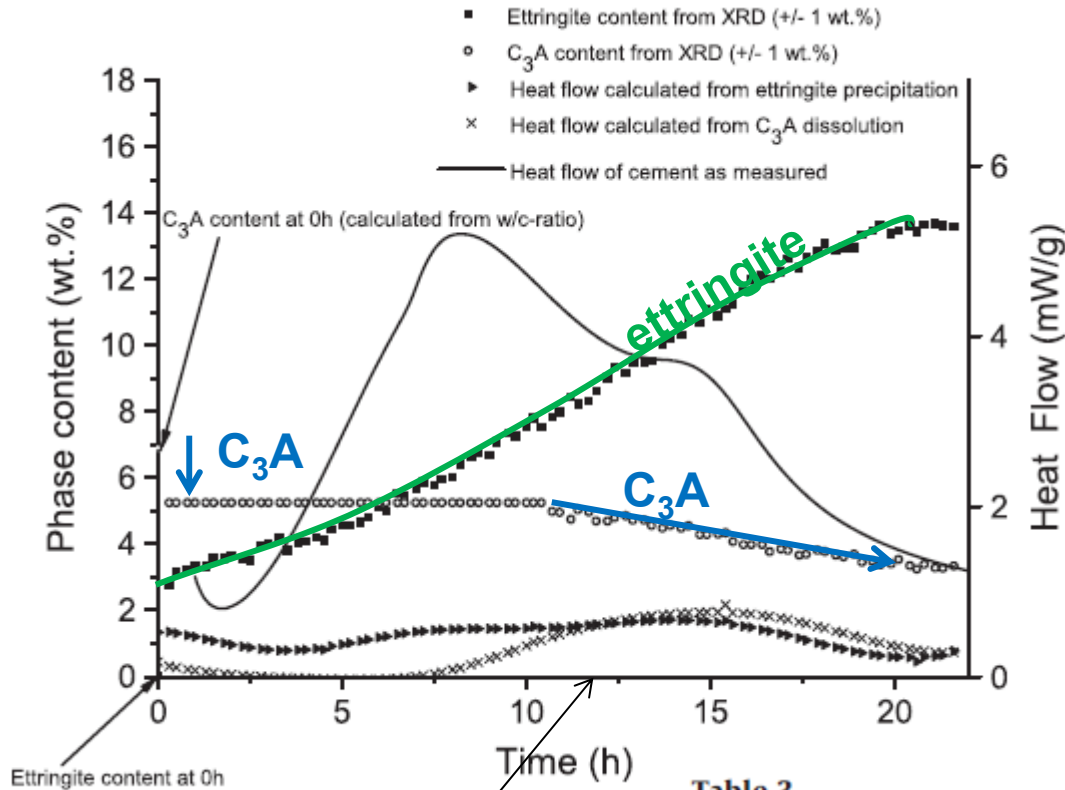
Reaction	Enthalpy
Eq. (1) (Silicate reaction)	- 561 J/g _{Alite}
Eq. (3) (Dissolution C ₃ A)	- 868 J/g _{C₃A}
Eq. (4) (Dissolution anhydrite)	- 50 J/g _{Anhydrite}
Eq. (5) (Dissolution gypsum)	59 J/g _{Gypsum}
Eq. (6) (Precipitation ettringite)	- 214 J/g _{Ettringite}

23°C, w/c = 0.50

Jansen et al. 2012, CCR

Heat of hydration (II)

Main early reaction: $C_3S(\text{alite}) + \text{water} \rightarrow \text{C-S-H} + \text{portlandite}$



Main C_3A dissolution

- 1st minutes
- Depletion of $CaSO_4$

Etringite forms continuously

Table 3

Enthalpies of reaction for the assumed reactions.

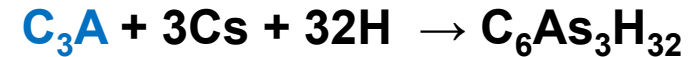
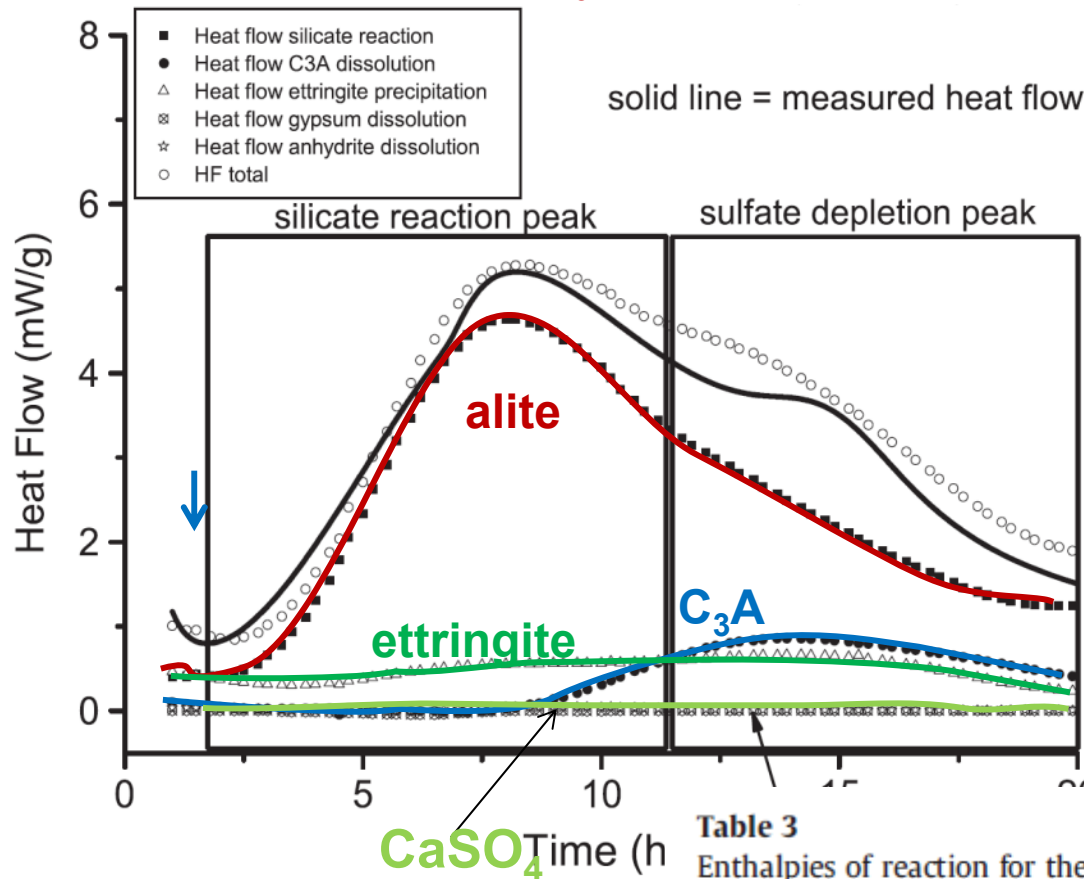
Reaction	Enthalpy
Eq. (1) (Silicate reaction)	- 561 J/g _{Alite}
Eq. (3) (Dissolution C_3A)	- 868 J/g _{C_3A}
Eq. (4) (Dissolution anhydrite)	- 50 J/g _{Anhydrite}
Eq. (5) (Dissolution gypsum)	59 J/g _{Gypsum}
Eq. (6) (Precipitation ettringite)	- 214 J/g _{Etringite}

23°C, w/c = 0.50

Jansen et al. 2012, CCR

Heat of hydration (III)

Main early reaction: $C_3S(\text{alite}) + \text{water} \rightarrow \text{C-S-H} + \text{portlandite}$



Main C_3A dissolution

- 1st minutes
- Depletion of $CaSO_4$

Ettringite forms continuously
Little effect of $CaSO_4$ dissolution

Table 3
Enthalpies of reaction for the assumed reactions.

Reaction	Enthalpy
Eq. (1) (Silicate reaction)	- 561 J/g _{Alite}
Eq. (3) (Dissolution C_3A)	- 868 J/g _{C_3A}
Eq. (4) (Dissolution anhydrite)	- 50 J/g _{Anhydrite}
Eq. (5) (Dissolution gypsum)	59 J/g _{Gypsum}
Eq. (6) (Precipitation ettringite)	- 214 J/g _{Ettringite}

23°C, w/c = 0.50

Jansen et al. 2012, CCR

How to calculate heat

	log K _{S0}	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/K/mol]	a ₀ [J/K/mol]	a ₁	a ₂	a ₃	V° [cm ³ /mol]	Ref
(Al-)ettringite ^{a,b,q}	-44.9	-15205.94	-17535	1900	1939	0.789			707	[1,2]
C₄As₃H₃₀^q		-14728.1	-16950.2	1792.4	1452	2.156			708	[24]
C₄As₃H₁₃		-10540.6	-11530.3	1960.4	970.7	1.483			411	[24]
C₄As₃H₉		-9540.4	-10643.7	646.6	764.3	1.638			361	[24]
tricarboaluminate ^a	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650	[2,1]
Fe-ettringite ^b	-44.0	-14282.36	-16600	1937	1922	0.855	2.02e6		717	[3,1]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	-3.40e6		330	[9]
C ₃ AH ₆ ^c	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
C ₃ AS _{0.41} H _{5.18} ^{*c}	-25.35	-5192.9	-5699	399	310	0.566	-4.37e6		146	[11]
C ₃ AS _{0.84} H _{4.32} ^{*d}	-26.70	-5365.2	-5847	375	331	0.484	-5.55e6		142	[11]
C ₃ FH ₆ ^{e**}	-26.30	-4122.8	-4518	870	330	1.237	-4.74e6		155	[11]
C ₃ FS _{0.84} H _{4.32} ^{d,e}	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
C₃(A,F)S_{0.84}H_{4.32}^d	-30.10	-4925.4	-5335	617	367	0.471	-8.10e6		146	[11]
C ₃ FS _{1.34} H _{3.32}	-34.20	-4681.1	-4994	820	395	0.383	-8.39e6		145	[11]
C ₄ AH ₁₉ ^f	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	369	[10,23]
C₄AH₁₃		-7325.7	-8262.4	831.5	208.3	3.13			274	[23]
C₄AH₁₁		-6841.4	-7656.6	772.6	0.0119	3.56	1.34e-7		257	[23]

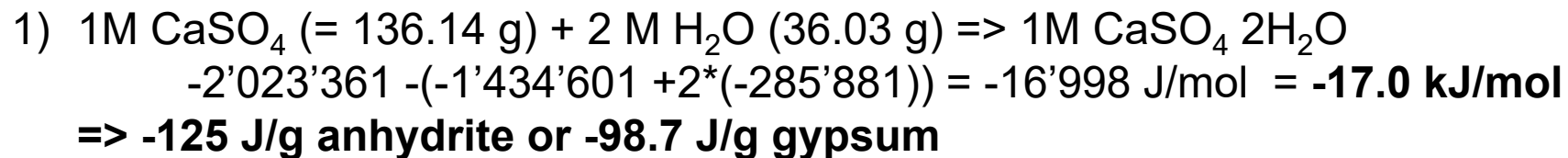
- Measured heat is due to enthalpy changes
- ! Water very important, involved in most reactions !

$$\Delta_f H^\circ (\text{H}_2\text{O}) = -285.88 \text{ kJ/mol}$$

How to calculate heat

	log K _{S0}	Δ _f G° [kJ/mol]	Δ _f H° [kJ/mol]	S° [J/K/mol]	a ₀ [J/K/mol]	a ₁	a ₂	a ₃	V° [cm ³ /mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH ₂ (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-CsH _{0.5} (hemihyd)	-3.59 ^{tv}	-1436.34 ^{tv}	-1575.3 ^{tv}	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum



$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ_{\text{gypsum}} - \Delta_f H^\circ_{\text{anhydrite}} - 2 \Delta_f H^\circ_{\text{water}} \\ &= -2022.63 - (-1434.11) - 2(-285.830) \\ &= -16.86 \text{ kJ mol}^{-1} \end{aligned}$$

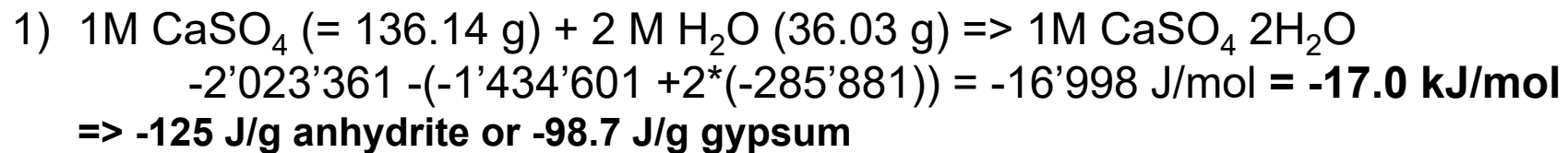
from which we see that the reaction between **anhydrite** and water to form gypsum is exothermic; that is, 16.86 kJ of **heat** would be released for every mole of **anhydrite** reacted.

Anderson (2017): Thermodynamics of Natural Systems

How to calculate heat

	log K _{S0}	Δ _f G° [kJ/mol]	Δ _f H° [kJ/mol]	S° [J/K/mol]	a ₀ [J/K/mol]	a ₁	a ₂	a ₃	V° [cm ³ /mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH ₂ (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-CsH _{0.5} (hemihyd)	-3.59 ^{tv}	-1436.34 ^{tv}	-1575.3 ^{tv}	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum



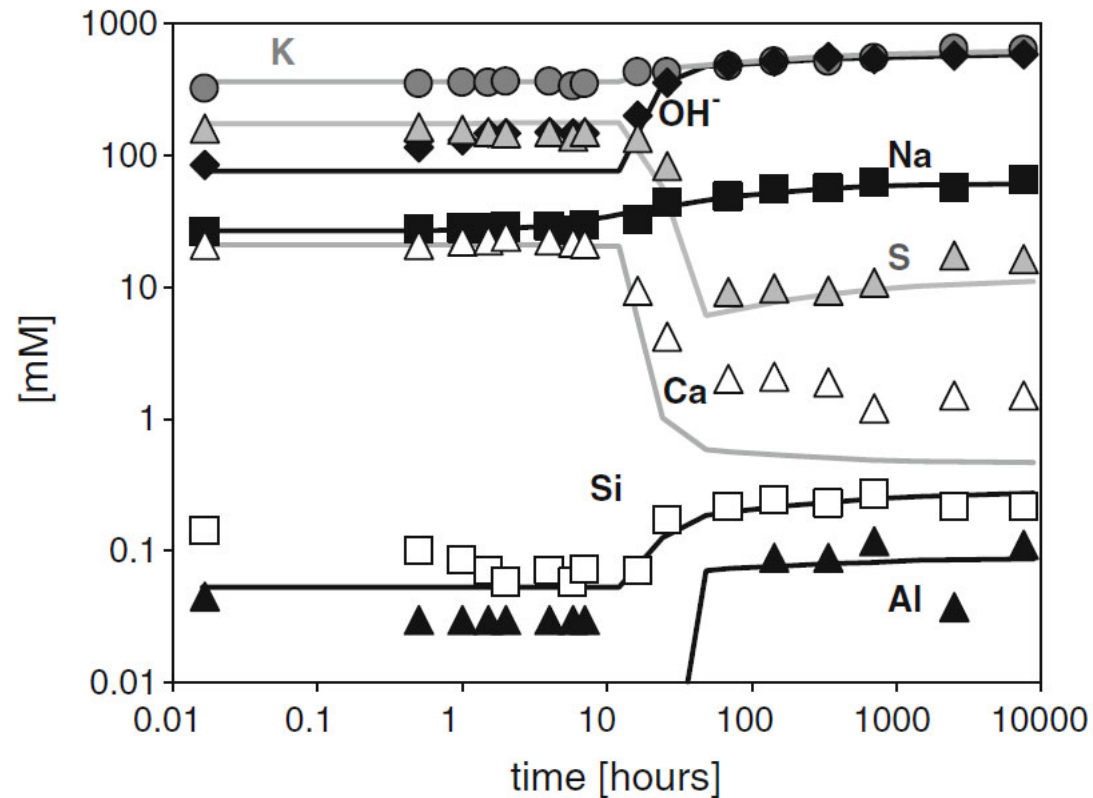
2) Dissolution of CaSO₄ in water: 1 g anhydrite (in 1 L H₂O)

<i>Input</i>	M	g/mol	H (J/mol)	g/L	J/g CaSO ₄
CaSO ₄	0.0073	136	-1434601	1	-10537
<i>output</i>					
Ca ²⁺	0.0055	40	-543069	0.22105834	-2995
SO ₄ ⁻²	0.0055	96	-909697	0.5298638	-5018
CaSO ₄ aq	0.0018	136	-1448430	0.2490777	-2650
Dissolution					-126

Thermodynamic data

1. Databases
2. Portlandite solubility and speciation
3. **Saturation indices**
 - a) **Pore solution**
 - b) **Calculation of SI**
4. Hydrates in cement
5. Details on how to manage thermodynamic data in GEMS
=> Self study

Poresolution



Composition changes during cement reaction

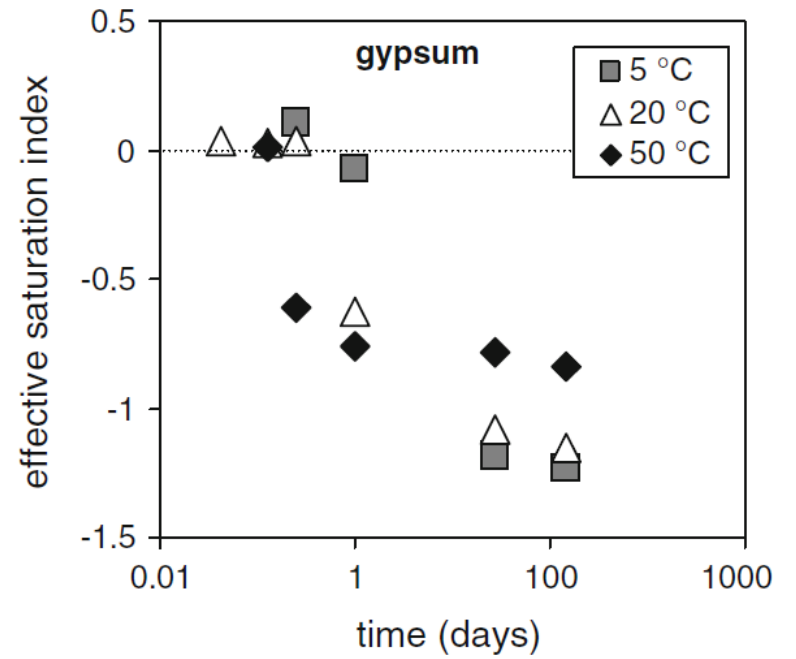
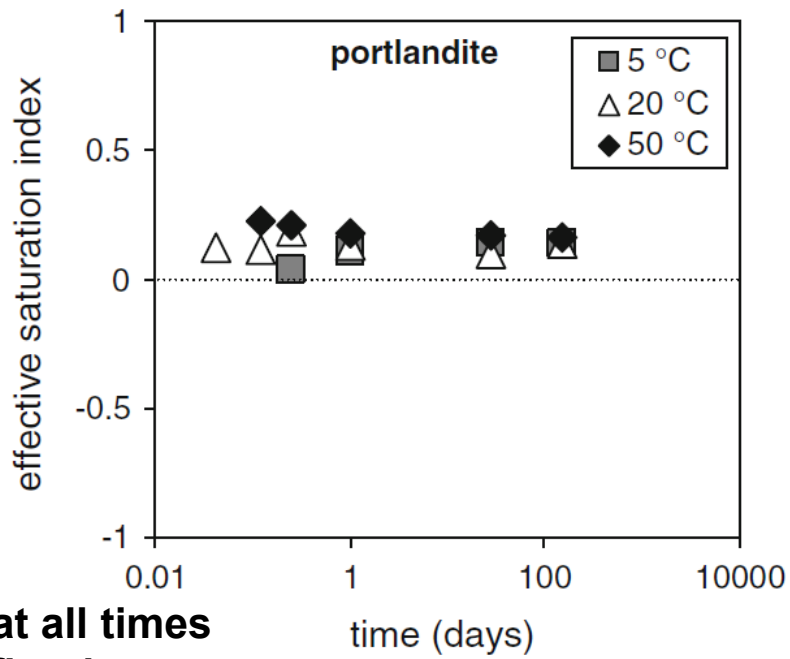
In particular for calcium and sulfate:

Calculation of saturation indices

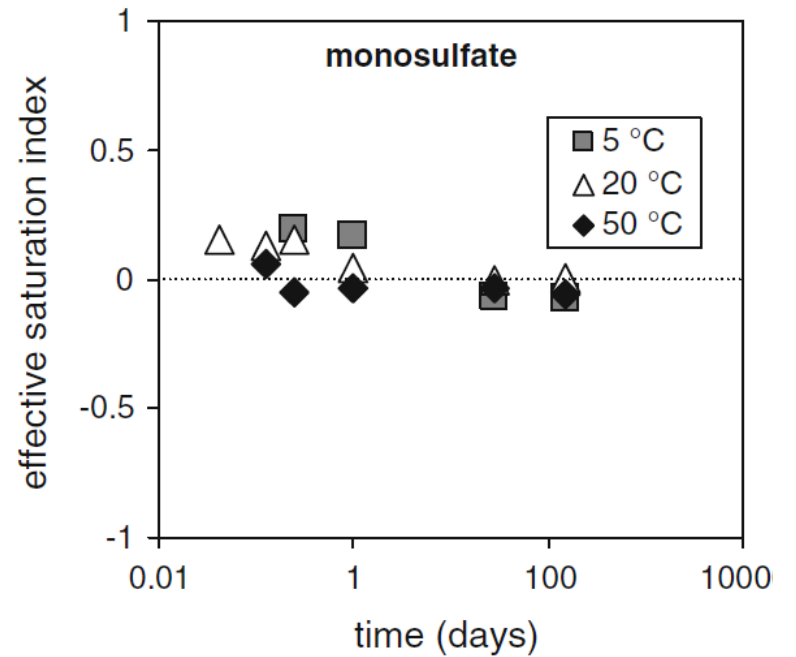
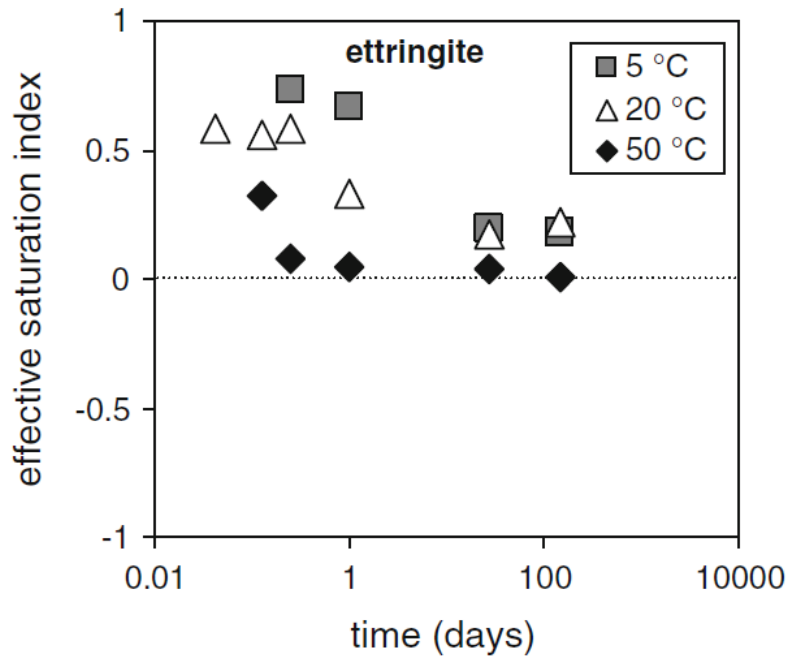
=> indicate changes in solid phases

Fig. 1 Evolution of the pore solution during the hydration of OPC. *Symbols* refer to measured concentrations, *lines* to modeled concentrations. Adapted from [17]

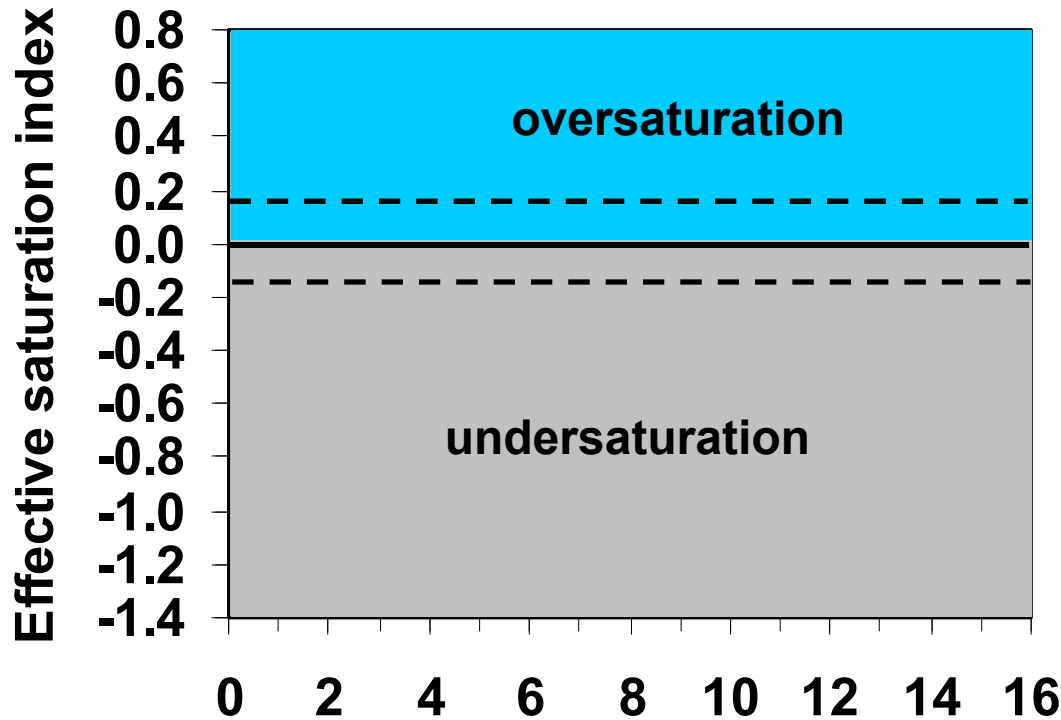
Lothenbach (2010) *Materials and Structures* 43, 1413-1433



**CH, AFt, AFm at all times
Gypsum only first hours**



Calculation of saturation indices



Phase in equilibrium
with pore solution

Might form

Phase not in equilibrium
with pore solution

Cannot form

Dissolves

Time (hours)

Derived from measured data e.g. pH, Ca_{tot}

$$SI = \log\left(\frac{IAP}{K_{S0}}\right) = \log\left(\frac{\{Ca^{2+}\}\{OH^{-}\}^2}{K_{S0_{portlandite}}}\right)$$

theoretical
solubility

IAP = ion activity product = measured concentrations

GEMS used to calculate
 $\{Ca^{2+}\}$ from Ca_{tot}

Saturation indices: measured conc.

time								
days	Al	Ca	S	K	Na	Si	OH-	pH
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	
0.04	0.0094	21	168	395	76	0.11	170	13.2
0.08	0.0043	21	175	404	77	0.13	164	13.2
0.17	0.0074	21	176	401	78	0.13	164	13.2
0.25	0.032	18	180	408	83	0.17	164	13.2
1	0.216	2.5	2.6	447	106	0.31	472	13.6
7	0.621	1.5	3.4	556	173	0.31	587	13.7
28	0.384	1.4	10	595	189	0.33	650	13.8
197	0.372	1.3	21	645	333	0.20	675	13.8
400	0.326	1.2	22	665	396	0.43	725	13.8

Make a new project:

by copying records from default d by linking files from the default d

Open Project

New Project

Learn more

Cancel

Create new project,
Al, Ca, Na, K, Si, S

Step 1 - Selection of databases

Phase/DC Filters

- Aqueous electrolyte
- Gas mixture
- Non-ideal fluids

I II III IV V VI

1	H									
2	Li	Be	B	C	N					
3	Na	Mg	Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni

Built-in Database	Version
<input checked="" type="checkbox"/> 3rdparty	
<input checked="" type="checkbox"/> cemdata	18.01
<input checked="" type="checkbox"/> .	
<input type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
<input checked="" type="checkbox"/> ss	18.01
<input type="checkbox"/> claysor	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

- Ion-association (IA) with Davies equation, D (default)
- IA with extended Debye-Hueckel equation (Helgeson), common b_gamma and a0, H
- IA with extended Debye-Hueckel equation (Shvarov), common b_gamma and a0, Y
- IA with extended Debye-Hueckel equation (Karpov), common b_gamma, individual a0, 3
- IA with Debye-Hueckel equation, no b_gamma, individual a0, 2
- IA with Debye-Hueckel limiting law (very low ionic strength), 1
- Do not generate; select a user-defined Phase record from database (Q, S, Z), U
- Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq_gen aq EDH_H

Parameters for the aqueous phase model

b_gamma(1,298) value:

0.123

b_gamma(P,T) mode

KOH

Common a0 value:

3.67

Gamma (neutral species)

Calculate as b_gamm

Gamma (water solvent)

Calculation of saturation indices

Input Recipe of Single Thermodynamic System: SI:G:SI:0:0:1:20:0: ? X

tname calculation of saturation indices

Property Selection

Property	Selection
Compos (xa_)	Al(OH)3 C4A3s
DComp (xd_)	Al2O3 CA
IComp (bi_)	Al2Si2O5(OH)4 CA2
Phase (xp_)	Aqua Ca(NO3)2
Kin.lower (dll_)	C12A7 Ca(OH)2
Kin.upper (dul_)	C2S CaCl2
G0 shift (gEx_)	C3A CaO
Other Inputs	C3S CaSO4

Recipe Input

ty	Name	Quantity	Units
1	Al(OH)3	0.0094	h
2	Aqua	1000	g
3	CaO	21	h
4	KOH	395	h
5	NaOH	76	h
6	O2	0.1	g
7	SO3	168	h
8	SiO2	0.11	h

Input quantities of Compos(itions) contributing to B_ vector

Learn more Print OK Cancel

1 kg of water

=> mmol/l

h: mmol

O₂ =>
oxidising cond.

CaO, SO3, Al(OH)3, KOH, NaOH, SiO2 used as proxy for measured total Ca, Al, ...concentrations [mmol/l]

=> Input of uncharged species

Window Help

SI:G:SI:0:0:1:20:0:

Compos 2) DComp Phase IComp Surfaces Config 25/04/2019, 16:44

1)

	mDC	DCvp				dll	dul		
46	G	g S-2	H2S	...	B	0	1000000	M	
47	I	s CaSiOH	CSHQ-JenD	...	B	0	0	M	
48	I	s CaSiOH	CSHQ-JenH	...	B	0	0	M	
49	I	s CaSiOH	CSHQ-TobD	...	B	0	0	M	
50	I	s CaSiOH	CSHQ-TobH	...	B	0	0	M	
51	I	s KSiOH	KSiOH	...	B	0	0	M	
52	I	s NaSiOH	NaSiOH	...	B	0	0	M	
53	I	s CaAlOSH	straetlingite	...	B	0	0	M	
54	I	s CaAlOSiHstraetlingite7...		...	B	0	0	M	
55	I	s CaAlOsH	ettringite	...	B	0	0	M	
56	I	s CaAlOsH	ettringite30	...	B	0	0	M	
57	J	s CaAlOH	C4AH13	...	B	0	0	M	
58	M	s CaAlOsH	monosulphate12...	...	B	0	0	M	
59	M	s CaAlOH	C4AH13	...	B	0	0	M	
60	J	s CaAlOsH	monosulphate12...	...	B	0	0	M	
61	O	s AlOH	AlOHam	...	B	0	0	M	
62	O	s AlOH	AlOHmic	...	B	0	0	M	
63	O	s AlOH	Gbs	...	B	0	0	M	
64	O	s AlSiOH	Kln	...	B	0	0	M	
65	O	s CaAlO	C12A7	...	B	0	0	M	
66	O	s CaSiO	C2S	...	B	0	0	M	
67	O	s CaAlO	C3A	...	B	0	0	M	
68	O	s CaSiO	C3S	...	B	0	0	M	
69	O	s CaAlO	CA	...	B	0	0	M	

3) Scroll down to 2nd table

4) Select all dul of solids

5) Press F8, 0, Ok-do it

dul = upper limit

dul = 0

Solid cannot form

dll = lower limit

Window Help



Input: System Definition Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Ac
a aq_gen	37	a	56.417069	4.549e-11		
g gas_gen	3	g	0.0018917082	-1.166e-07		
s CSHQ	6	s	0	0.7215		
s straetlingite	2	s	0	-2.475		
s ettringite	2	s	0	10		
s SO4_OH_AFm	2	s	0	-1		
s OH_SO4_AFm	2	s	0	-1		
s Al(OH)3am	1	s	0	-4.444		
s Al(OH)3mic	1	s	0	-3.581		
s Gibbsite	1	s	0	-3.058		
s Kaolinite	1	s	0	-15.97		
s Mayenite	1	s	0	-143.8		
s Belite	1	s	0	-0.7583		
s Aluminat	1	s	0	-37.99		
s Alite	1	s	0	-12.45		
s CA	1	s	0	-13.22		
s CA2	1	s	0	-19.97		
s C2AH75	1	s	0	-3.78		
s C3AH6	1	s	0	-1.724		
s C4AH11	1	s	0	-3.383		
s C4AH13	1	s	0	-1.558		
s C4AH19	1	s	0	-1.269		
s CAH10	1	s	0	-5.388		
s C4AsH105	1	s	0	1.332		
s C4AsH12	1	s	0	2.723		
s C4AsH14	1	s	0	2.712		
s C4AsH16	1	s	0	2.726		
s C4AsH9	1	s	0	-0.7921		
s Chabazite	1	s	0	-23		
s ZeoliteP	1	s	0	-10.89		
s C2ASH55	1	s	0	-5.64		
s C6AsH13	1	s	0	-19.53		
s C6AsH9	1	s	0	-27.75		
s Portlandite	1	s	0	0.5735		
s Anhydrite	1	s	0	-0.1117		
s Gypsum	1	s	0	0.1515		
s hemihydrate	1	s	0	-0.887		
s arcanite	1	s	0	-1.037		
s syngenite	1	s	0	-0.05999		
s thenardite	1	s	0	-4.049		

PC pore solution after 1 hour
Oversaturated: logSI > 0
with respect to

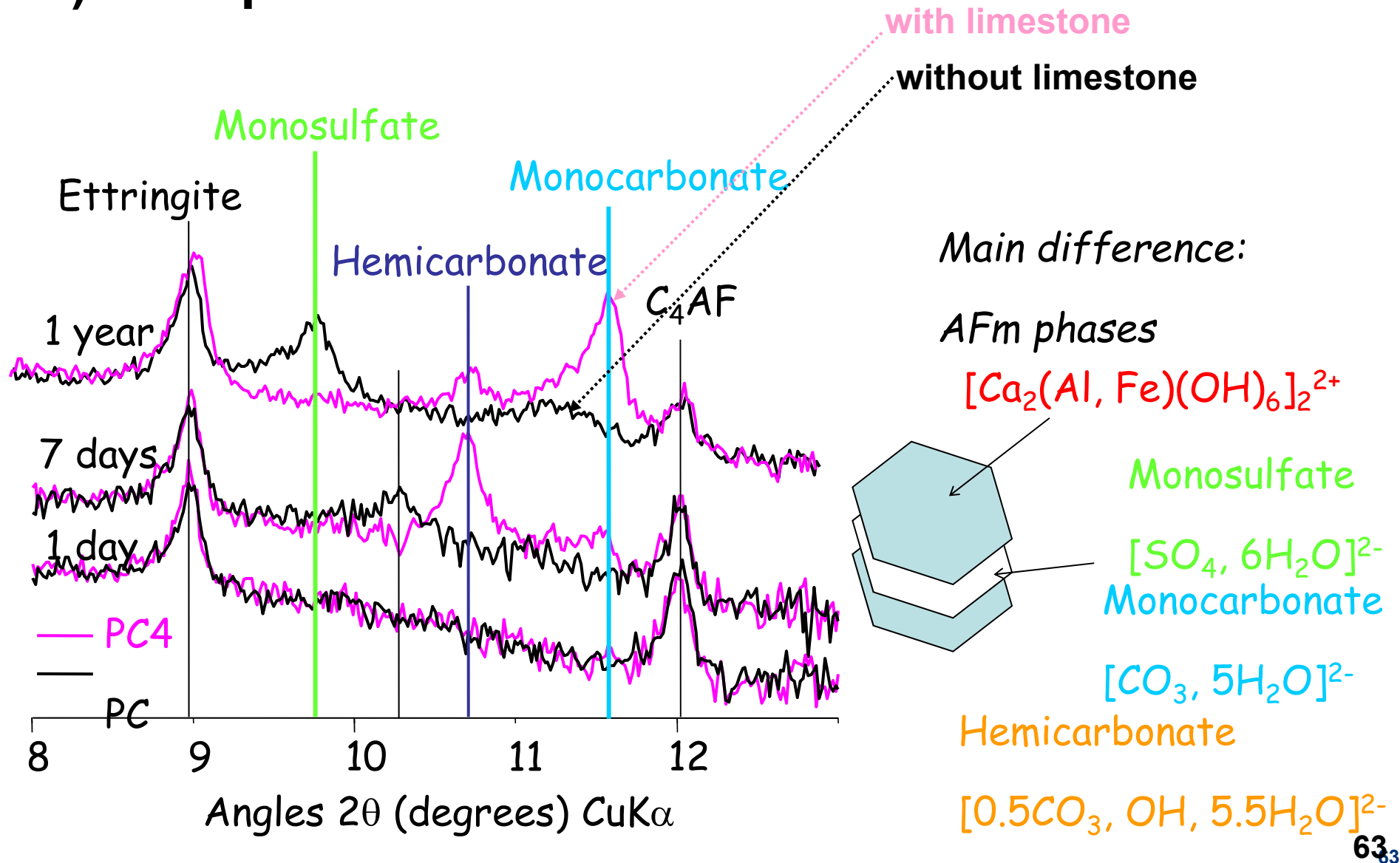
- C-S-H
- Ettringite
- Monosulfate
- Portlandite
- Gypsum

$$\log SI = \log \left(\frac{IAP}{K_{S0}} \right) = \log \left(\frac{\{Ca^{2+}\} \{OH^{-}\}^2}{K_{S0\text{portlandite}}} \right)$$

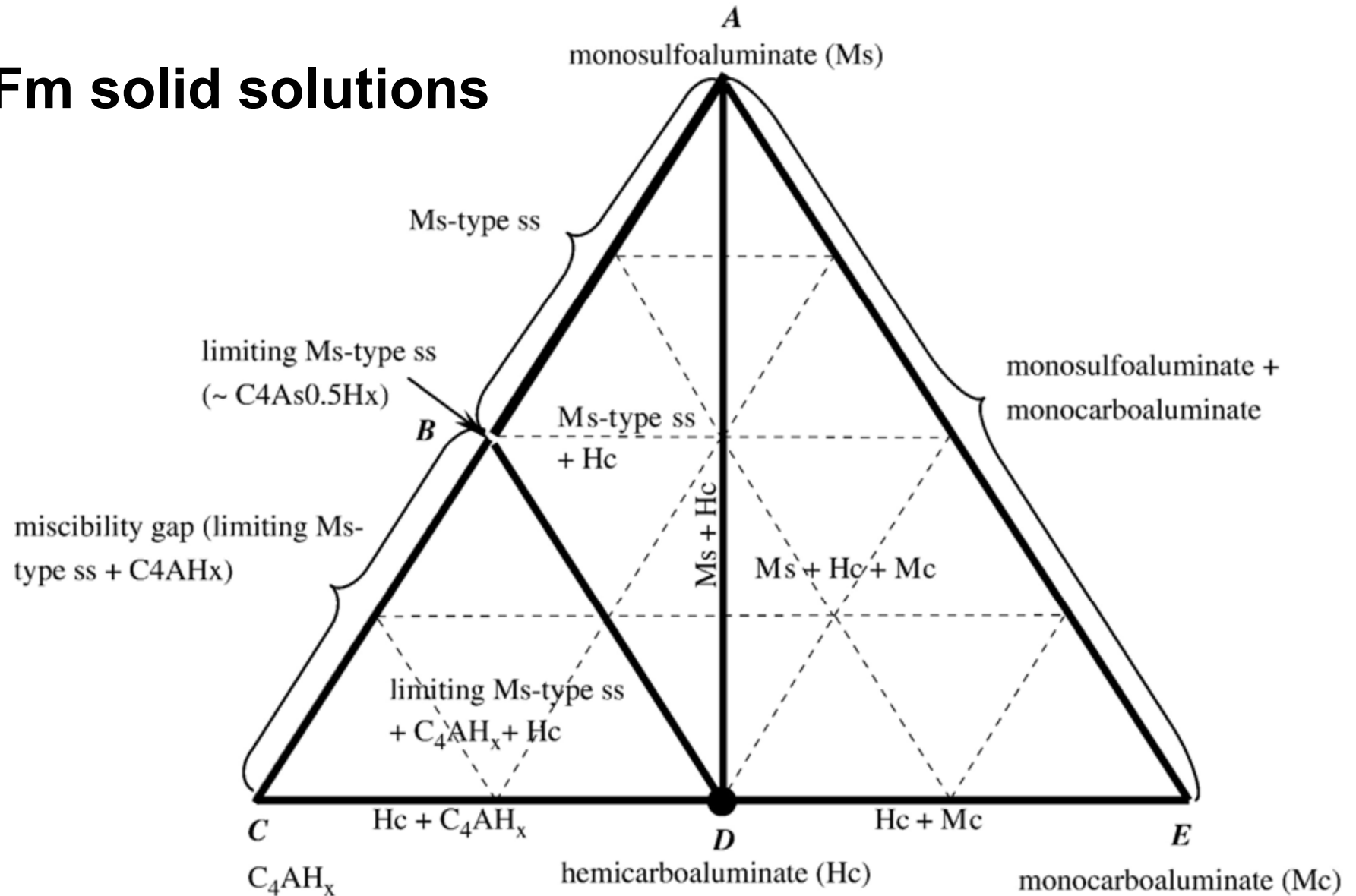
Thermodynamic data

1. Databases
2. Solubility and speciation
3. Saturation indices
4. **Hydrates in cements**
5. Details on how to manage thermodynamic data in GEMS
=> Self study

1) AFm phases



AFm solid solutions



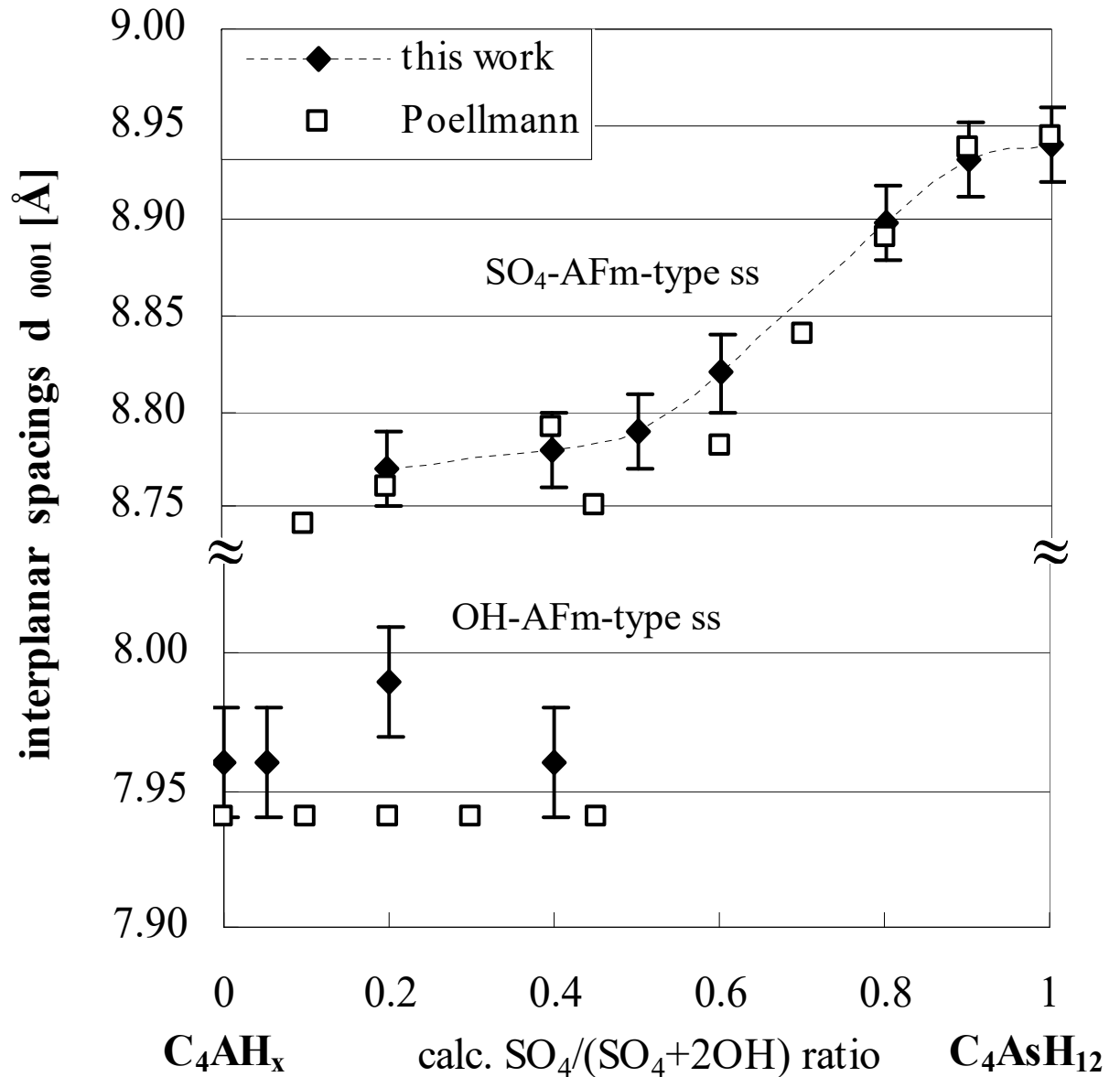
1) AFm phases

**Characteristics
solid solutions:**

- XRD peak shift

- change of
concentrations

**C_4AH_{13} –
monosulfate:
solid solution**

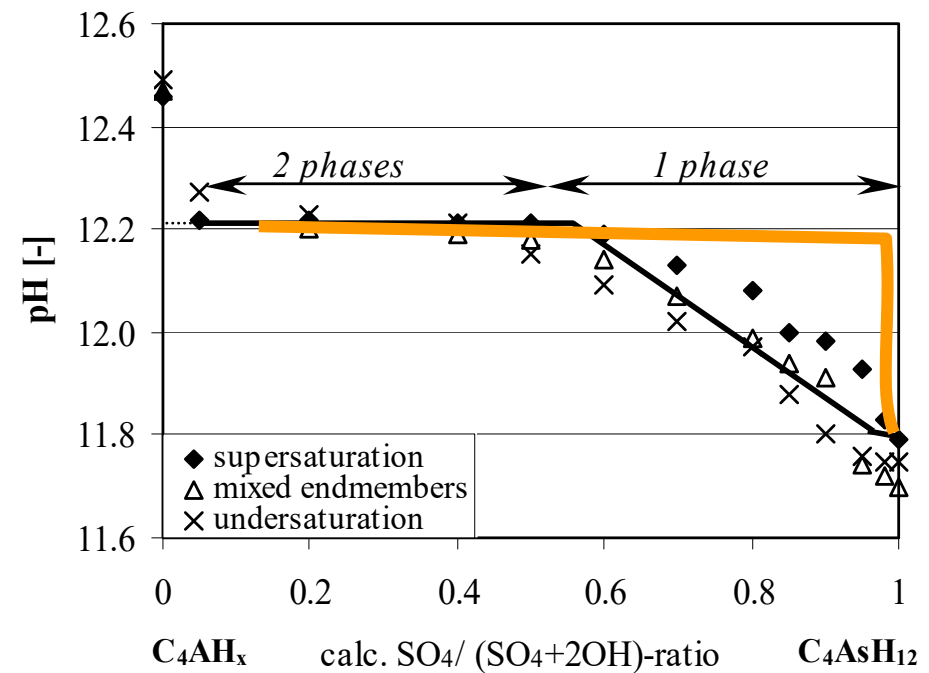
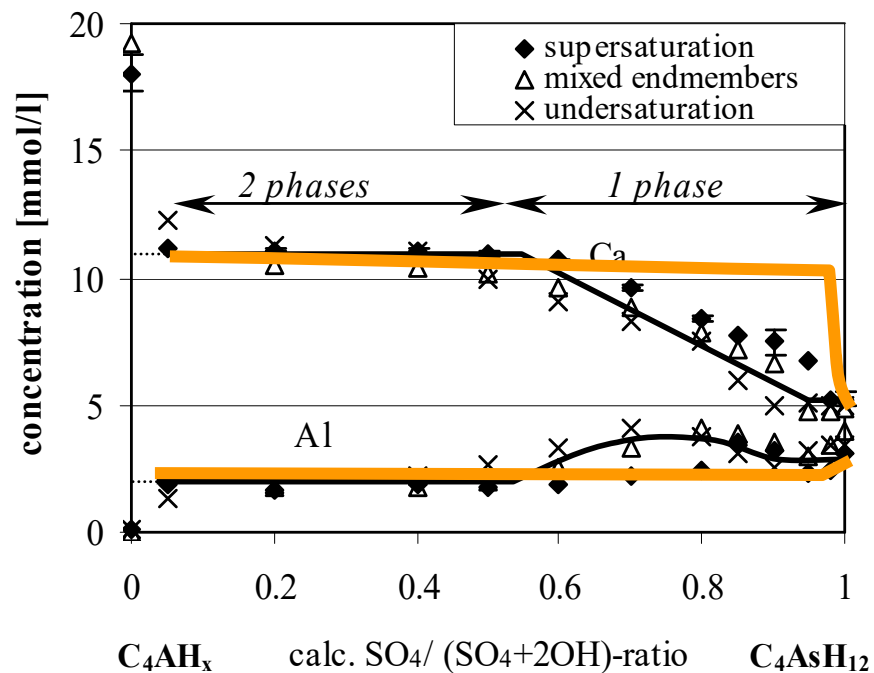


1) AFm phases

Characteristics of solid solution:

- peak shift in XRD
- continuous change of concentrations

Matschei et al (2007)



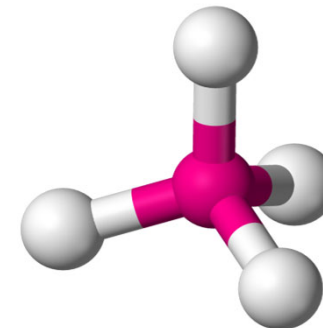
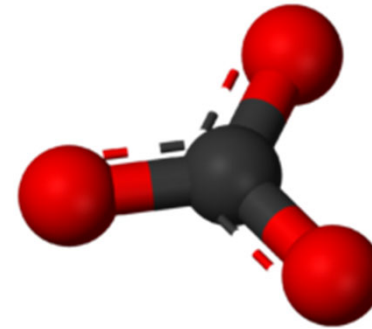
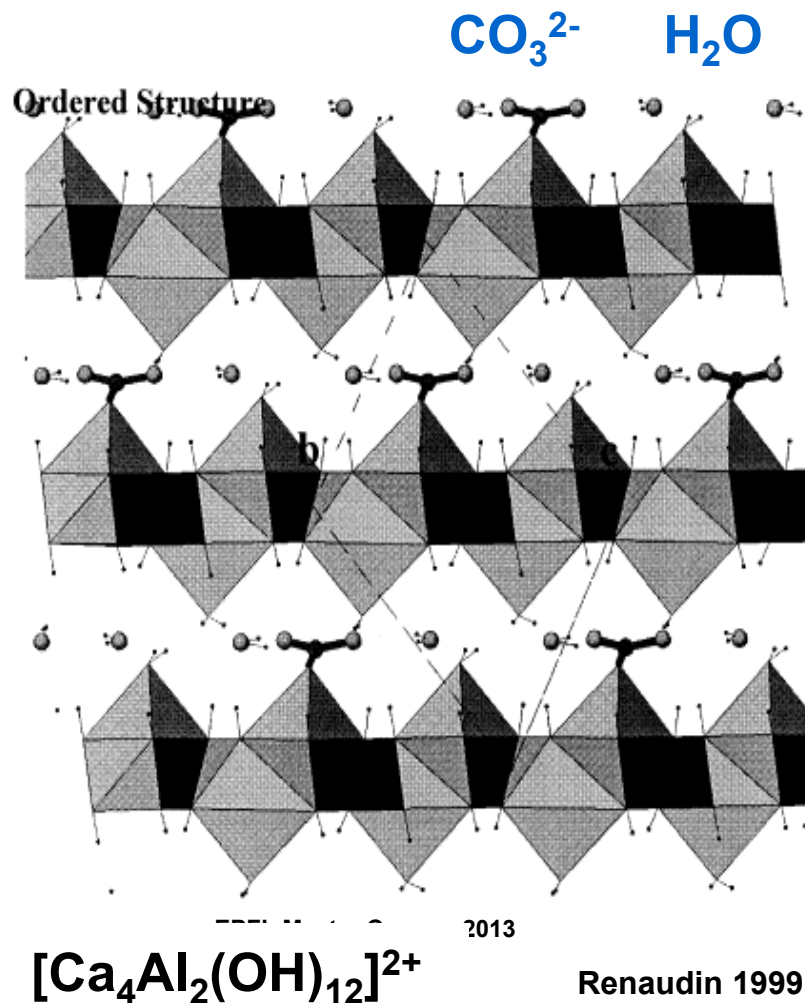
Effects of solid solution:

- stabilizes solids
- lowers aqueous concentrations - no solid solution

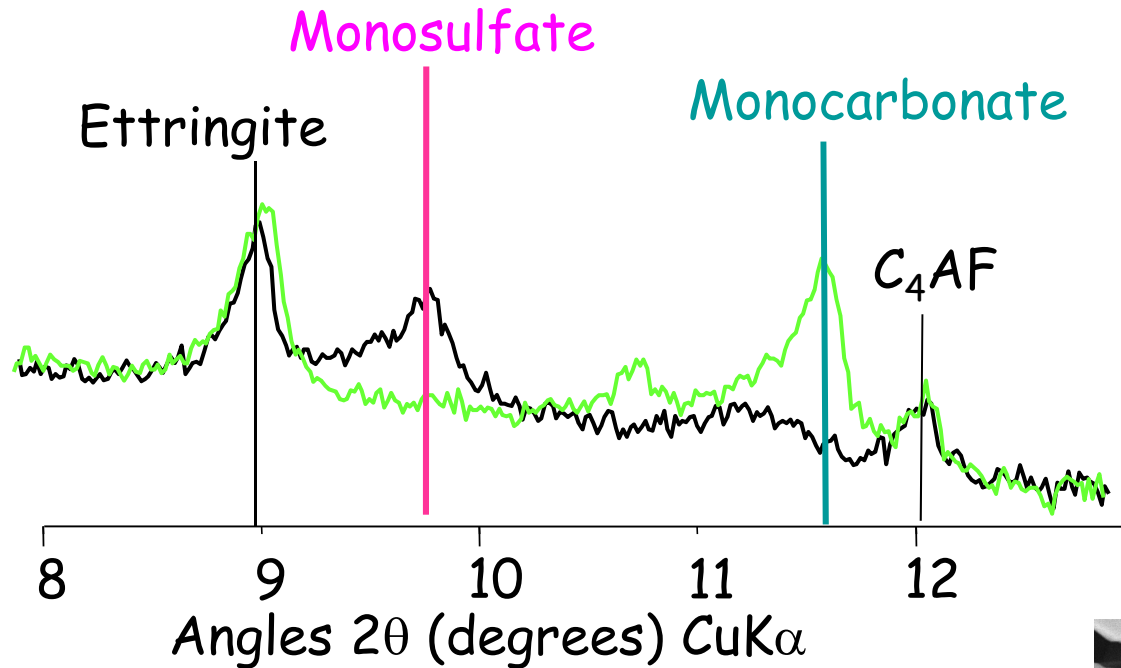
- miscibility gap 0.03-0.5

Solid solutions probable

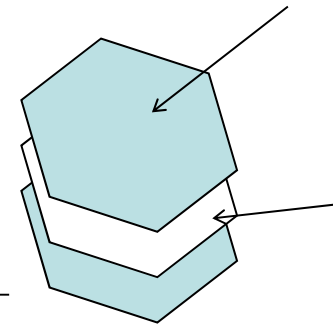
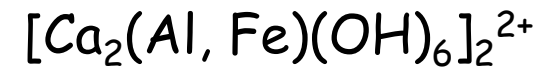
- Similar charge
- Similar structure
- Similar size



Solid solution $\text{CO}_3\text{-AFm}$ – $\text{SO}_4\text{-AFm}$?



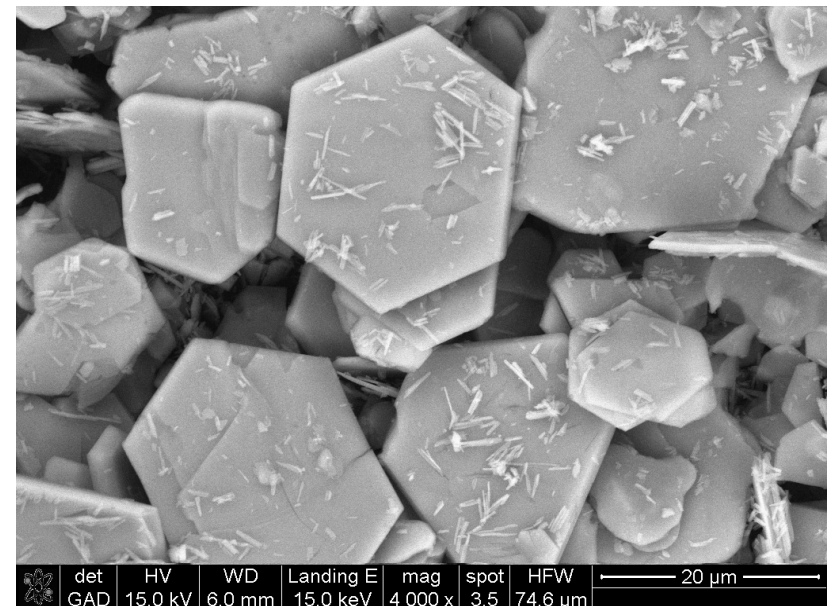
Main difference:
AFm phases



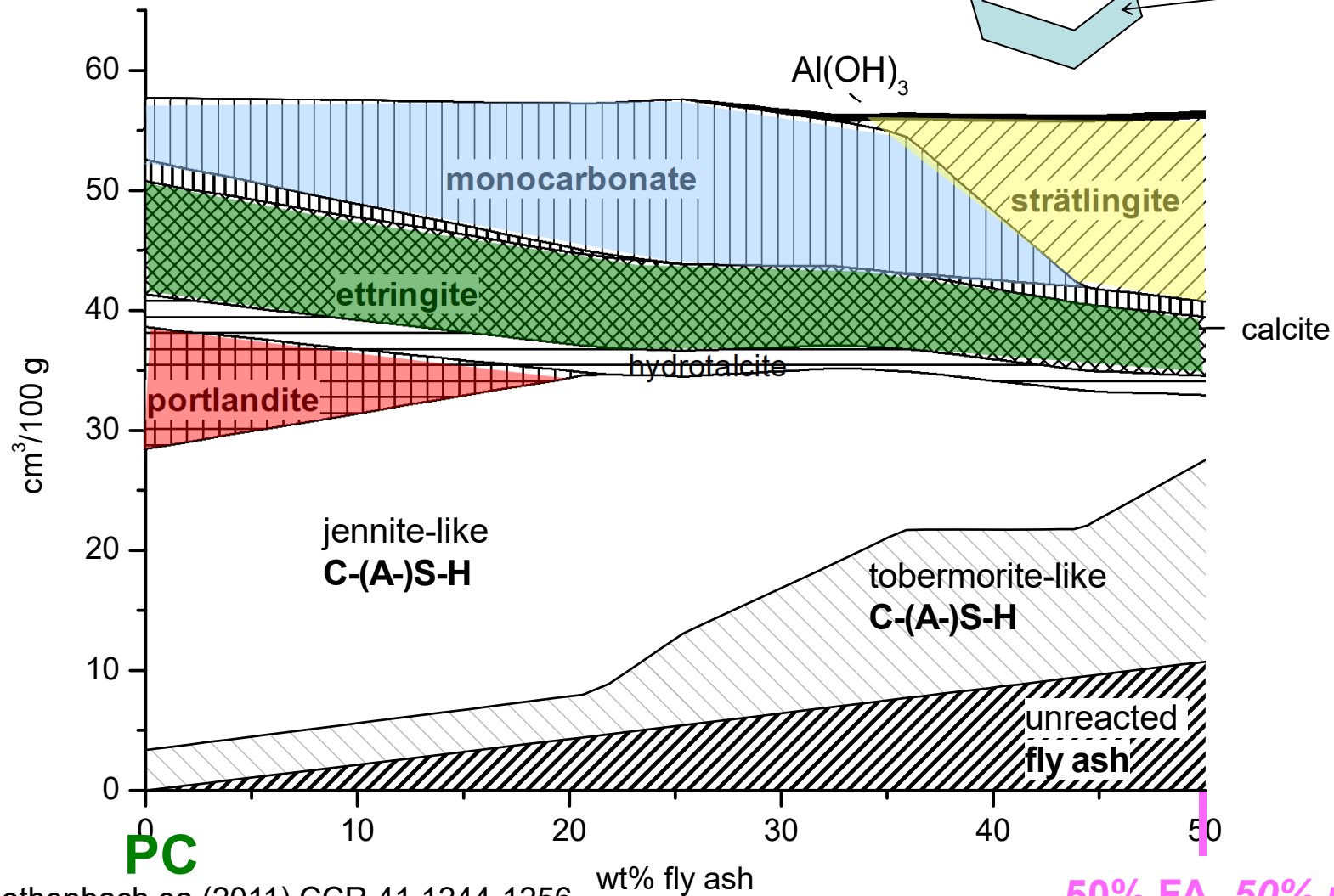
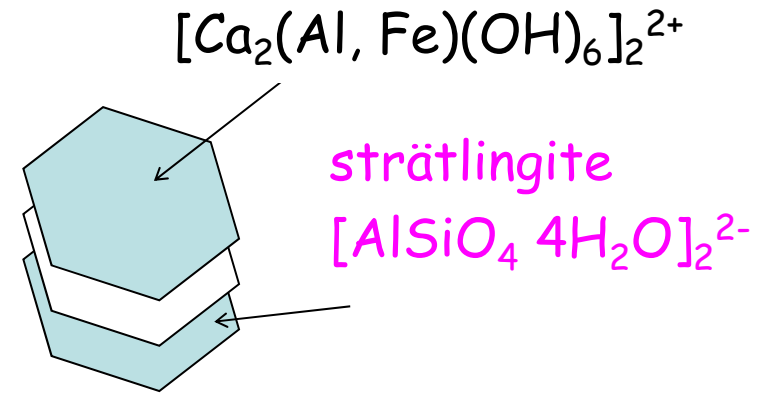
Monosulfate
 $[\text{SO}_4, 6\text{H}_2\text{O}]^{2-}$
Monocarbonate
 $[\text{CO}_3, 5\text{H}_2\text{O}]^{2-}$

Solid solution not probable:

- Similar charge ✓
- Similar structure -
- Similar size -



Further AFm phase at low CaO availability: Strätlingite incompatible with portlandite



Ettringite:

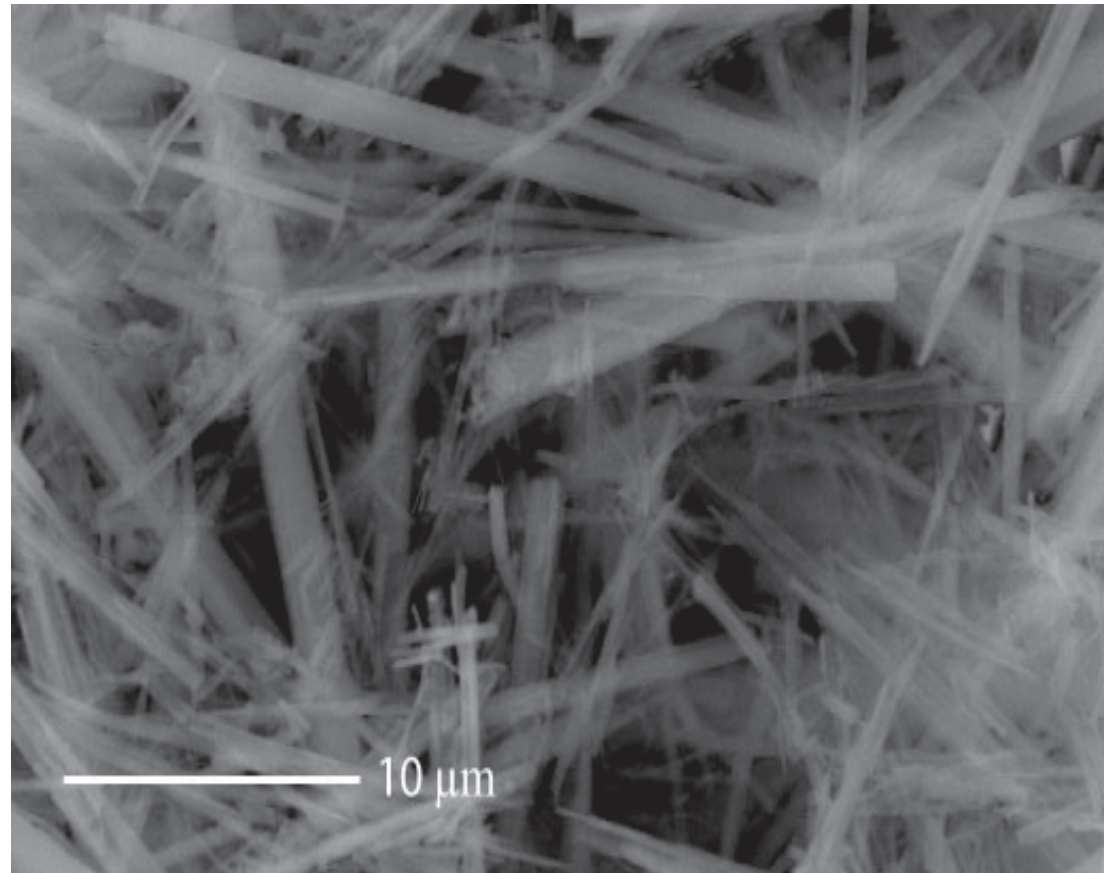


high water content

-> voluminous

-> low density 1.8 kg/dm³

-> good space filling

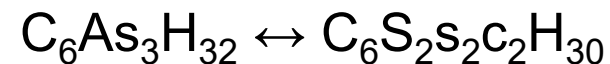


Takes up other ions
(solid solutions)

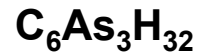
-> Al ↔ Fe

-> SO₄²⁻ ↔ CO₃²⁻, CrO₄²⁻, ...

solid solution with thaumasite



Ettringite:



high water content

-> voluminous

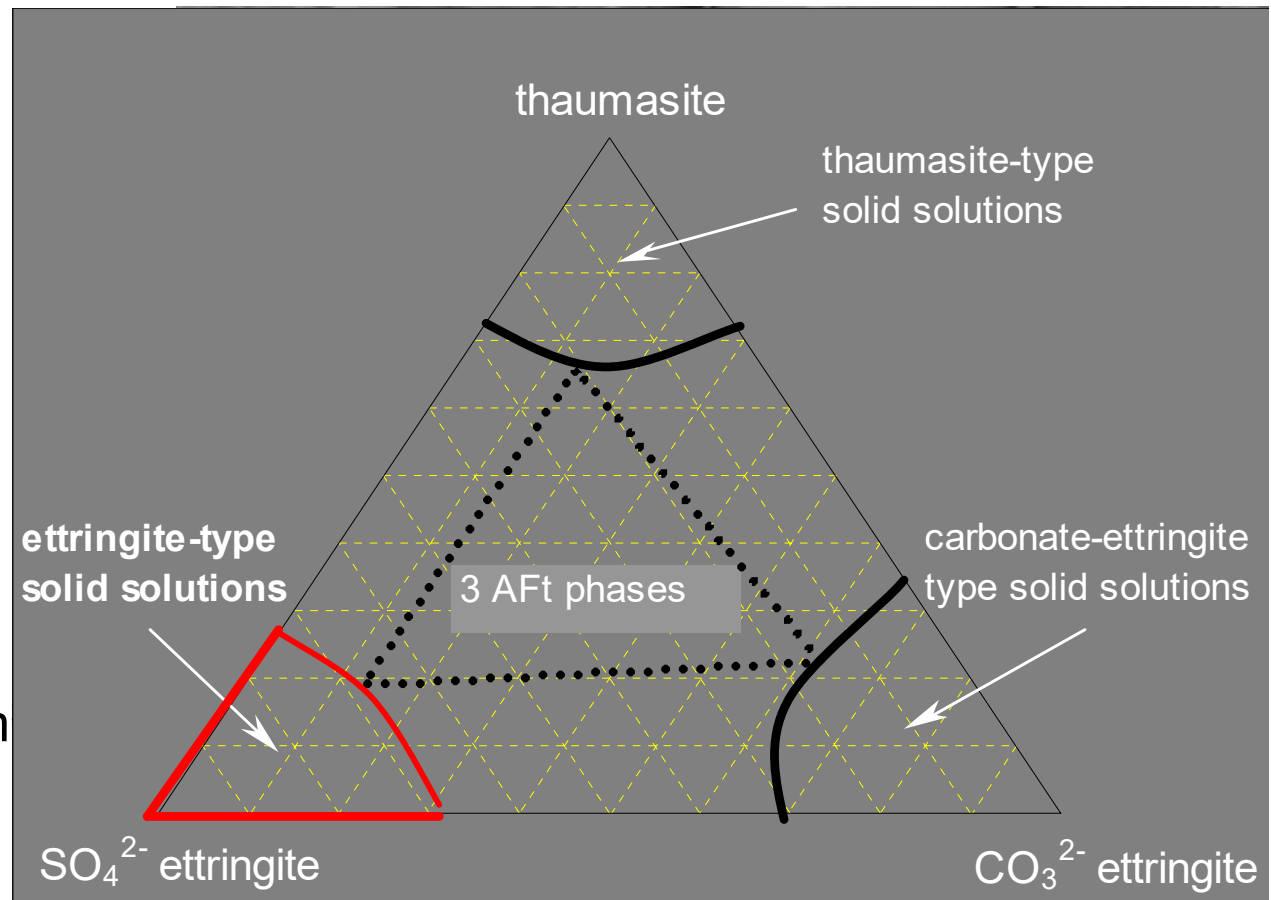
-> low density 1.8 kg/dm

-> good space filling

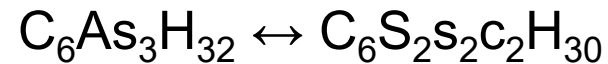
Takes up other ions
(solid solutions)

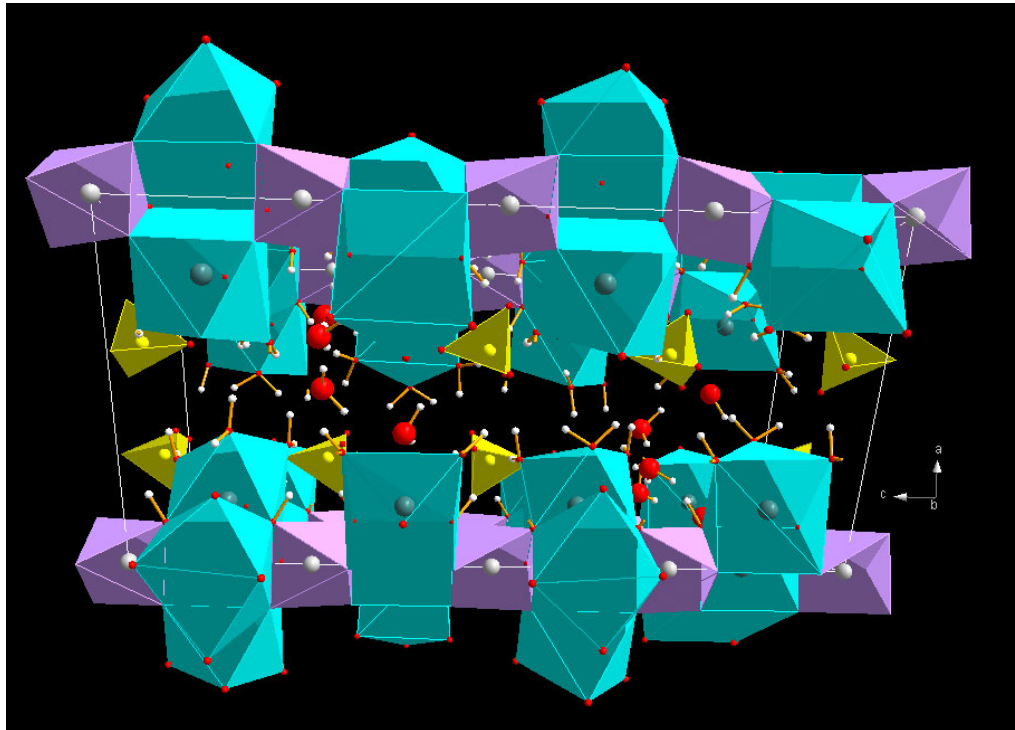
-> $Al \leftrightarrow Fe$

-> $SO_4^{2-} \leftrightarrow CO_3^{2-}, CrO_4^{2-}, \dots$



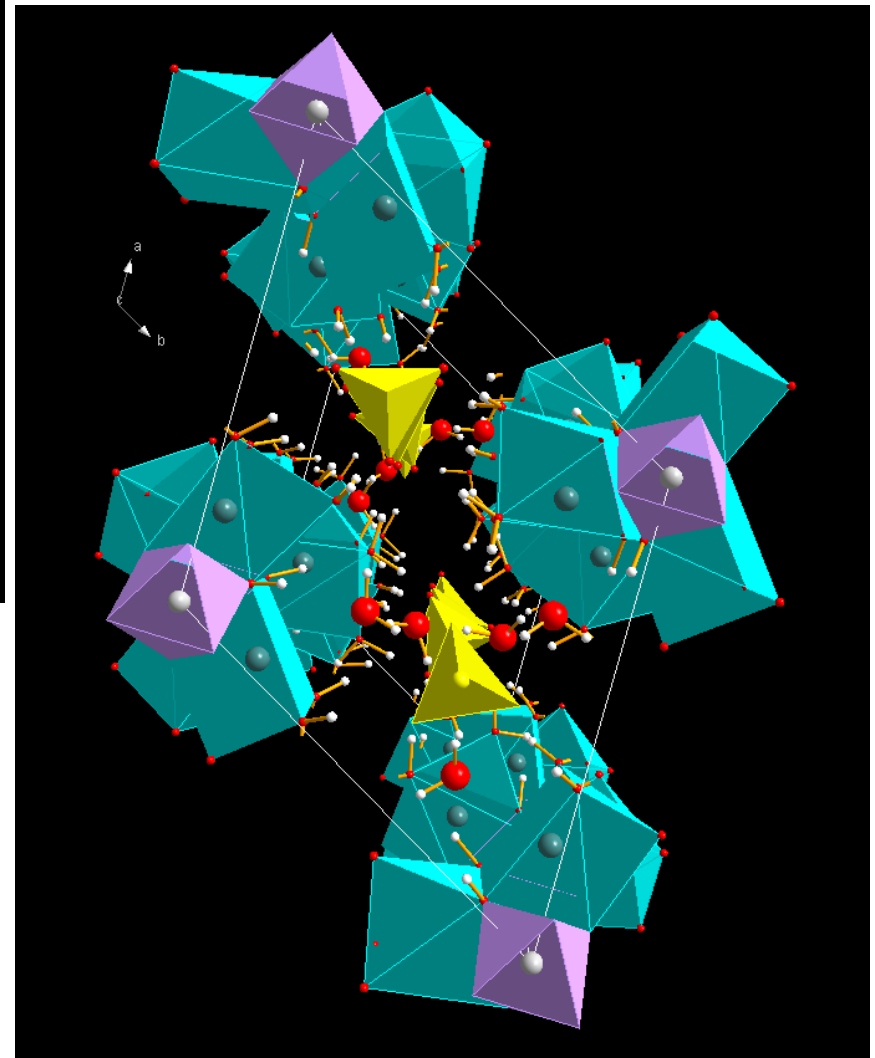
solid solution with thaumasite





ettringite
crystal system: hexagonal
 $a=1.12$ nm
 $c=2.14$ nm

* F. Goetz- Neunhoeffler et al. Powder diffraction 21 (2006) 4-11



Hydrogarnets:



Solid solutions

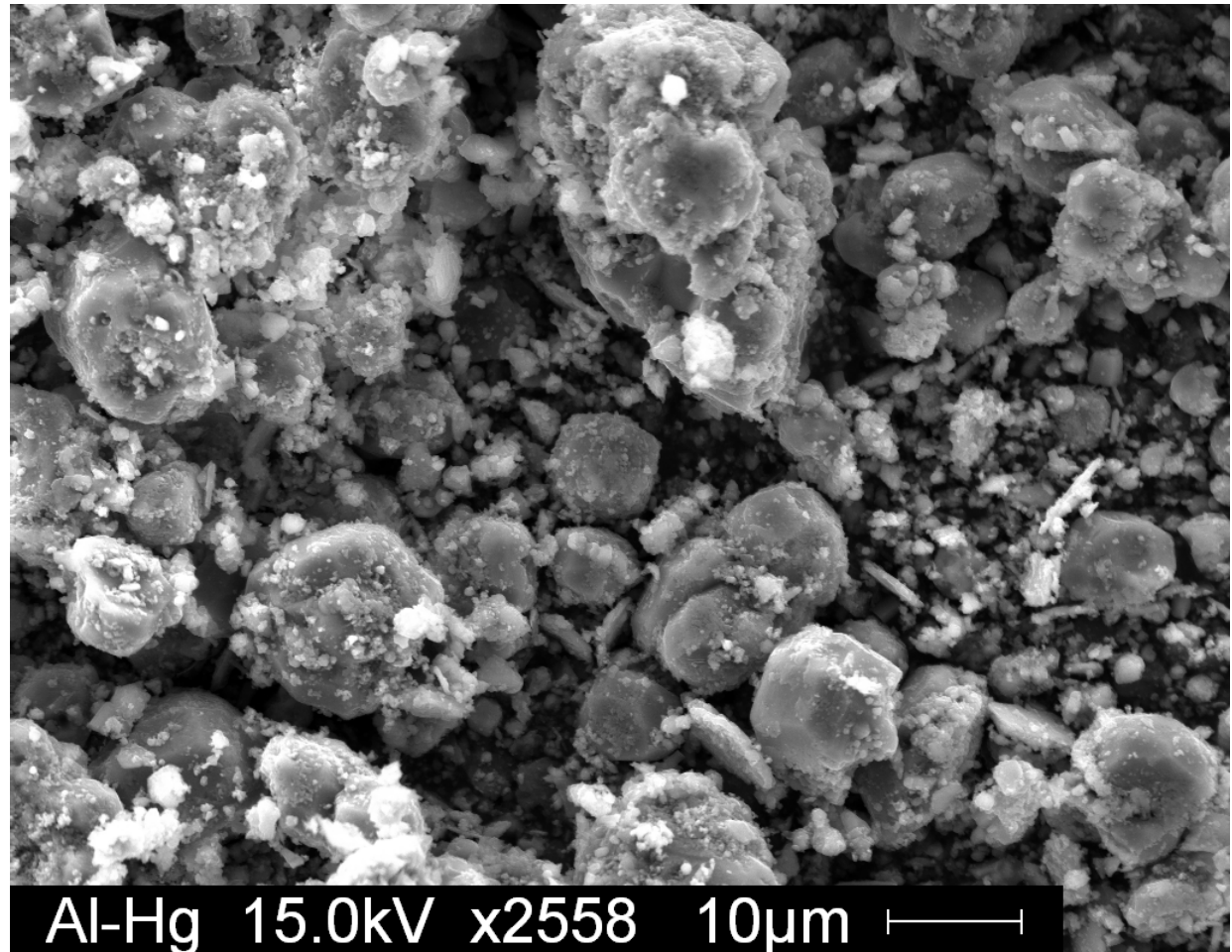
-> $\text{Al} \leftrightarrow \text{Fe}$

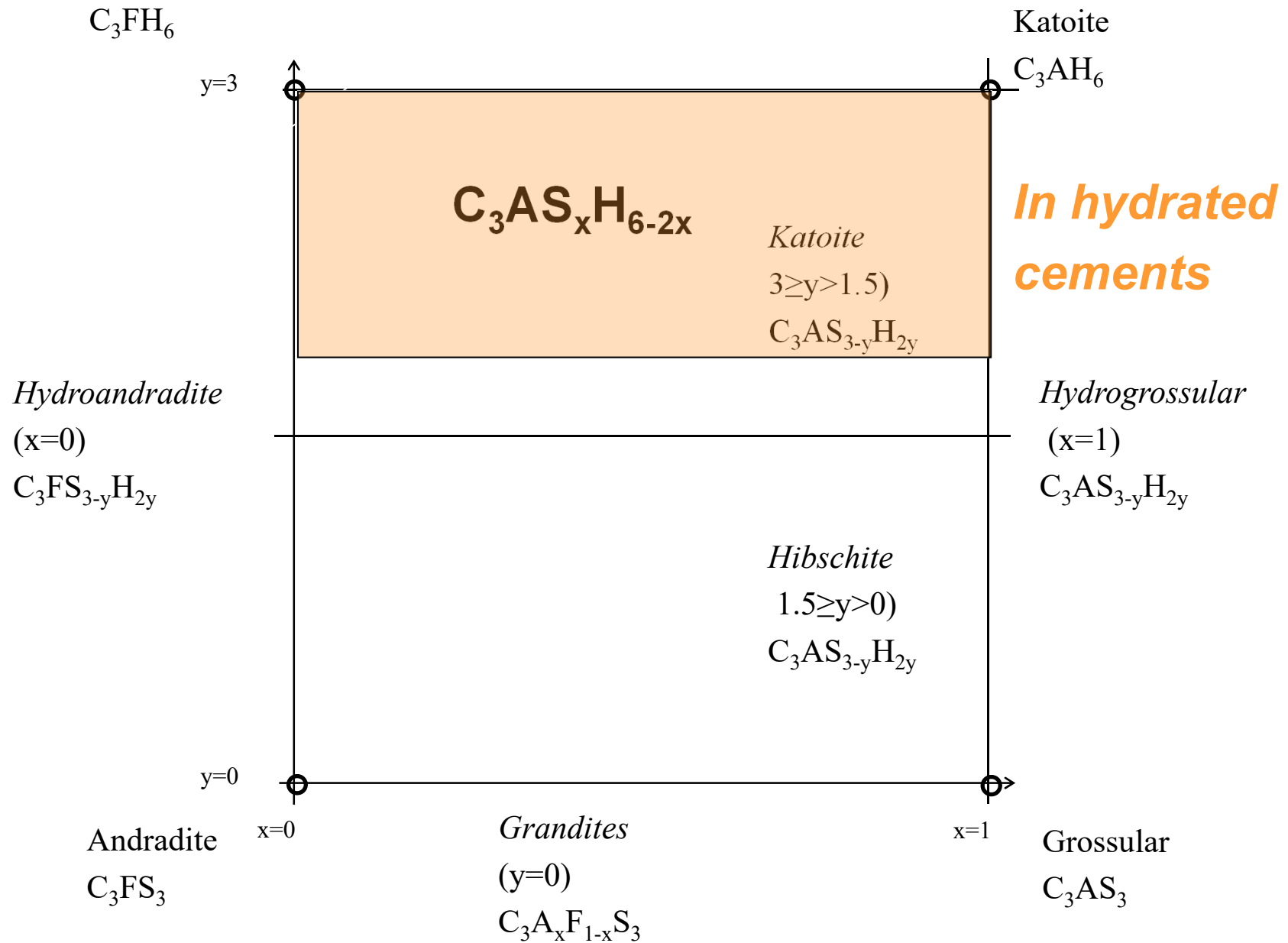
-> $\text{SiO}_2^0 \leftrightarrow 2\text{H}_2\text{O}$

low water content

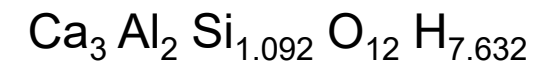
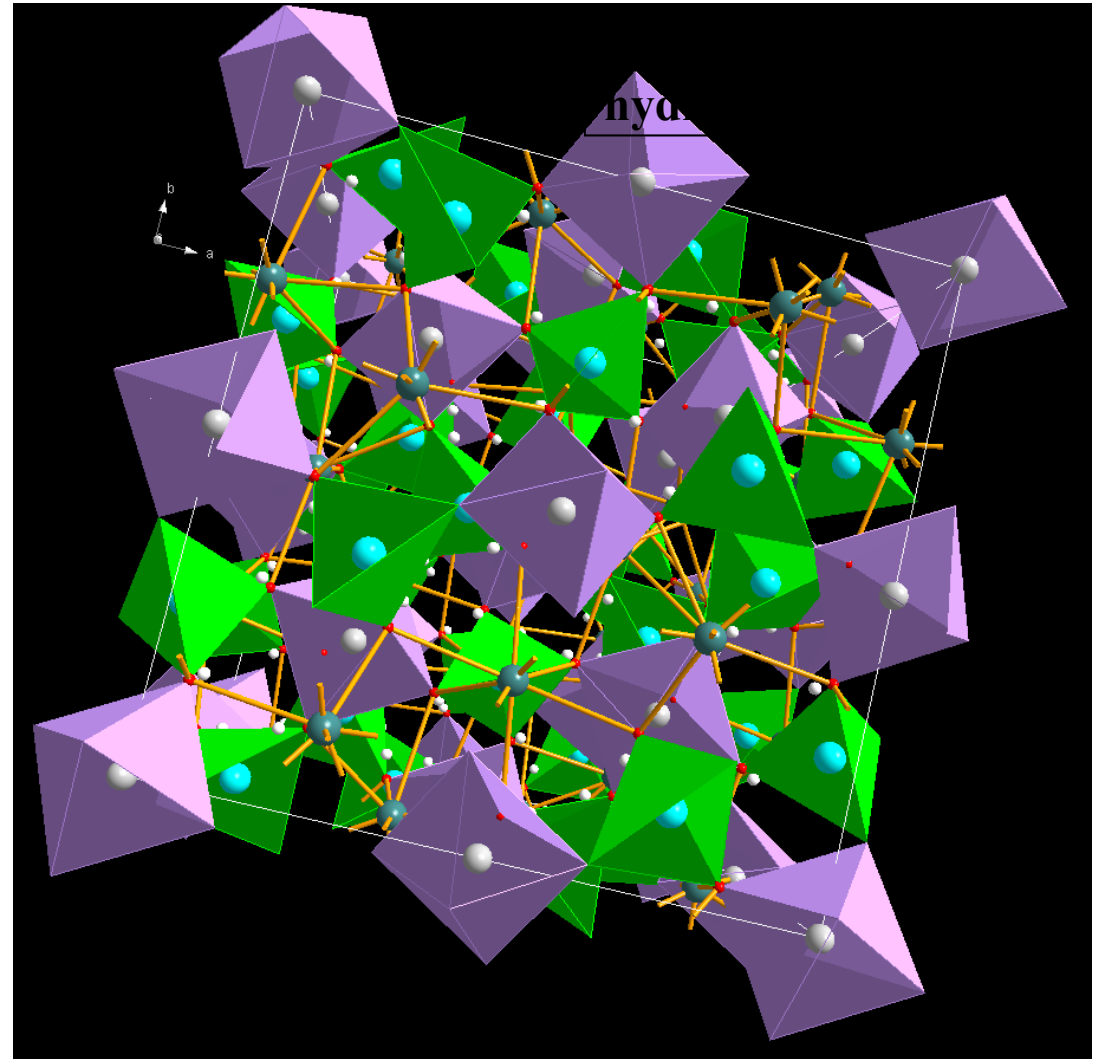
-> higher density

> 2.5 kg/dm^3





Hydrogarnets:



Katoite (y=1.9):

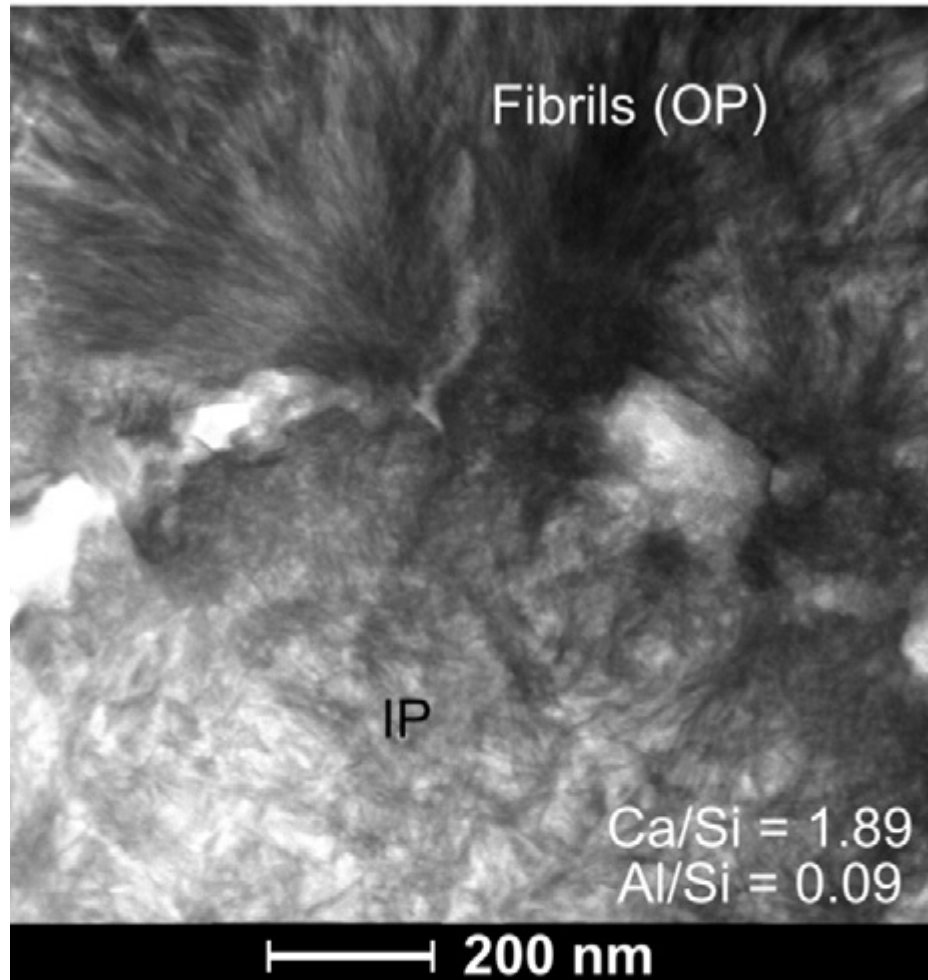
crystal system: cubic

a=1.22 nm

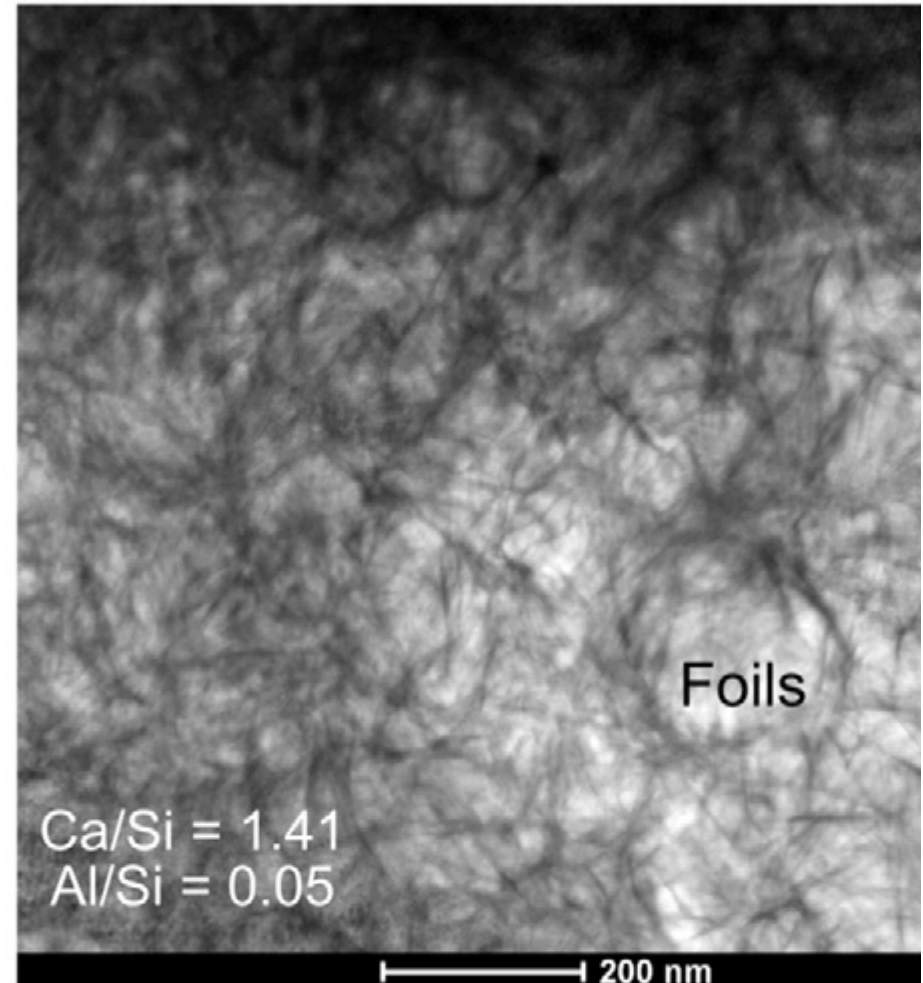
* Ferro et al. European J. Min. 15 (2003) 419- 426

C-S-H in cements

Foil like morphology at low Ca/Si



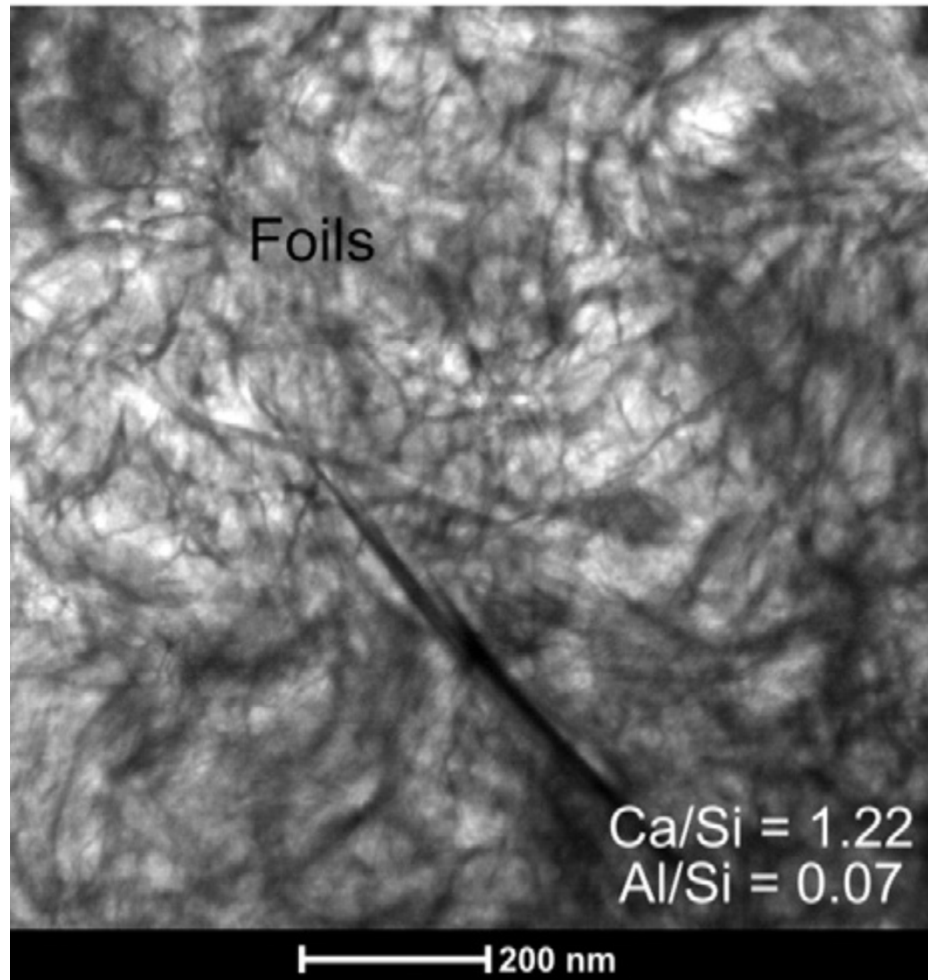
a) Plain cement (PC), 90 days, 20°C



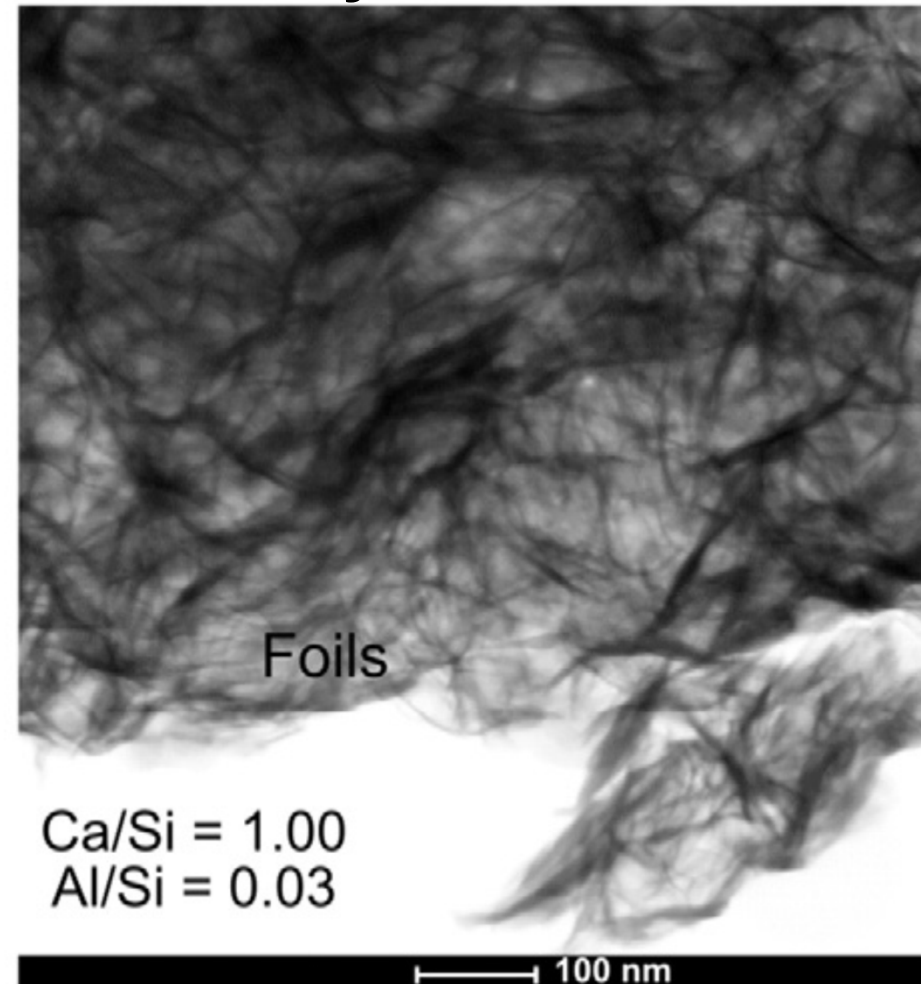
(b) PC 10SF, 90 days, 20°C

C-S-H in cements and synthetic C-S-H

Comparable morphology in PC and synthetic C-S-H

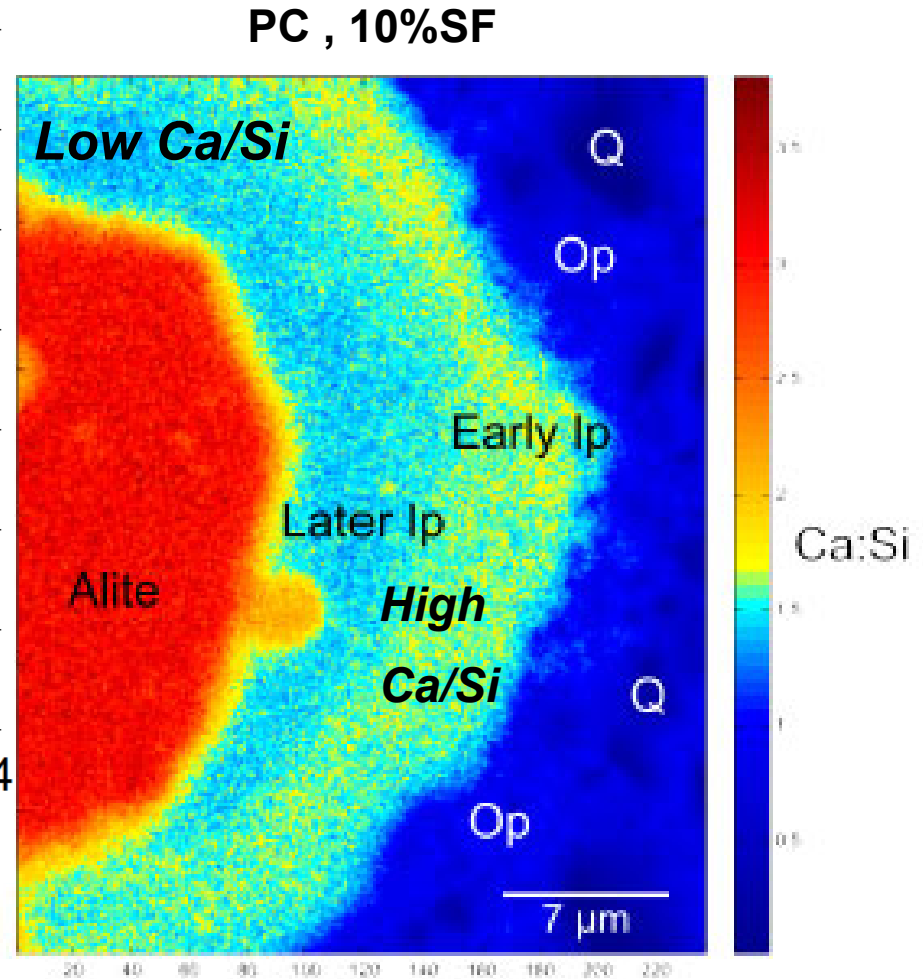
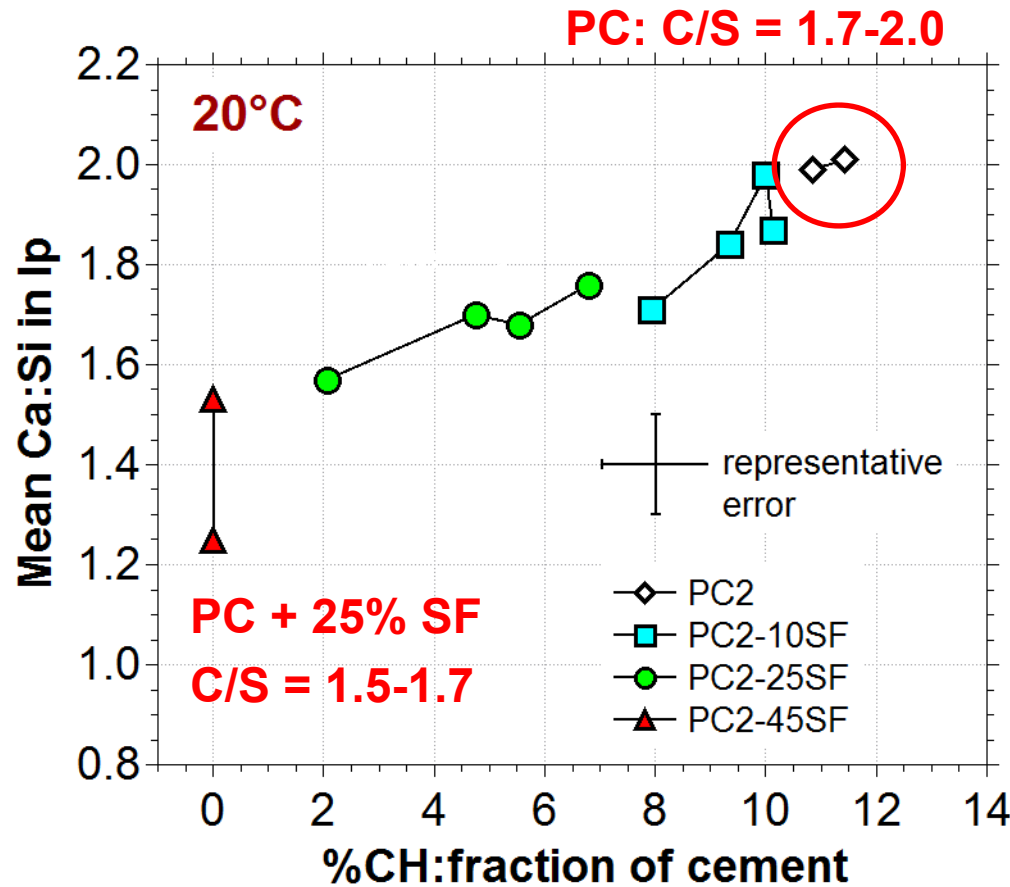


(c) PC(Q) 20SF, 90 days, 20°C



(d) Synthetic C-S-H, 20°C

C-S-H in Pastes



Rossen ea (2015) CCR

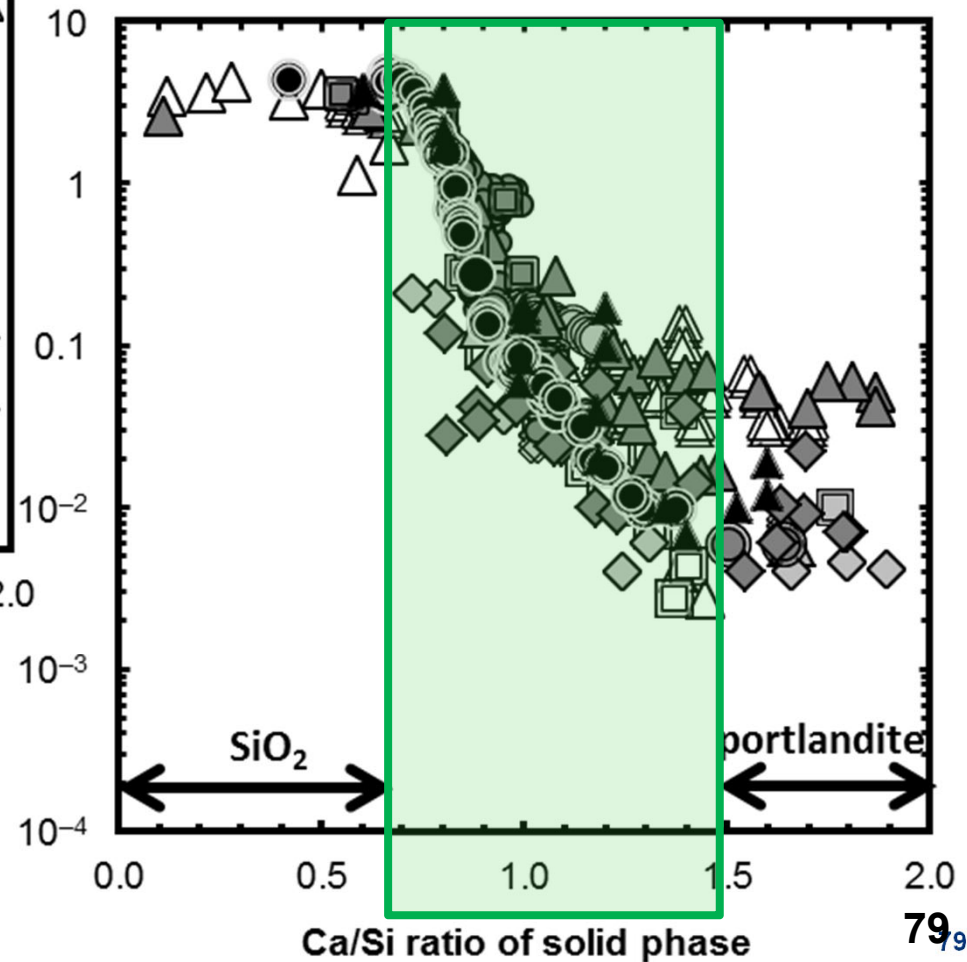
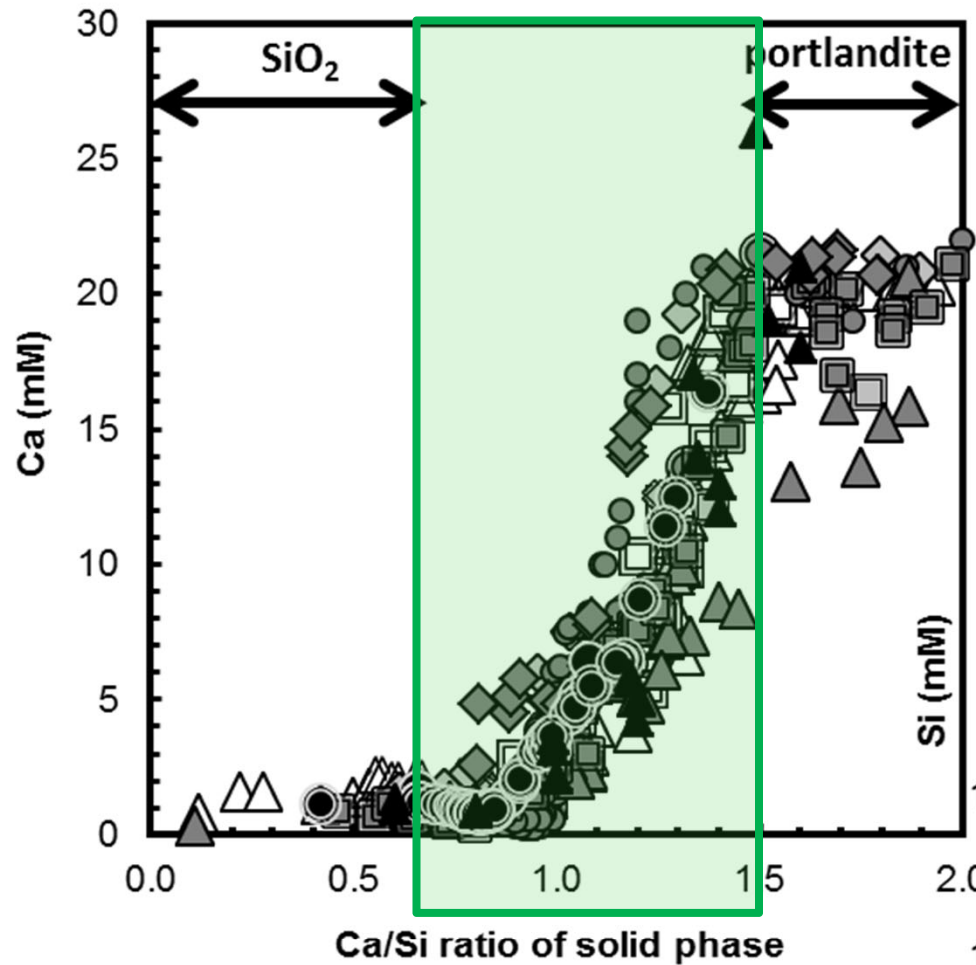
PC + SCM's:

C-S-H composition changes
with time as CH is consumed

C-S-H: range of compositions

Ca/Si =
0.7 to 1.5
for synthetic C-S-H

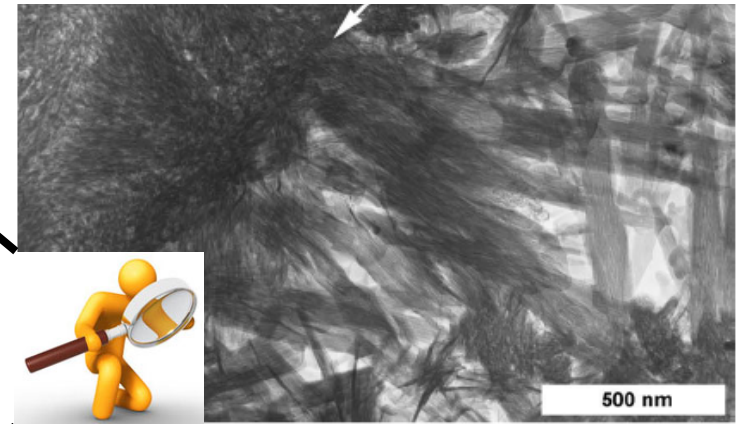
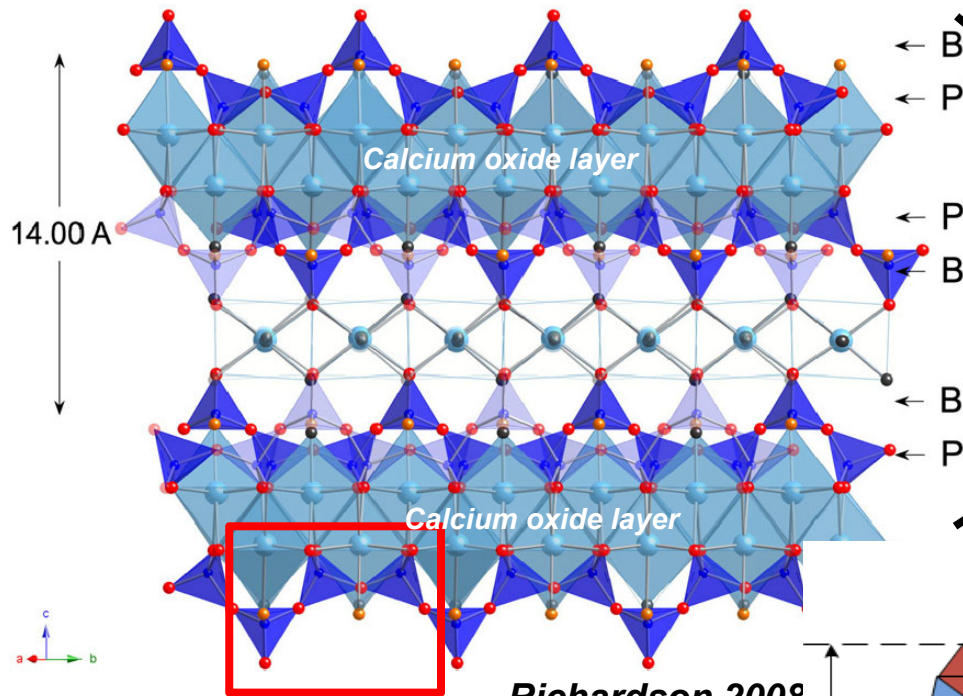
1.7-2 PC pastes



C-S-H

=> structurally imperfect tobermorite

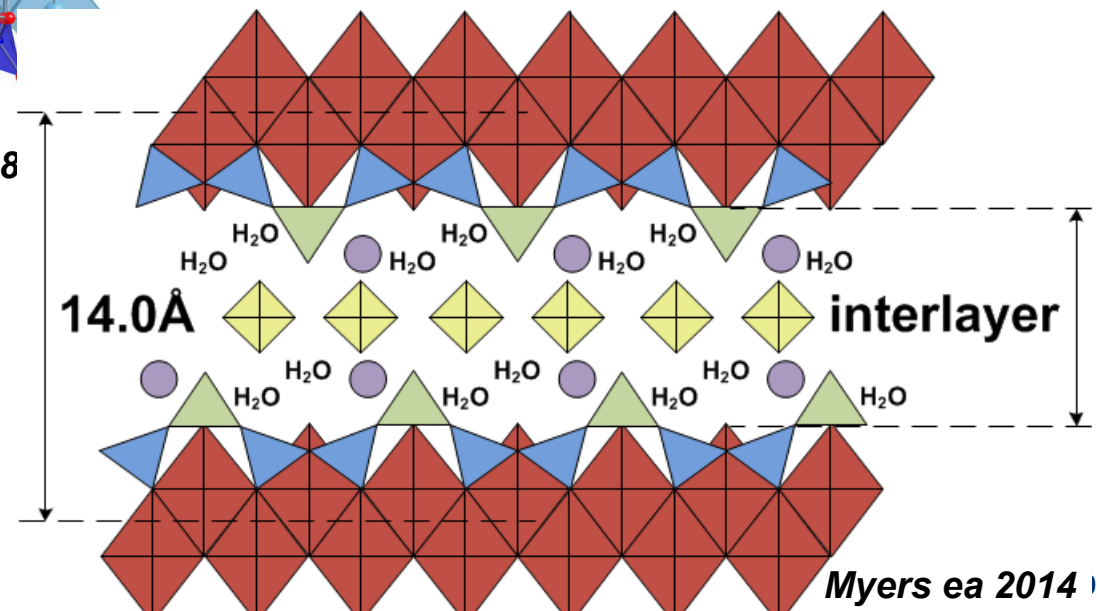
Richardson, 2004



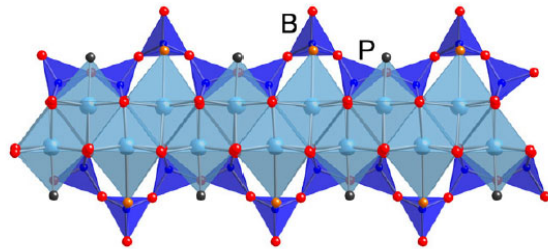
Dreierketten chain

● Ca ● Si ● O

Richardson (2014):
Structure: clino tobermorite
Not ortho tobermorite

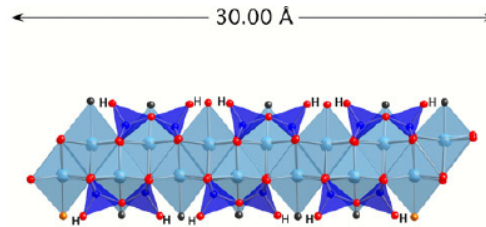


C-S-H structure: Variation of Ca/Si ratio



Ca/Si=0.67

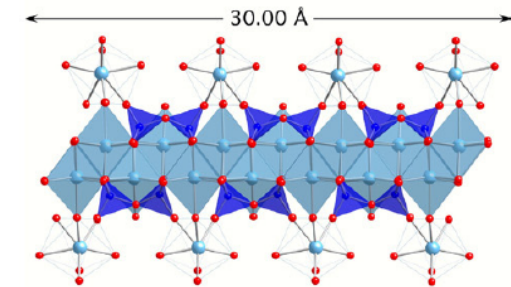
- Infinite chain



Ca/Si=1.0

- Dimer, pentamer,
...

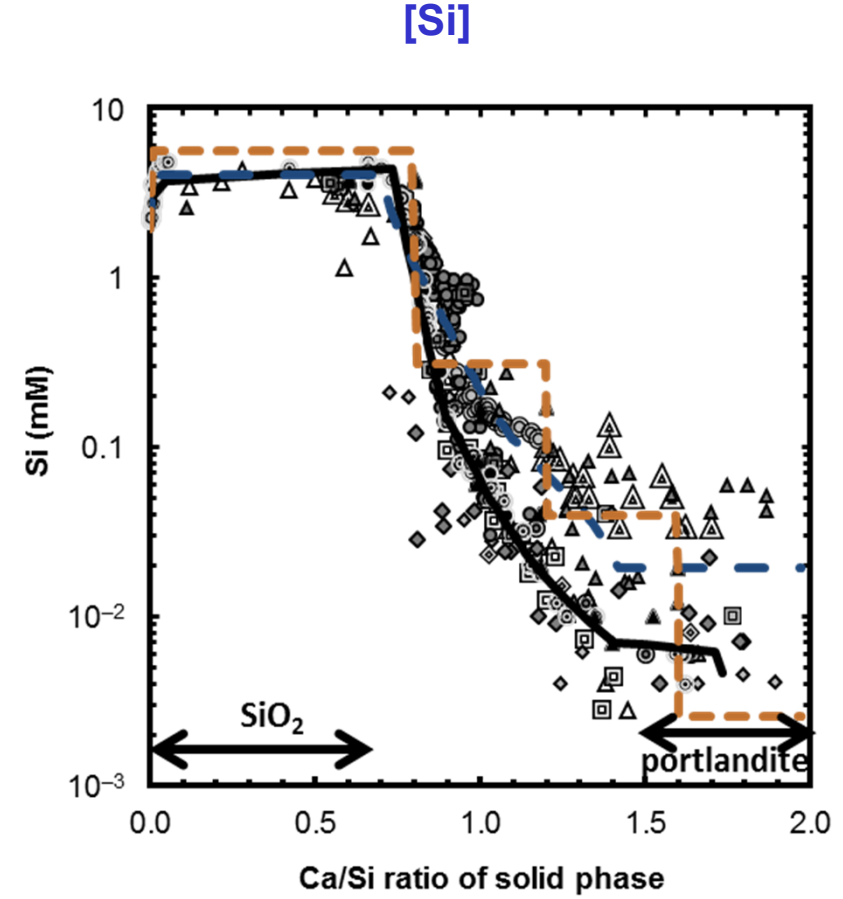
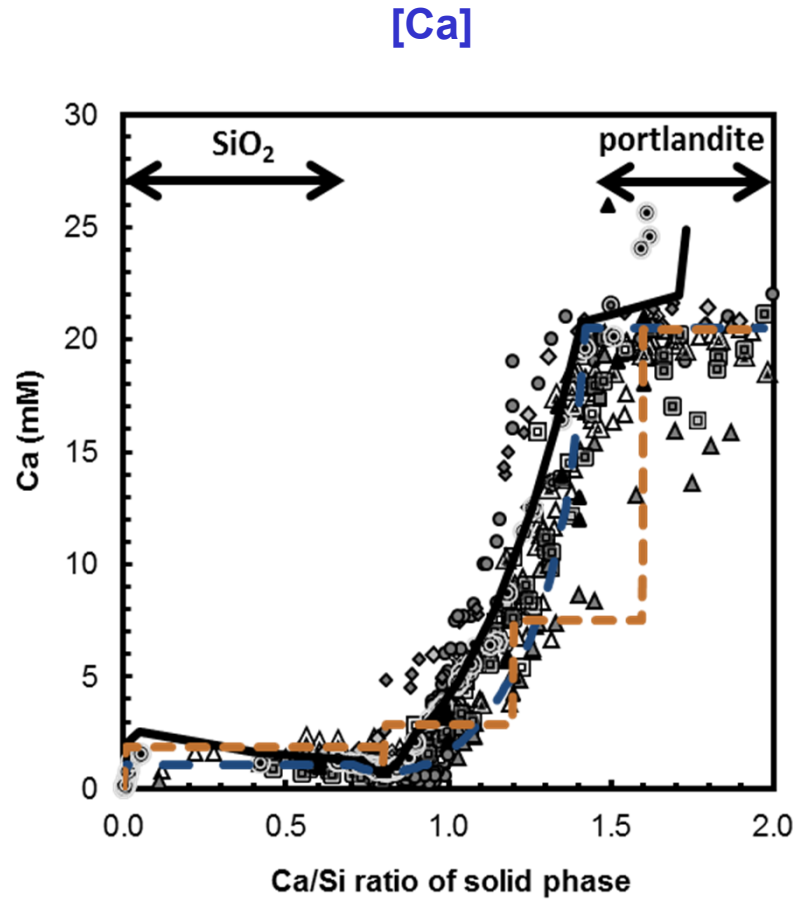
Richardson 2008



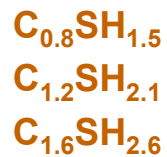
Ca/Si=1.50

- Mainly dimer
- Ca in the interlayer
- Intergrowth with CH possible

Different types of thermodynamic (geochemical) models for C-S-H

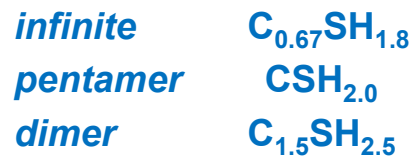


3 different CSH



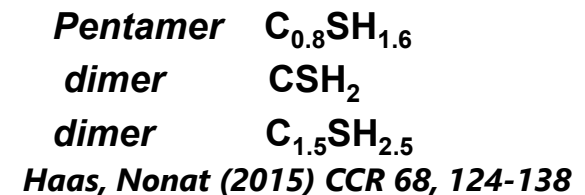
Blanc et al. (2010) CCR 40, 851-866

Solid solution



Kulik (2011) CCR 41, 477-495

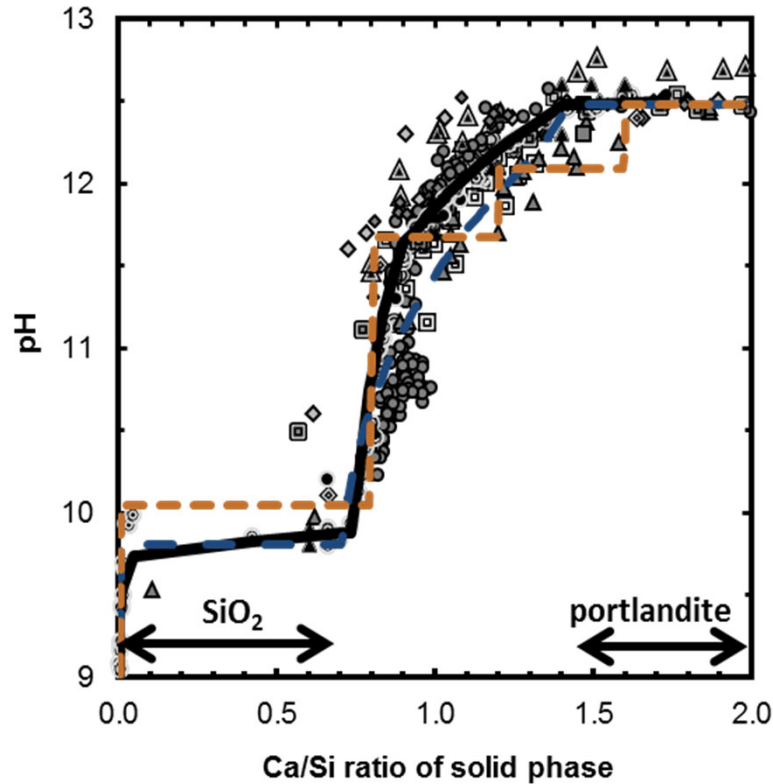
Surface reaction model



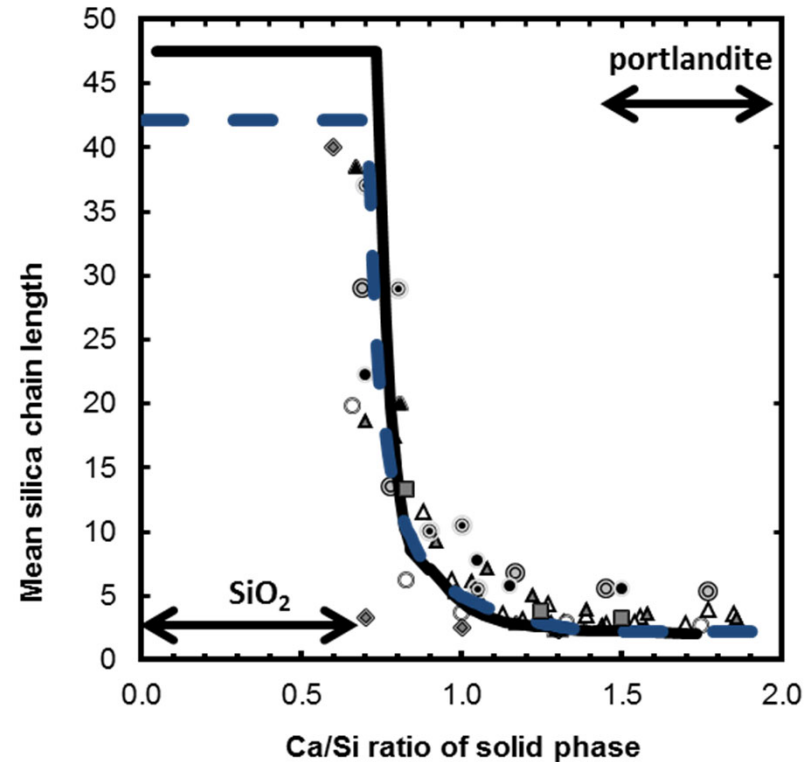
Haas, Nonat (2015) CCR 68, 124-138

Different types of thermodynamic (geochemical) models for C-S-H

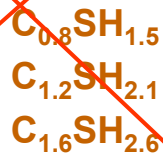
pH



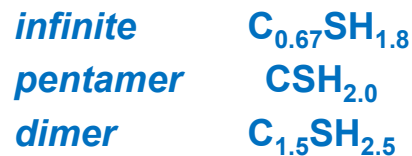
Mean Chain Length



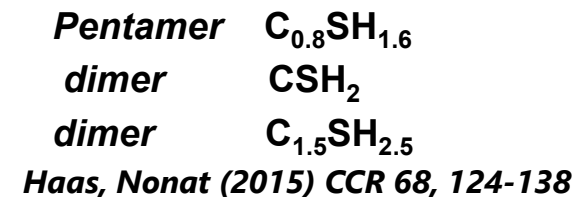
~~3 different CSH~~



Solid solution



Surface reaction model

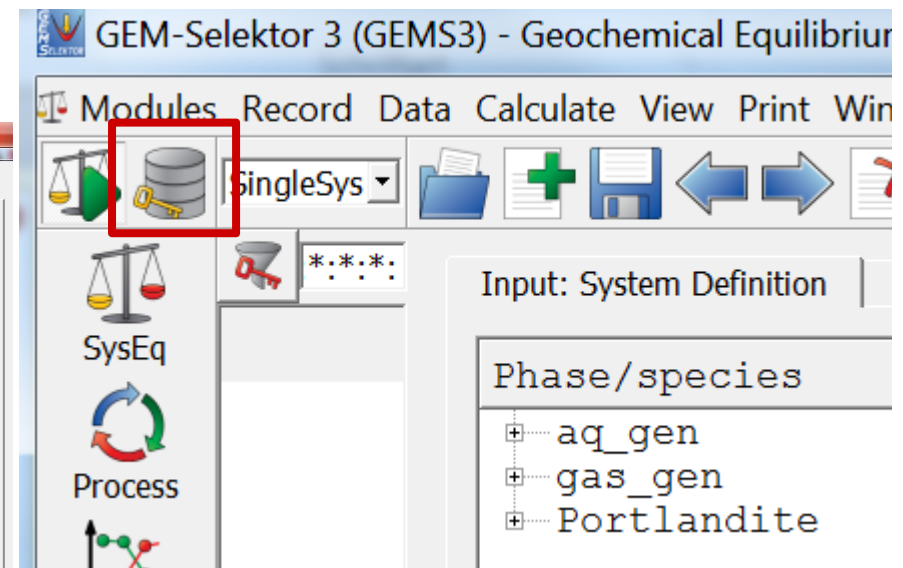
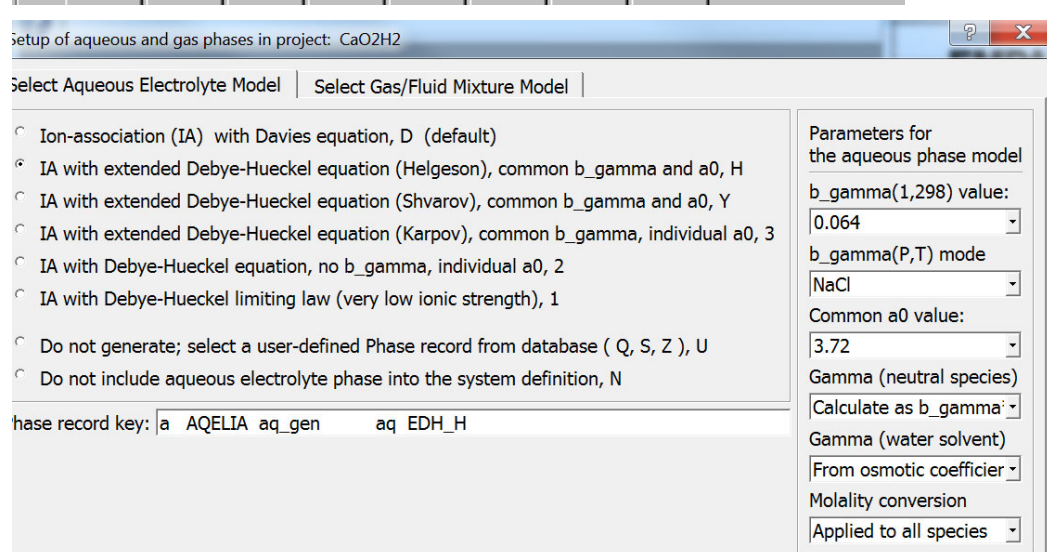
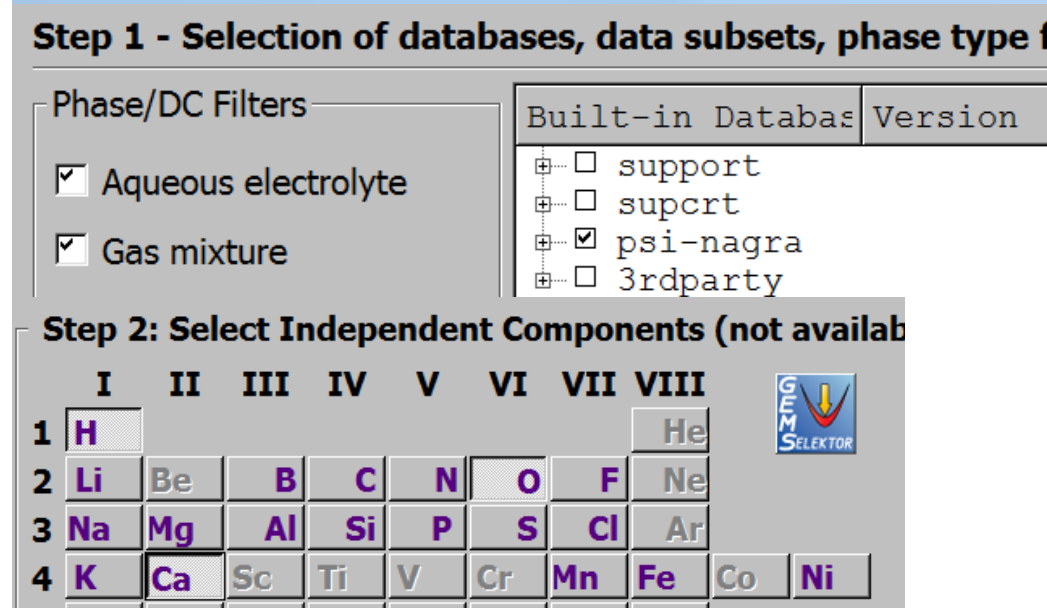
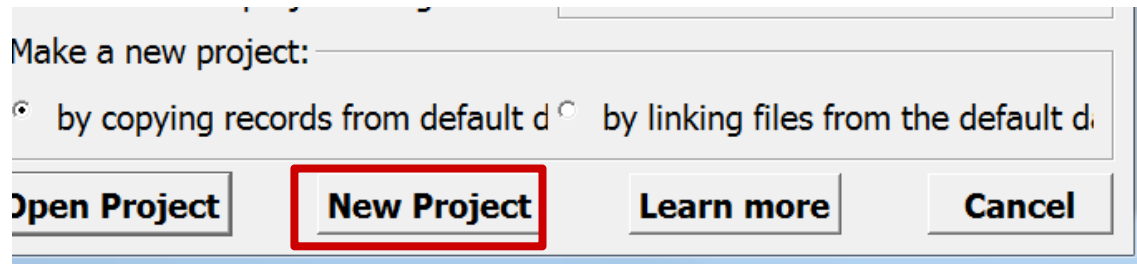


Thermodynamic data

1. Databases
2. Portlandite solubility and speciation
3. Saturation indices
4. Hydrates
5. **How to create new entries for thermodynamic data in GEMS:**
 - a) **Dcomp**
 - b) **ReacDC**
 - c) **Temperature and pressure plots**
 - d) **Thermodynamic phases**

=> Self study

Create new project,
Name it CaO2H2,
Psi nagra database
Select Ca, O, H
Select Helgeson, NaCl
Open
Go back to database



DComp– creation of new entries

1) Make a new entry: Record: Create(New)

Phase state (s ... solid; a ... aqueous; g ... gaseous)
Group id (e.g. elements of chem composition name)
Comment (e.g. cem ... cement; Exam: Example)

Leave default values if including a single phase or an ideal solid solution
Optional: Choice of mixing model if a non ideal solid solution is included

O: solid phase

S: Aqueous species

**M: Major end-member
(solvent)**

**J: Junior end-member
(solute)**

DComp– creation of new entries

GEM-Selektor DComp Setup: s:CaOH:Portlandite:exam:

Step 1 - Defining the dependent component (DC) type and the calculation method codes

Select here to which class this DC belongs

This class code will be copied into Phase definition (can be changed there too):

By setting the codes below, configure the DComp record data and tell the program how the molar properties of this DC should be corrected for T and P.

Select here the methods for temperature T and pressure P corrections

General method code for T corrections of molar thermodynamic properties:

Method variant code for EoS T corrections of molar thermodynamic properties:

Method code for P corrections of molar thermodynamic properties:

Codes for species-dependent EoS subroutines

Optional parameters for experienced users, else leave default values

Default: “CS”

$$\Delta_a G_T^o = \Delta_f G_{T_0}^o - \int_{T_0}^T S_T^o dT$$

and “C”

Alternatively, the “HKF” is used for aqueous species. This optional vector contains empirical parameters of revised Helgeson- Kirkham- Flowers equation of state for calculation of standard partial molal properties of aqueous species up to 1000 oC and 5000 bar [1981HEL/KIR; 1997SHO/SAS]. The coefficients were imported from SPRONS92.DAT file [1992JOH/OEL] and its latest extension, SLOP98.DAT [1997SHO/SAS];

DComp – creation of new entries

Optional parameters for experienced users, else leave default values

Step 2 - Specific dimensions and settings

Dimensions to change only in special cases

Number of $C_p(T)$ equations can be changed here if $C_p(T)$ coefficients are available for more than one temperature interval. Default is 1, maximum 5 intervals.

Number of phase transitions can be changed here, if necessary (usually one less than the number of $C_p=f(T)$ equations). Default is 0, maximal 4.

Number of EoS coefficients can be set here if certain EoS models for fluids will be used (default: 0). The coefficients will be collected automatically into Phase record.

Check here to allocate the $V_m=f(P, T)$ vector of coefficients (reserved)

Units of measurement (cannot be changed in this version of GEMS)

Units of energy (default: j)

Units of volume (default: j)

Units of pressure (default: b)

Units of temperature (default: C)

[Learn more](#)

DComp :: Thermochemical/EoS data format for Dependent Components

Page 1 Page 2 03/05/2017, 10:09

Portlandite
Ca(OH)2

M0 --- Zz --- ab

V0d	3.306	---
G0d	-897013	---
H0d	---	---
S0d	83.4	---
Cp0d	---	---
PrTr	1	25
LamST	---	---
BetAlp	---	---

Robie_Hem:1995:pap: All

Enter G (in J/mol) and S
H will be calculated
Cp on page 2

Temperature range

DComp :: Thermochemical/EoS data format f

Page 1 Page 2 03/05/2017, 10:09

C S C N O j j b C + -

TCint	
0	0
1	426.85

aiCpT	
0	186.7
1	-0.02191
2	0
3	-1600
4	0
5	0
6	0
7	0
8	0
9	0
10	0
11	0

$$C_p^0 = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5} + a_4T^2 + a_5T^3 + a_6T^4 + a_7T^{-3} + a_8T^{-1} + a_9T^{0.5}$$

$$= 186.7 - 0.022 \cdot 298.15 - 1600 / \sqrt{298.15} = 87.5$$

Press calculate

Modules Record Record List Database Files Window Help

DComp

s:CaOH:Portlandite:exam:

DComp :: Calculation finished OK (elapsed time: 8.533 s)

Page 1 Page 2 03/05/2017, 10:12

Portlandite **name**

Ca (OH) 2 **Chemical composition (defined format)**

Mass (g/mol) from composition **charge** **Activity coefficients**

M0	74.0927	Zz	0	ab	---
----	---------	----	---	----	-----

Uncertainty

V0d	3.306	0
G0d	-897013	---
H0d	-984671.48	---
S0d	83.4	---
Cp0d	87.5053	0
PrTr	1	25
LamST	---	---
BetAlp	---	---

Volume (1 J/bar = 10 cm³/mol)

Free energy (J/mol)

Enthalpy (J/mol) calculated from S and G

Entropy (J/mol/K) $\Delta G = \Delta H - TS$

Heat capacity (J/mol/K): calculated from page 2

Pressure Temperature

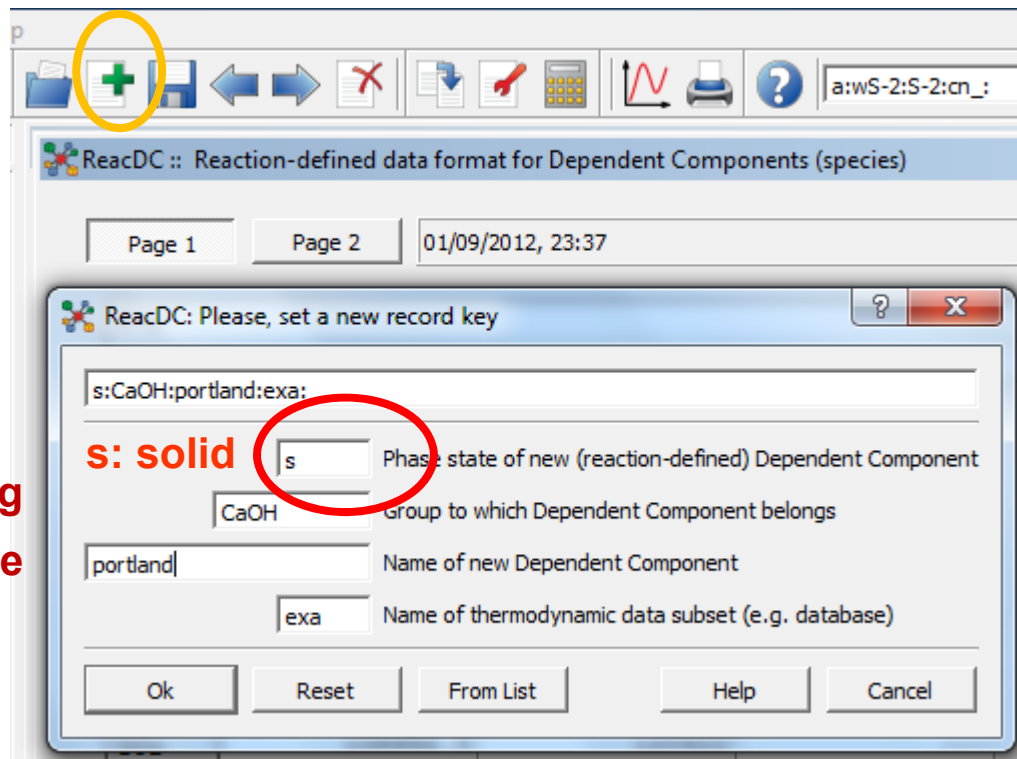
	$\log K_{S0}^*$	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm ³ /r]
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
SiO _{2,am}	1.476	-848.90	-903	41	47	0.034	-1.13·10 ⁶		29

3) GEMS: reactions (ReacDC): new

Portlandite solubility:



$$\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$$



Elements:ordering
Component name

Data base: «example»

GEM-Selektor ReacDC Setup: s:CaOH;portland:exa

Step 1 - Selection of reaction-defined DC type and codes of methods of T,P correction

Select here the class code for the reaction-defined Dependent Component (DC)

This DC class code will be copied to Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

The codes set below will configure the ReacDC record and define how to compute T,P corrections for the reaction and the new DC it defines.

Select here method codes of T,P correction for molar properties of the reaction-defined DC

General method code for temperature corrections:

K Calculation through the logK of reaction TP dependency

Method variant code for temperature EoS corrections:

3 Three-term extrapolation of logK (T) at dCpr (T) = const

Method code for pressure corrections:

C Molar volume of new DC calculated from constant dVr of reaction

Codes for species-dependent EoS subroutines

N No fluid model routine

Learn more < Back Next> Cancel

$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

(K) 3

[Three-term extrapolation](#) of $\log K(T)$ at $dCpr(T) = \text{const}$ (preferable). Enter non-[empty] values into the [Cp0x\[0,0\]](#) cell, and into either [H0x\[0,0\]](#) or [S0x\[0,0\]](#) cells (another must contain [empty]); enter a non-empty value in either [logKx\[0,0\]](#), [logKx\[0,1\]](#) or [G0x\[0,0\]](#) cells (the other two cells and [G0x\[0,1\]](#) must contain [empty]). Then re-calculate and save the record. Use this code combination also for the [PRONSPREP calculation](#).

C

Molar volume of species V^s (in [DComp](#)) or dVr of reaction (in [ReacDC](#)) is assumed to be constant, independent of P and T (may be used for minerals up to a 1-2 kbar pressures at low-to-moderate temperatures).

3) GEMS: reactions (ReacDC): new

Portlandite solubility:



$$\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$$

Ca²⁺, OH⁻, Ca(OH)₂

GEM-Selektor ReacDC Setup: s:CaOH:portland:exa

Step 2 - Specific dimensions and settings

Dimension to change only in special cases (e.g. to find properties of reaction between existing DCs)

Number of DCs in the reaction (usually set automatically after selecting the DCs)

Dimensions to set only for the logK array for T,P corrections by interpolation (KZZ method codes)

Number of interpolation points along T (> 2, < 20)

Number of interpolation points along P (> 1, < 10)

Units of measurement (cannot be changed in this version of GEMS)

J/mol(/K) Units of energy (default: j)

J/bar = 0.1 cm³/mol Units of volume (default: j)

bar = 10⁵ Pa Units of pressure (default: b)

Celsius Units of temperature (default: C)

[Learn more](#) < Back Next> Cancel

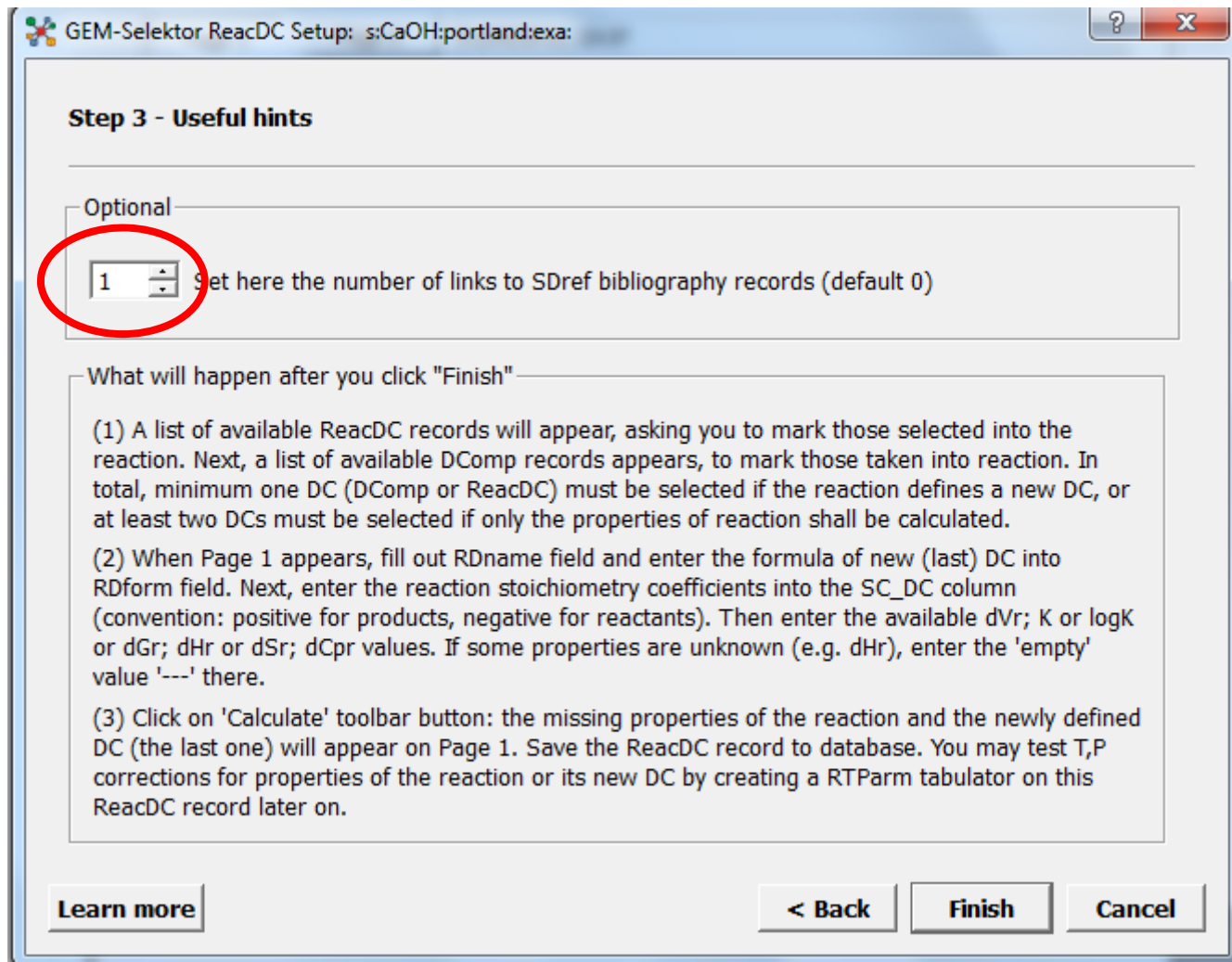
3) GEMS: reactions (ReacDC)

Portlandite solubility:



$$\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$$

Literature reference

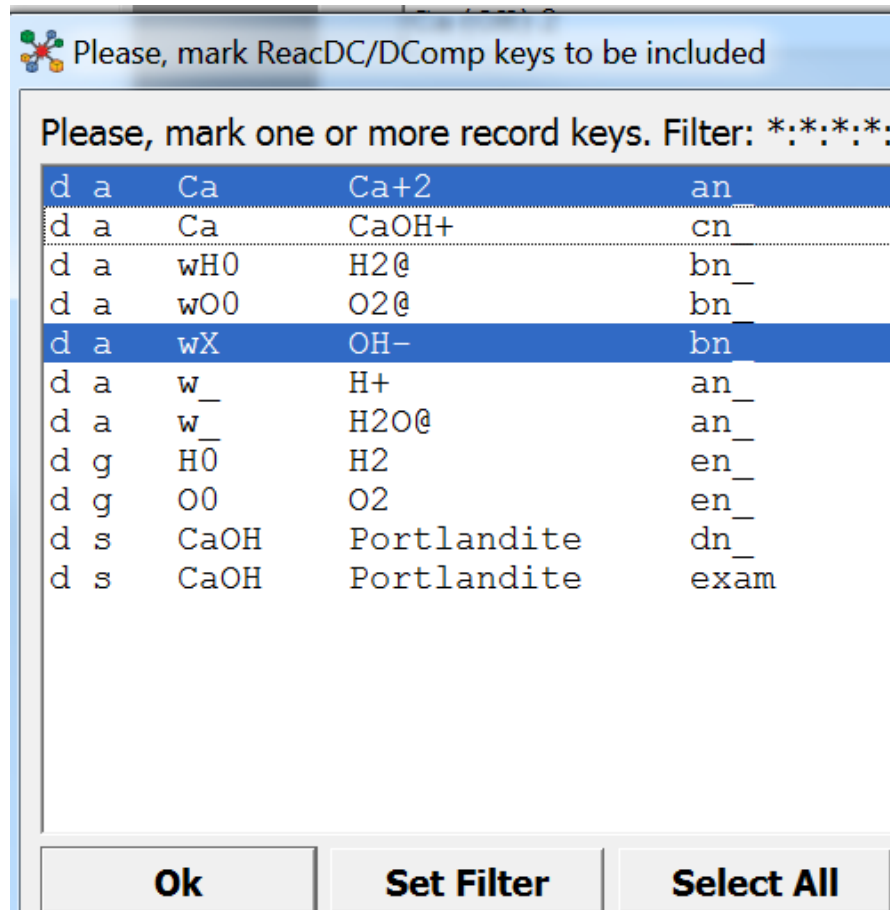


3) GEMS: reactions (ReacDC)

Portlandite solubility:



$$\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$$



Chose existing compounds;

New compound «Ca(OH)₂» will be made by the programme

3) GEMS: reactions (ReacDC)

Portlandite solubility:



$$\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$$

DComp :: Thermochemical/EoS data f

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1 Page 2 02/04/2013, 15:48

Portlandite
Ca (OH) 2

M0	74.0927	Zz
V0d	3.306	
G0d	-897013	
H0d	-984675	
S0d	83.4	
Cp0d	87.5053	
PrTr	1	
LamST	---	
BetAlp	---	
0	Robie_Hem:1995:pap:	
1	AUG20_GEMS:2001:dat:	

SC	DC	REsDC			
0	1 d	a Ca	Ca+2	an_	
1	2 d	a wX	OH-	bn_	
2	-1 n	s CaOH	Portl	exa	

V0r	-6.0914	---	---
logKr	---	-5.2	---
G0r	---	---	---
H0r	---	---	---
S0r	-161.306	---	---
Cp0r	-391.104	---	---
NisoX	---	---	---

PrTr_	1	25	M0_	74.0927
BetAl_	---	---	ab_	---

Reaction coefficients

New component

Volume changes

Log K

S reaction

Cp reaction

3) GEMS: reactions (ReacDC)

Portlandite solubility:
 $\text{Ca(OH)}_2 = \text{Ca}^{2+} + 2\text{OH}^-$; $\log K = -5.2$
 $\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{\{\text{Ca(OH)}_2\}} = 10^{-5.2}$

Volume

Gf

S

Cp

	$\log K_{S0}^*$	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm ³ /r]
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
SiO ₂ am	1.476	-848.90	-903	41	47	0.034	-1.13·10 ⁶		29

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1 Page 2 03/09/2012, 14:14

portlandite
Ca (OH) 2

	SC	DC		REsDC			
0		1	d	a	Ca	Ca+2	an_
1		2	d	a	wX	OH-	bn_
2		-1	n	s	CaOH	portland	exa

V0r	-6.0914	3.30596	--
logKr	6.3095734e-006	-5.2	--
G0r	29681.819	-897011.82	--
H0r	-18411.597	-984675.4	--
S0r	-161.306	83.4	--
Cp0r	-391.104	87.5053	--

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1 Page 2 03/09/2012, 14:14

K 3 C N

0 j j b C + - - - - - - -

03/09/12 3 0 0 0 0 0 0 0 1

	TCint	P int	aiLgKr
0	0	0	128.397
1	426.85	1	0
2			-5129.11
3			-20.4287
4			0
5			0
6			0
7			0
8			0
9			0
10			0

Extrapolation method: 3-term

Calculates automatically temperature dependent function of the solubility product, depending on the initial data input

see <C:\GEMS337\Gems3-app\Resources\doc\pdf\T-corrections-Reac.pdf>

3-term extrapolation $\Delta C_{p_T} = \Delta C_{p_{T_0}} = const$

$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

$$A_0 = \frac{0.4343}{R} \cdot \left[\Delta_r S_{T_0}^0 - \Delta_r C_{p_{T_0}} (\ln T_0 + 1) \right]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H_{T_0}^0 - \Delta_r C_{p_{T_0}} T_0)$$

$$A_3 = \frac{0.4343}{R} \cdot \Delta_r C_{p_{T_0}} = \frac{0.4343}{8.3145} \cdot -391.1 = -20.43$$

4.) Plot of temperature/pressure dependent thermodynamic data

The screenshot shows the RTParm software interface. The main window title is "RTParm :: Tabulation/plot of thermodynamic data for one DC (species)". The interface includes a menu bar (Modules, Record, Record List, Database Files, Window, Help), a toolbar with various icons, and a central workspace. A dialog box titled "RTParm" is open, displaying the message "Please, select a source record from:" with three buttons: "DComp", "ReacDC", and "Cancel". The "DComp" button is highlighted with a red circle. In the background, the main window shows a script editor with the text "logKsp = f(TC) of ettringite" and "Please, change the script and/or remake, if necessary". Below this, there is a table with columns for "rpMode", "rpNpT", and "rpNpI". The table contains the following data:

rpMode	rpNpT	rpNpI
2	1	17
5		
85		
2	1000	2
		5

Below the table, there is a section for "tExpr" with the following code:

```
xT[jTP] =: twTC;  
xP[jTP] =: twP;  
yF[jTP][0] =: tlogK;
```

A red circle highlights the "DComp" icon in the left sidebar. A red circle also highlights the "+" icon in the toolbar. A red arrow points from the "+" icon to the "DComp" icon. A red text box with the word "new" is positioned near the "+" icon.

Helps to determine S or H for Temperature extrapolations

Temperature/pressure dependent thermodynamic data

The image shows two overlapping dialog boxes from a software application. The background dialog, titled "ReacDC: Select one key of a source ReacDC record", has a list box containing a single entry: "s CaOH Portl exa". The foreground dialog, titled "RTParm: Please, set a new record key", contains a text field with the value "s:CaOH:Portl:exa:r:001:". Below this field are several labeled input fields: "s" (Phase state of source Dependent Component), "CaOH" (Group to which source Dependent Component belongs), "Portl" (Name of source Dependent Component), "exa" (Code of source thermodynamic data set), "r" (Source of input data for DC { r d }), and "001" (Variant number of this RTParm calculation task). A red circle highlights the "001" field, with the word "number" written in red next to it. Both dialog boxes have "Ok", "Reset", "From List", "Help", and "Cancel" buttons at the bottom.

Temperature/pressure dependent thermodynamic data

GEM-Selektor RTparm Setup: s:CaOH:Portl:exa:r:001:

Step 1 - Thermodynamic data tabulator (RTParm) configuration

This is a tool for tabulating and plotting thermodynamic data against temperature T and/or pressure P. The input is taken from a DComp or ReacDC record specified in this RTParm record key.

Upon calculation, results will be tabulated on the 'Tables' page, as specified in 'tExpr' math script. Results can be plotted, exported into text files, or copy-pasted to other programs.

Simple 'tExpr' scripts can be created using a selection dialog on the next page of this wizard. Example scripts are also provided under 'Help' 'View Scripts...' menu command in the RTParm window.

2 T then P increments Select mode for iterating xP and xT arguments. Default mode: 2.

Temperature T		Pressure P	
Units	C Celsius <input type="button" value="v"/>	Units	b bar <input type="button" value="v"/>
Minimal	0.00 <input type="button" value="v"/>	Minimal	1.00 <input type="button" value="v"/>
Maximal	350.00 <input type="button" value="v"/>	Maximal	1.00 <input type="button" value="v"/>
Step	25.00 <input type="button" value="v"/>	Step	0.00 <input type="button" value="v"/>
Number of points	15 <input type="button" value="v"/>	Number of points	1 <input type="button" value="v"/>
<input checked="" type="radio"/> Plot as abscissa xT		<input type="radio"/> Plot as abscissa xP	

*Initial
Final
step*

GEM-Selektor RTparm Setup: s:CaOH:Portl:exa:r:001:

[Learn more](#)

< Ba

Step 2 - Selection of items to sample (to retain the old script, just click 'Next >')

Property	Item Selection	Sampling Script																
Scalars	<table border="1"> <tr><td>twG</td><td>twEw</td></tr> <tr><td>twH</td><td>twRT</td></tr> <tr><td>twS</td><td>twP</td></tr> <tr><td>twCp</td><td>twTC</td></tr> <tr><td>twV</td><td>twTK</td></tr> <tr><td>twK</td><td>tw[0]</td></tr> <tr><td>tlogK</td><td>xT</td></tr> <tr><td>tdGr</td><td>xP</td></tr> </table>	twG	twEw	twH	twRT	twS	twP	twCp	twTC	twV	twTK	twK	tw[0]	tlogK	xT	tdGr	xP	<pre>yF[jTP][0] =: tlogK;</pre>
twG	twEw																	
twH	twRT																	
twS	twP																	
twCp	twTC																	
twV	twTK																	
twK	tw[0]																	
tlogK	xT																	
tdGr	xP																	

Temperature/pressure dependent thermodynamic data

GEM-Selektor RTParm Setup: s:CaOH:Ca(OH)2:cm:r:01:

Step 1 - Thermodynamic data tabulator (RTParm) configuration

This is a tool for tabulating and plotting thermodynamic data against temperature T and/or pressure P. The input is taken from a DComp or ReacDC record specified in this RTParm record key.

Upon calculation, results will be tabulated on the 'Tables' page, as specified in 'tExpr' math script. Results can be plotted, exported into text files, or copy-pasted to other programs.

Simple 'tExpr' scripts can be created using a selection dialog on the next page of this wizard. Example scripts are also provided under 'Help' 'View Scripts...' menu command in the RTParm window.

calc. values

2 T then P increments Select mode for iterating xP and xT arguments. Default mode: 2.

Temperature T		Pressure P	
Units	C Celsius	Units	b bar
Minimal	0.00	Minimal	1.00
Maximal	350.00	Maximal	1.00
Step	25.00	Step	0.00
Number of points	15	Number of points	1
<input checked="" type="radio"/> Plot as abscissa xT		<input type="radio"/> Plot as abscissa xP	

Start value
Stop value
Step

RTParm :: Calculation finished OK (elapsed time: 0.687 s).

Learn more

< Back

Next >

Scripts

Tables

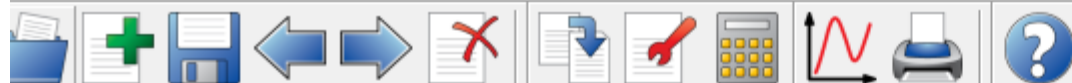
TPwork

Setup

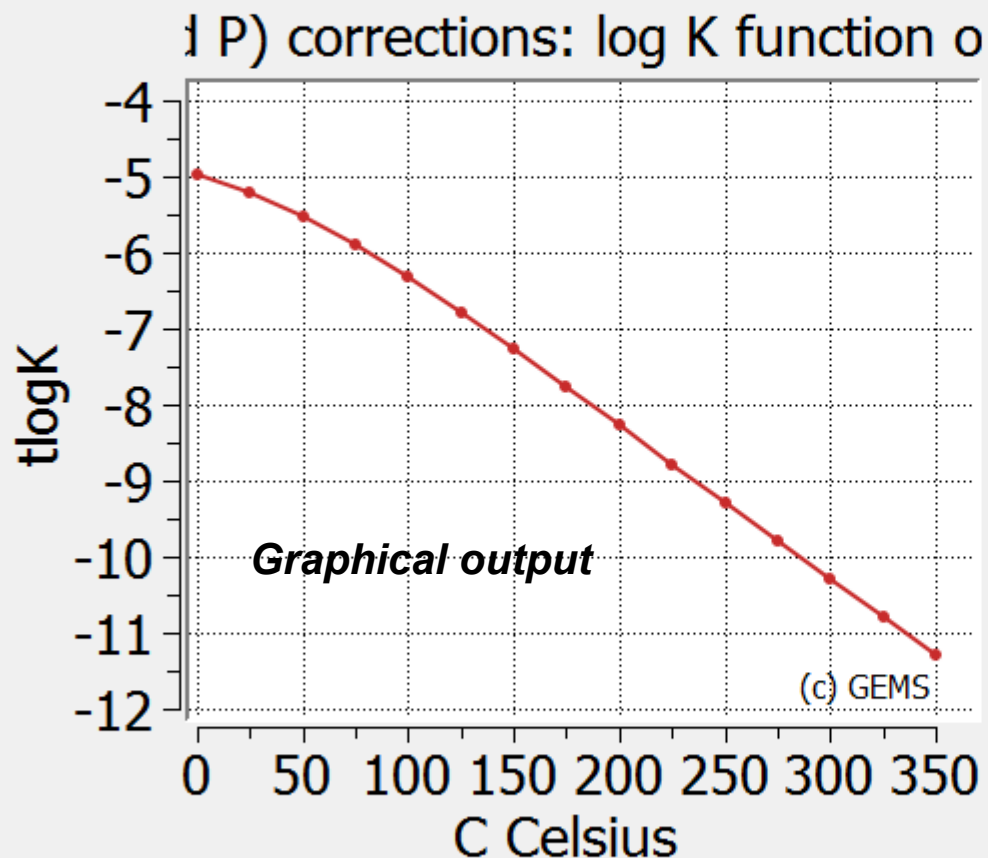
03/05/2017, 14:50

tXName C Celsius tlogK

	xT	xP	vF
0	0	1	-4.9854588
1	25	1	-5.2
2	50	1	-5.5140215
3	75	1	-5.8965457
4	100	1	-6.3261795
5	125	1	-6.7878629



GEM-Selektor v.3 Graphics Dialog



Legend | x# | Label

● 0 tlogK

Comparison between extrapolated $\log K_T$ function and experimental values:

Good tool for visual data fitting, e.g. estimation of ΔH_0^r based on experimental data

Click legend symbols to adjust curves; select abscissae under x#; edit labels, drag-drop them to plot area

Fragment

Customize

Print

Save Image

Help

5.) Thermodynamic Phases – creation of entries

Phase: Please, set a new record key

s:CaOH:Portlandite:c:exa:

s Code of phase state { a g f p l m h s d x }

CaOH Group identifier for such phases (letters, digits)

Portlandite Name of this phase definition (letters, digits)

c Phase class { c d l gm ss ssd ls aq xsa xc }

exa Comment to phase definition

Ok Reset From List Help Cancel

Phase state (s ... solid; a ... aqueous; g ... gaseous)

Group id (e.g. elements of chem composition name)

c: condensed solid (single compound); ss: solid solution; aq: Aqueous

Comment (e.g. cem: cement; exa: example)

Leave default values if including a single phase or an ideal solid solution

Optional: Choice of mixing model if a non ideal solid solution is included

I for Single phase or ideal solid solution:

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

Step 1 - Defining the Phase and the Model of Mixing

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of ideal) mixing should be used, and how it should be calculated.

Select a phase aggregate state code:

s Condensed solid phase, also multi-component solid solution

Select a model of mixing for this phase:

I Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

I Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

5.) Thermodynamic Phases – creation of entries

I	Ideal mixture (also multi-site) or pure phase, default
M	Binary subregular Margules solid-solution model
G	Binary Redlich-Kister solid-solution model
T	Ternary regular Margules solid-solution model
R	Regular multicomponent solid- or liquid solution model
V	Van Laar multicomponent solid- or liquid solution model
K	Redlich-Kister multicomponent solid- or liquid solution model
B	Microscopic α (symmetric) multicomponent solid-solution model (reserved)
L	NRTL multicomponent liquid solution model
W	Wilson multicomponent liquid solution (or ion exchange) model

Optional parameters only for experienced users, otherwise leave default value “I” !

5.) Thermodynamic Phases – creation of entries

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

Step 2 - Phase Model-Specific Settings

Optional dimensions to set when built-in functions or scripts for the mixing model shall be used.

Attention! ForTSolMod built-in mixing models that use dc_cf and/or ipxT, pc_cf data objects, the appropriate dimensions will usually be allocated automatically. Otherwise, the array will be allocated only if all its dimensions are not zeros.

0 dc_cf array: number of columns (coefficients per phase end member).

0 ipxT and ph_cf arrays: number of rows (interaction parameters) for the non-ideal mixing model.

0 ipxT array for indexation of interaction parameters: set here the maximum order of a parameter (e.g. 3 if binary and ternary parameters will be used).

0 ph_cf array of interaction parameter coefficients: number of columns (max. number of coefficients per parameter).

Set items in this box only if this is a sorption phase

Check if surface complexation will be considered in this (sorption) phase

0 Set the number of surface types (minimum 1, maximum 6) to allocate surface complexes

0 Enter here the specific surface area A of the sorbent (in m² per gram), A>0

[Learn more](#)

Optional parameters only for experienced users, otherwise leave default values

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

Step 3 - Final Settings and Hints

Optional

0 Set here the number of links to SDref bibliography records (default 0)

Extract parameters from DComp/ReacDC records and refresh DC class codes upon 'Calculate'?

What will happen after you click "Finish"

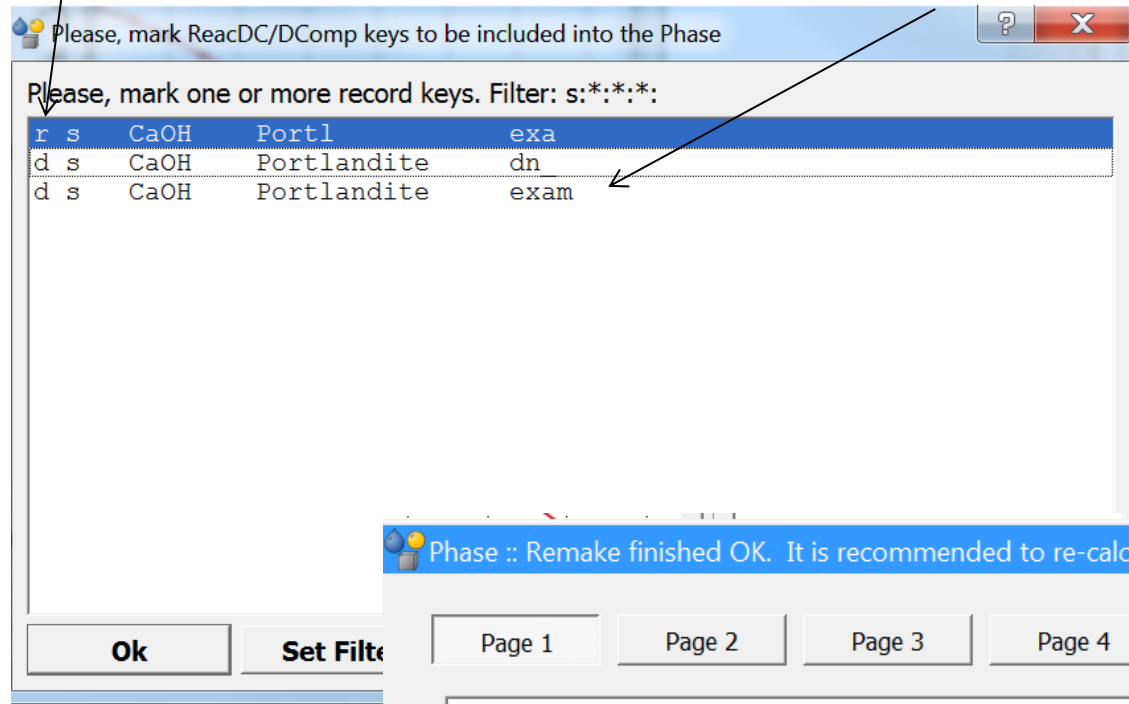
- (1) A list of available ReacDC ('r') and DComp ('d') records will appear; mark those to be the phase components (end-members). At least one species for a pure phase, or two for a solution phase must be marked.
- (2) In Phase window, fill out PhName and PhNote comments. Depending on setup, enter numbers in DisPar, text in DcEq and/or PhEq, parameter coefficients in ipxT, ph_cf, dc_cf arrays on Phase window pages.
- (3) Click on 'Calculate' toolbar button, then look at the PhDCC column; correct DC codes, if needed ('T' for H+; 'W' for H₂O-solvent; 'M','J',or 'I' for solid-solution end members). Save Phase record to project database.

5.) Thermodynamic Phases – creation of entries

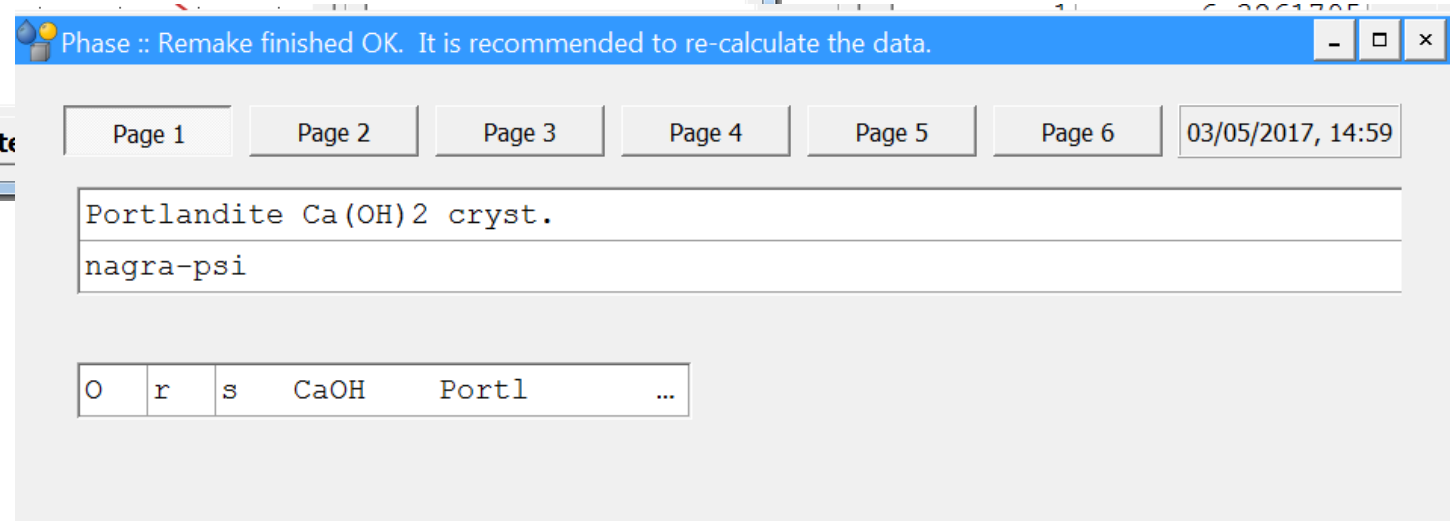
Mark dependent component to be included in the project database

a) either from ReacDC

b) or from DComp



See “help” for additional information or hints
(Partially still under construction)



GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gib

Modules Record Record List Database Files Window Help

Phase

GEM-Selektor 3 (GEMS3) : Help Viewer

File Find Go View Help

Find:

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 - Reaction-Defined Com...
 - Predefined Compositio...
 - Phase Definitions (Phase)**
 - T-P Tabulations (RTParm)
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GEM-Selektor version 3

Phase Definitions (Phase) Module

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 - [1.4. Phase module calculations](#)
 - [1.5. TSolMod rules for interaction parameters](#)
 - [1.6. Metastability and kinetics \(TKinMet implementation\)](#)
2. Phase Create/Remake Wizard
 - [2.1. Phase Wizard Step 1 - Defining the phase and the mode of mixing](#)
 - [2.2. Phase Wizard Step 2 - Phase model-of-mixing specific dimensions](#)
 - [2.3. Phase Wizard Step 3 - Sorption models and settings](#)
 - [2.4. Phase Wizard Step 4 - Metastability and kinetics model settings](#)
 - [2.5. Phase Wizard step 5 - Phase links, other settings and comments](#)
3. Phase Module Window

- See “Help:Help” for additional information or hints (*Partially still under construction*)

5.) Thermodynamic Phases – creation of entries

b) Solid solution

The screenshot shows a software interface for creating thermodynamic phase entries. The interface is divided into several sections:

- Phase List (Left):** A table listing various phases with their IDs, states, and names. The phases listed include AIOH, C12A7, C2S, C3A, C3S, C4AF, CA, CA2, CAFSH, CSH, CaAlFeSO, and CaAlNH.
- Toolbar (Top):** A set of icons for file operations, including a folder, a plus sign (Add), a floppy disk (Save), arrows (Navigation), a red X (Delete), a document with a checkmark (Check), a calculator, a graph, and a printer.
- Page Navigation (Top Right):** Buttons for Page 1, Page 2, Page 3, and Page 4.
- Search/Filter (Middle Right):** A search bar containing the text "Kulik:2011:pap:" and a dropdown menu set to "all".
- Phase Details (Bottom Right):** A table showing the details of a selected phase entry. The entry is "CSHQ" (ID 11) with state "ss" and "cem". The table lists various phase entries with their IDs, states, and names.

An arrow points from the "Add" button in the toolbar to the "Kulik:2011:pap:" field in the search/filter section.

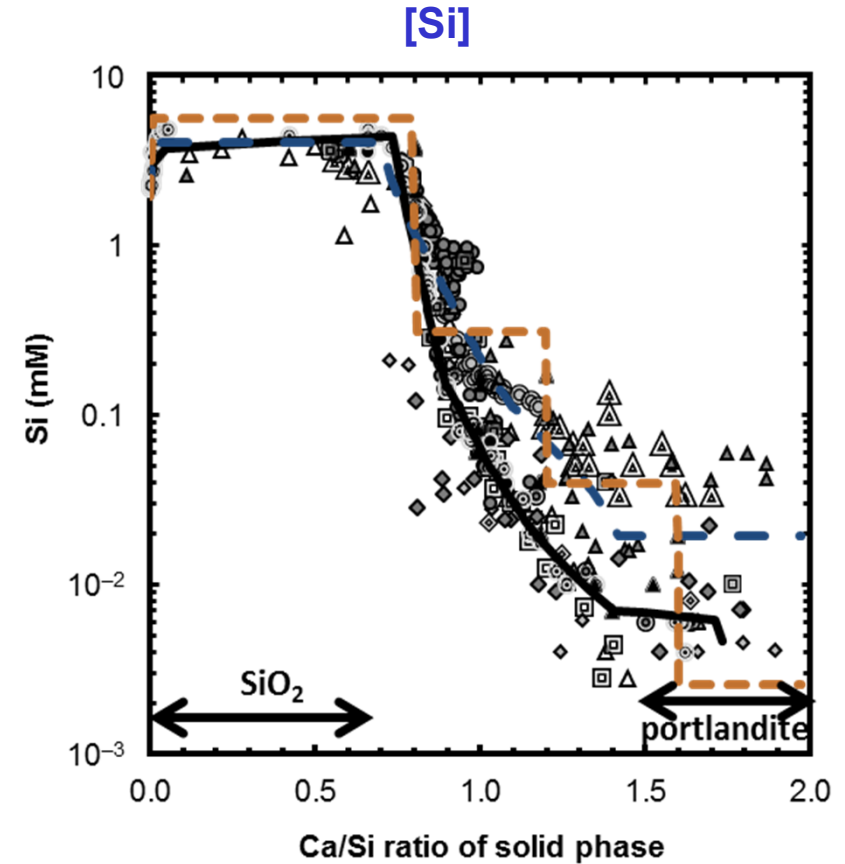
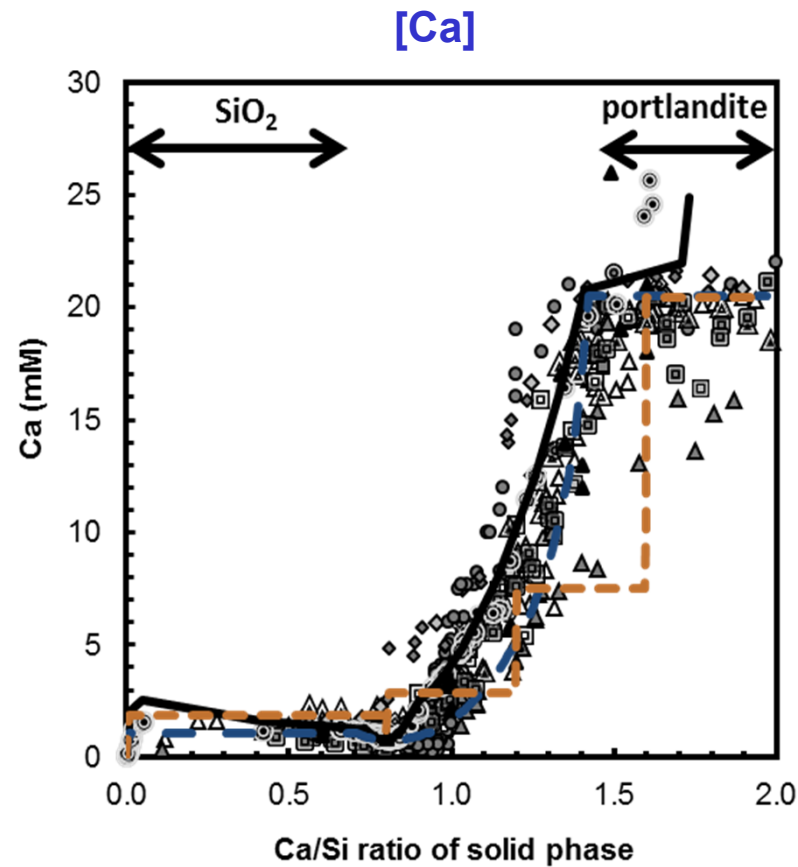
1	2	3	4	5	
1	s	AIOH	Al(OH)3am	c	cem
2	s	AIOH	Al(OH)3mic	c	cem
3	s	C12A7	Mayenite	c	cem
4	s	C2S	Belite	c	cem
5	s	C3A	Aluminate	c	cem
6	s	C3S	Alite	c	cem
7	s	C4AF	Ferrite	c	cem
8	s	CA	CA	c	cem
9	s	CA2	CA2	c	cem
10	s	CAFSH	C3(AF)S0.84H	ss	cem
11	s	CSH	CSHQ	ss	cem
12	s	CaAlFeSO	ettringite-Al	ss	cem
13	s	CaAlFeSO	ettringite-Fe	ss	cem
14	s	CaAlFeSO	monosulphate-Al	ss	cem
15	s	CaAlFeSO	monosulphate-Fe	ss	cem
16	s	CaAlNH	CAANOH10	c	cem

0	r	s	CaSiOH	CSH-JenD	...	
1	I	r	s	CaSiOH	CSH-JenH	...
2	I	r	s	CaSiOH	CSH-TobD	...
3	I	r	s	CaSiOH	CSH-TobH	...
4	I	d	s	KSiOH	KSiOH	...
5	I	d	s	NaSiOH	NaSiOH	...

CSHQ (Kulik): Ca/Si 0.67 – 2.2 (portlandite limits Ca/Si to ≤ 1.6)

Plus $(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$ and $(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$ to **estimate** alkali uptake

Other thermodynamic models for C-S-H



3 different CSH



Blanc et al. (2010) CCR 40, 851-866

Solid solution: CSHT

infinite

pentamer

dimer



Kulik (2011) CCR 41, 477-495

Surface reaction model

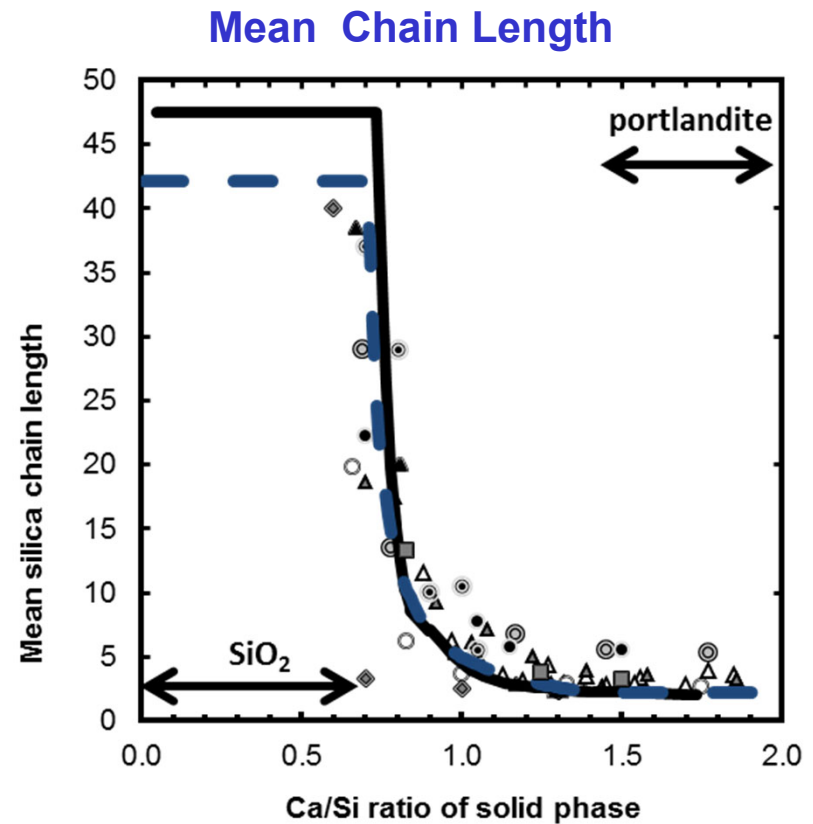
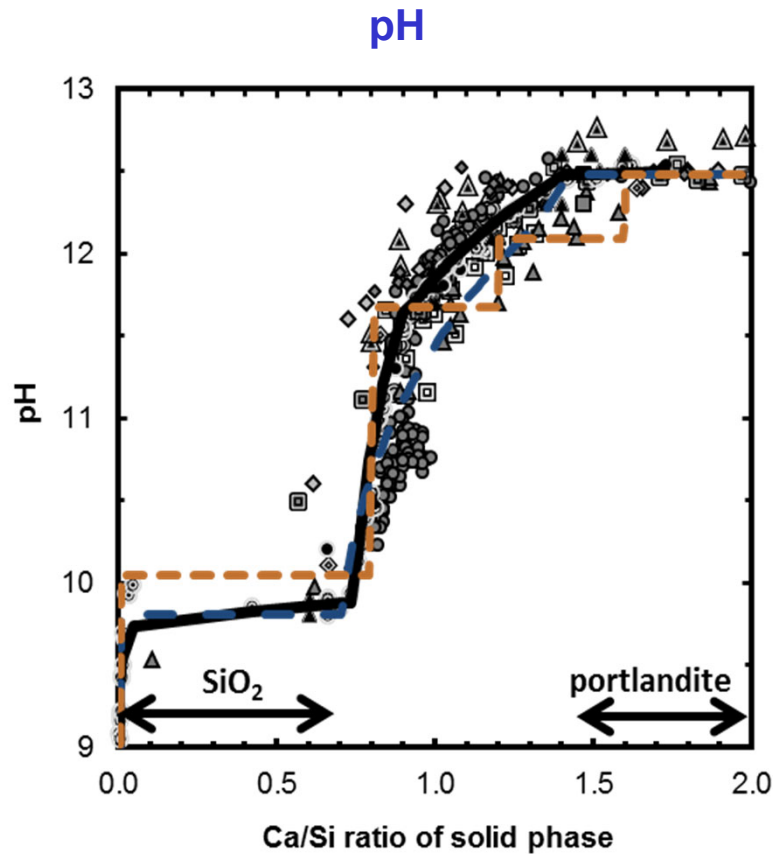
Pentamer $C_{0.8}SH_{1.6}$

dimer CSH_2

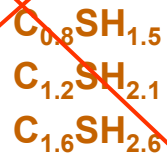
dimer $C_{1.5}SH_{2.5}$

Haas Nonat (2015) CCR 68, 124-138

Thermodynamic models for C-S-H

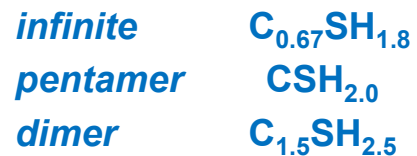


~~3 different CSH~~



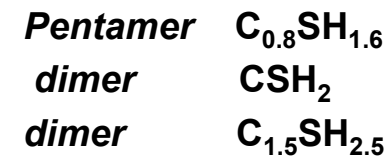
Blanc et al. (2010) CCR 40, 851-866

Solid solution



Kulik (2011) CCR 41, 477-495

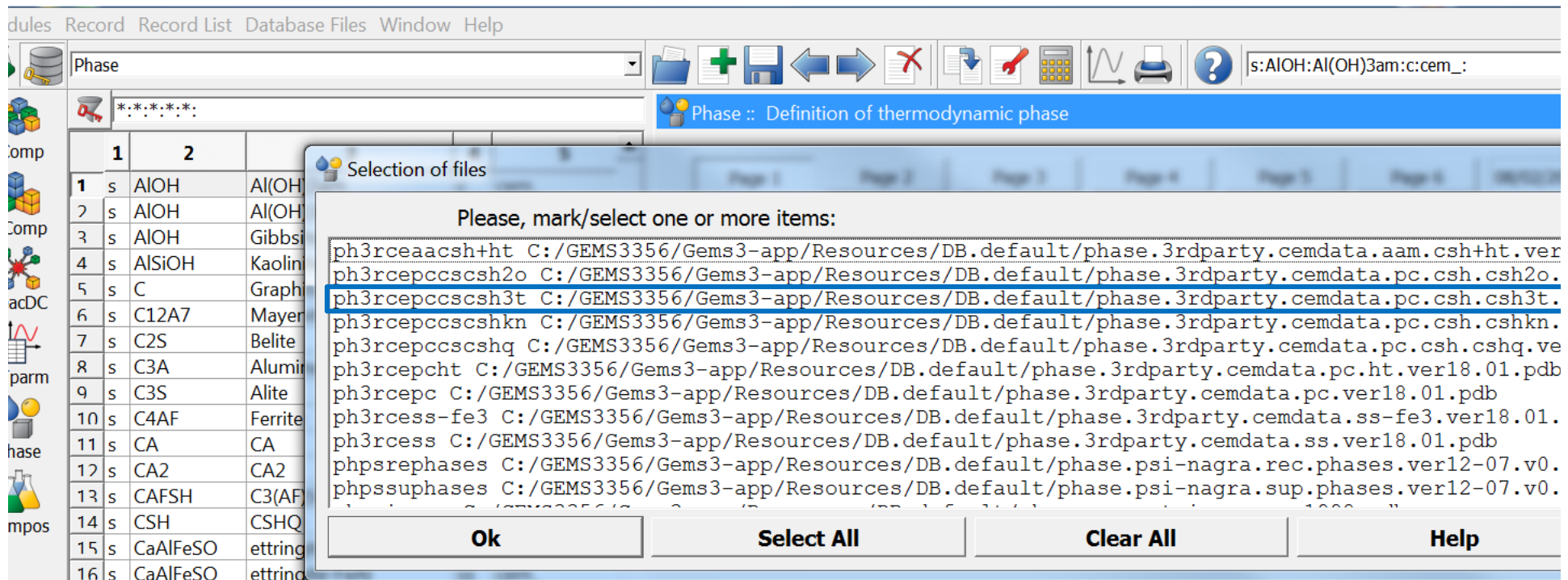
Surface reaction model



Haas Nonat (2015) CCR 68, 124-138

Selection of CSH model

- 1) When defining the project OR
- 2) Add later in database *Phase : Record List : Database*
=> select any of the available CSH models
=> store them in your database using
“Record: save as”



The screenshot shows a software interface with a menu bar (Modules, Record, Record List, Database, Files, Window, Help) and a toolbar. A table titled 'Record List' is visible, with columns labeled '1', '2', and '3'. The table contains 16 rows of data, including chemical formulas and names. A 'Selection of files' dialog box is open in the foreground, displaying a list of files with their full paths. The file 'ph3rcepccscsh3t' is selected. The dialog box has buttons for 'Ok', 'Select All', 'Clear All', and 'Help'.

	1	2	3
1	s	AIOH	Al(OH
2	s	AIOH	Al(OH
3	s	AIOH	Gibbsi
4	s	AlSiOH	Kaolin
5	s	C	Graph
6	s	C12A7	Mayer
7	s	C2S	Belite
8	s	C3A	Alumi
9	s	C3S	Alite
10	s	C4AF	Ferrite
11	s	CA	CA
12	s	CA2	CA2
13	s	CAFSH	C3(AF
14	s	CSH	CSHQ
15	s	CaAlFeSO	ettring
16	s	CaAlFeSO	ettring

Selection of files

Please, mark/select one or more items:

- ph3rceaacsh+ht C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.aam.csh+ht.ver
- ph3rcepccscsh2o C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.csh.csh2o.
- ph3rcepccscsh3t C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.csh.csh3t.**
- ph3rcepccscshkn C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.csh.cshkn.
- ph3rcepccscshq C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.csh.cshq.ve
- ph3rcepcht C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.ht.ver18.01.pdb
- ph3rcepc C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.pc.ver18.01.pdb
- ph3rcess-fe3 C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.ss-fe3.ver18.01.
- ph3rcess C:/GEMS3356/Gems3-app/Resources/DB.default/phase.3rdparty.cemdata.ss.ver18.01.pdb
- phpsrephases C:/GEMS3356/Gems3-app/Resources/DB.default/phase.psi-nagra.rec.phases.ver12-07.v0.
- phpsrephases C:/GEMS3356/Gems3-app/Resources/DB.default/phase.psi-nagra.sup.phases.ver12-07.v0.

Ok Select All Clear All Help

Selection of CSH models

MODULES Record Record LIST Database Files window Help

Phase

Phase :: Definition of thermodynamic phase

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CSH3T (downscaled) solid solution model
cement database

Kulik:2011:pap: all

0	I	d	s	CaSiOH	CSH3T-T2C	...
1	I	d	s	CaSiOH	CSH3T-T5C	...
2	I	d	s	CaSiOH	CSH3T-TobH	...

	1	2	3	4	5
54	s	CaFeSiOH	C3FS1.34H3.32	c	cem_
55	s	CAFSH	C3(AF)S0.84H	ss	cem_
56	s	CaMgCO	Dolomite-dis	c	nagra-psi_
57	s	CaMgCO	Dolomite-ord	c	nagra-psi_
58	s	CaO	lime	c	cem_
59	s	CaOH	Portlandite	c	nagra-psi_
60	s	CaSO	Anhydrite	c	nagra-psi_
61	s	CaSO	Gypsum	c	nagra-psi_
62	s	CaSO	hemihydrate	c	cem_
63	s	CSH	CSH3T	ss	cem
64	s	CSH	CSHQ	ss	cem_
65	s	Fe	Iron	c	nagra-psi_
66	s	FeCO	Fe-carbonate	d	nagra-psi_
67	s	FeCO	Siderite	c	nagra-psi_
68	s	FeO	Hematite	c	nagra-psi_
69	s	FeO	Magnetite	c	nagra-psi_
70	s	FeOH	Ferrihydrite-am	d	nagra-psi_
71	s	FeOH	Ferrihydrite-mc	c	cem_
72	s	FeOH	Goethite	c	nagra-psi_

CSH T (Kulik 2011): Ca/Si = 0.67 to 1.5
further information

5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H

GEM-Selektor Phase Setup: s:CSH:CSHT:ss:cem_

Step 1 - Defining the Phase and the Model of Mixing

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (non-ideal) mixing should be used, and how it should be calculated.

Select a phase aggregate state code:

s Condensed solid phase, also multi-component solid solution

Select a model of mixing for this phase:

I Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

I Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

N No DcEq script will be provided in this Phase definition (default)

Select a mode of execution of PhEq user-defined script for the whole phase:

N No PhEq script will be provided in this Phase definition (default)

Select a mode of a linking user-defined DcEq script to phase end members:

N No DcEq script will be provided (pure phase, built-in or ideal model), default

Select specific mixing rules (temperature corrections) for EoS and activity models:

N Default mixing rule or form of interaction parameter coefficients

To set up a (new) sorption, metastable layer- or a kinetically-controlled phase, please proceed to next wizard pages.

GEMS – Database management

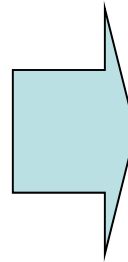
5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H

Please, mark one or more record keys. Filter: s*:*:*

r	s	CaSiOH	CSH-JenD	ce
r	s	CaSiOH	CSH-JenH	ce_
r	s	CaSiOH	CSH-TobD	ce_
r	s	CaSiOH	CSH-TobH	ce_
d	s	CSH	T2C-CNASHss	CA_
d	s	CSH	T5C-CNASHss	CA_
d	s	CSH	TobH-CNASHss	CA_
d	s	CaO	Lim	ce_
d	s	CaOH	Portlandite	dn_
d	s	CaSOH	Jennite	ce_
d	s	CaSOH	Tob-I	ce_
d	s	CaSOH	Tob-II	ce_
d	s	CaSiO	C2S	ce_
d	s	CaSiO	C3S	ce_
d	s	CaSiOH	T2C	ce_
d	s	CaSiOH	T5C	ce_
d	s	CaSiOH	TobH	ce_
d	s	SiO	Amor-S1	ce_
d	s	SiO	Qtz	dn_

Ok Set Filter Select All



Phase: Remark finished OK. It is recommended to re-calculate the data.

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CSH-ternary tobermorite model
cement database

Kulik:2011:pap: all

0	I	d	s	CaSiOH	T2C	...
1	I	d	s	CaSiOH	T5C	...
2	I	d	s	CaSiOH	TobH	...

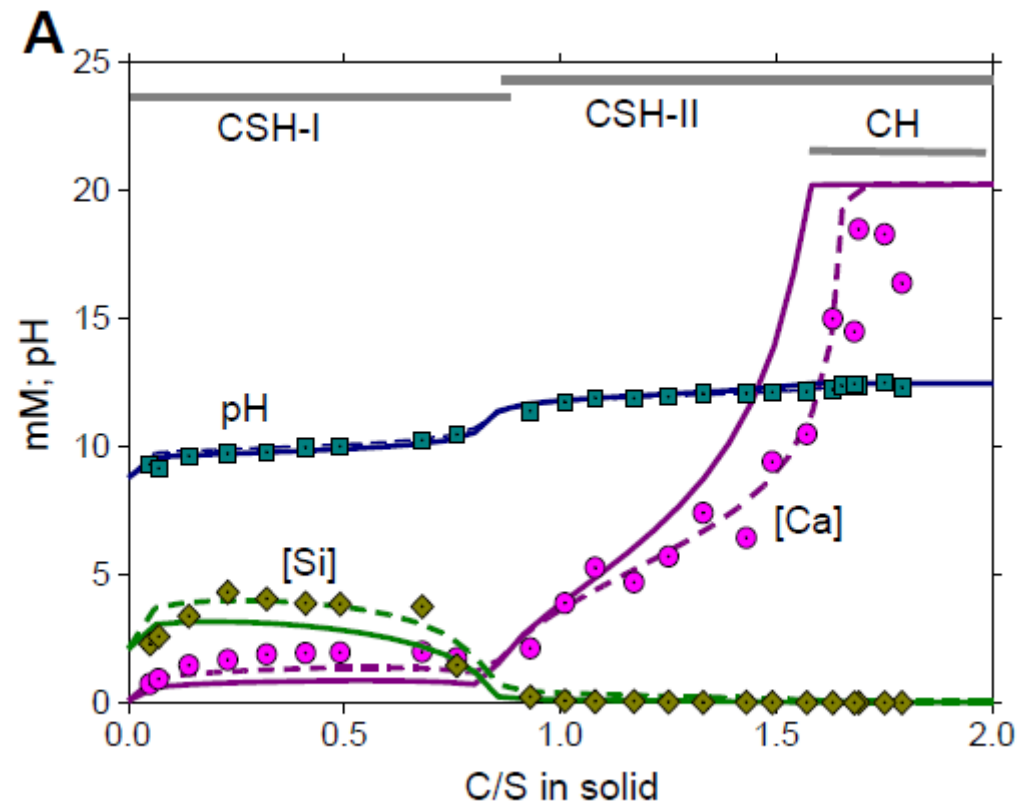
Includes the data of the end members of the solid solution series

Ideal solid solution phase

CSH «Tob-Jennite»: used in Cemdata07

CSHII: Ca/Si 0.83 to 1.67

- i) CSH-I solid solution system with the end-members SiO_2 (am) and tobermorite (Tob-I: $(\text{CaO})_2(\text{SiO}_2)_{2.4} \cdot (\text{H}_2\text{O})_{3.2}$) and
- ii) CSH-II solid solution system with the end-members jennite $(\text{CaO})_{1.67}(\text{SiO}_2)_1 \cdot (\text{H}_2\text{O})_{2.1}$ and tobermorite (Tob-II: $(\text{CaO})_{0.83}(\text{SiO}_2)_1 \cdot (\text{H}_2\text{O})_{1.3}$).



Details in (Kulik and Kersten 2001, Lothenbach et al. 2008)

CSH «Tob-Jennite»: used in Cemdata07

The screenshot displays the Cemdata07 software interface. The main window shows a list of phases with columns for ID, state, formula, name, and database. The phase 'CSH-II: Tob_jen_ss' is selected. The right-hand pane shows the definition of this phase, including its ideal solution model and search results for 'Lothenbach_ea:pap:2007:'. Below this, a second table shows the definition for 'CSH-I: Tob_SiO2_ss' and its search results.

	1	2	3	4	5
1	s	C2S	Belite	c	cem_
2	s	C3S	Alite	c	cem_
3	s	CSH	CSHQ	ss	cem_
4	s	CSH	CSHT	ss	cem_
5	s	CSH-I	Tob_SiO2_ss	ss	cem_
6	s	CSH-II	Tob_jen_ss	ss	cem_
7	s	CaO	lime	c	cem_
8	s	CaOH	Portlandite	c	nagra-psi_
9	s	SiO	Quartz	c	psi-nagra_
10	s	SiO	Silica-amorph	c	nagra-psi_

Phase :: Definition of thermodynamic phase

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Tob-jen ideal ss
cement database

Lothenbach_ea:pap:2007:

0	I	d	s	CaSOH	Jennite	...
1	I	d	s	CaSOH	Tob-II	...
2	I	r	s	KOHSi	K_sorption	...
3	I	r	s	NaOHSi	Na_sorption	...

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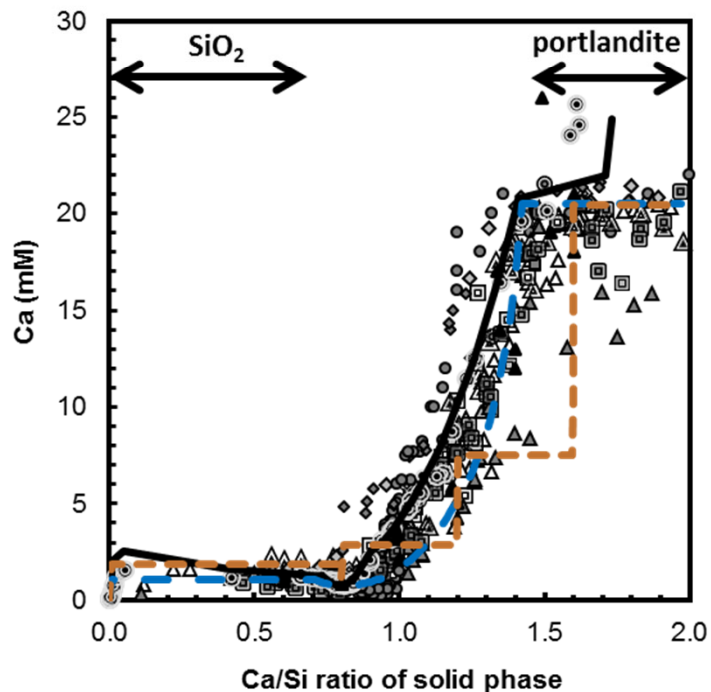
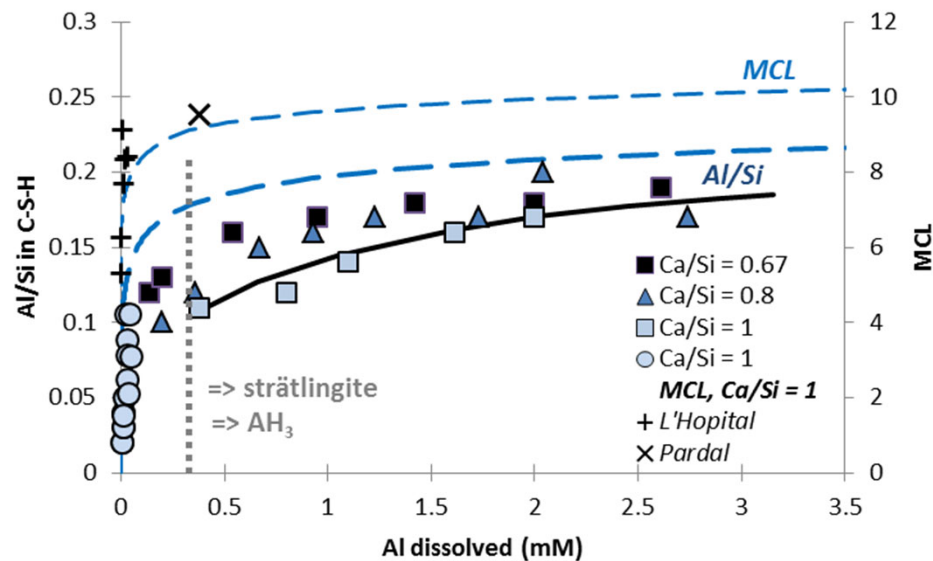
Tob-SiO2 ideal ss
cement database

Lothenbach_ea:pap:2007: all

0	I	d	s	CaSOH	Tob-I	...
1	I	d	s	SiO	Amor-S1	...

Details in (Kulik and Kersten 2001, Lothenbach ea 2008)

Al-uptake in CSH



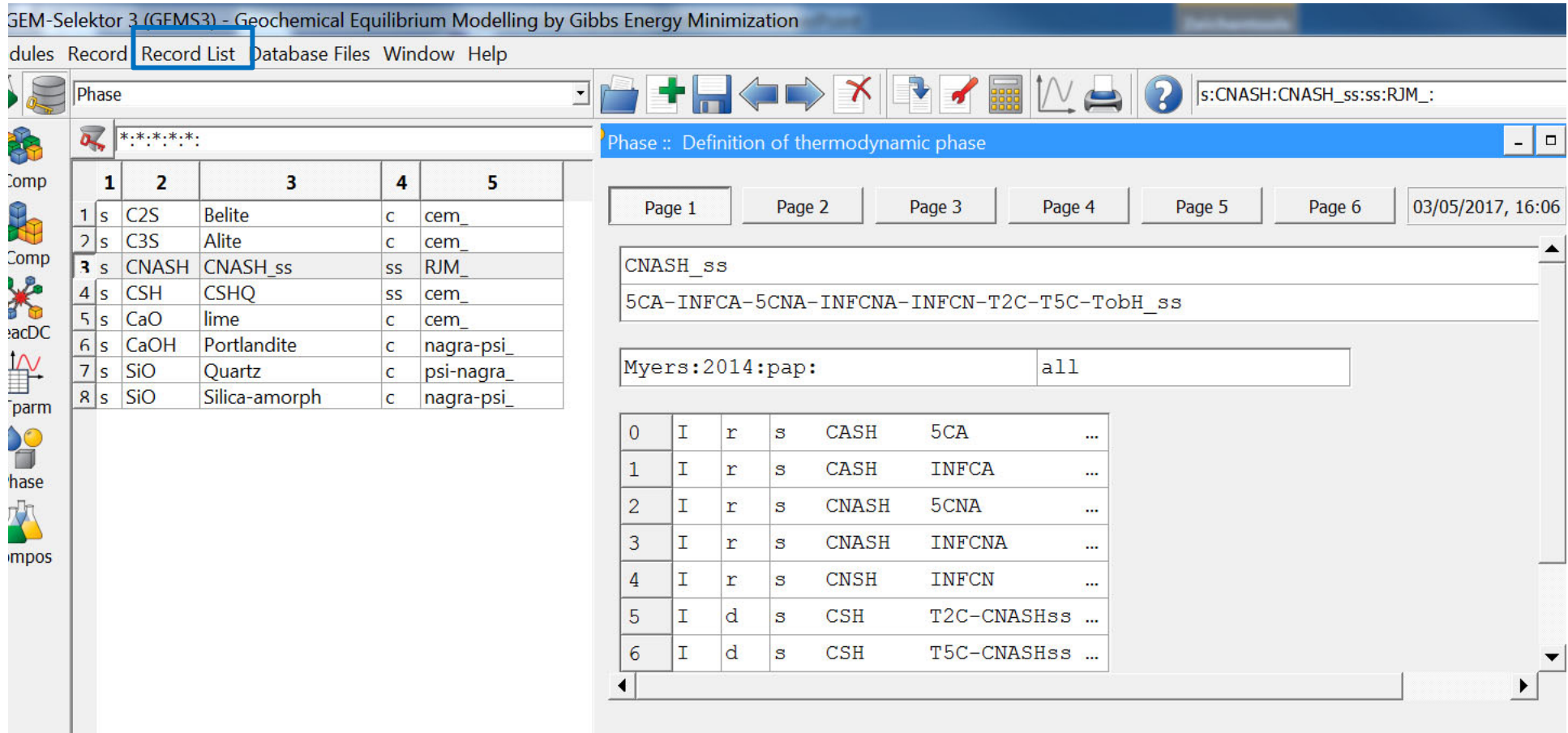
Sorption (Haas & Nonat) and solid solution (Kulik ea, Myers ea)

Models:

- relate to structure:
dimer, pentamer, infinite
- calculate MCL
- Al and alkali binding
- New models under construction
- Need for more systematic experimental data for different Al sorption sites

CNASH (Myers ea 2014): Ca/Si = 0.67 to 1.5

Based on CSHT (Kulik 2011)



The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The main window is titled "Phase :: Definition of thermodynamic phase". The left sidebar contains a "Record List" table with 8 rows. The right pane shows the phase definition details for "CNASH_ss".

1	2	3	4	5
1 s	C2S	Belite	c	cem_
2 s	C3S	Alite	c	cem_
3 s	CNASH	CNASH_ss	ss	RJM_
4 s	CSH	CSHQ	ss	cem_
5 s	CaO	lime	c	cem_
6 s	CaOH	Portlandite	c	nagra-psi_
7 s	SiO	Quartz	c	psi-nagra_
8 s	SiO	Silica-amorph	c	nagra-psi_

Phase :: Definition of thermodynamic phase

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CNASH_ss
5CA-INFCA-5CNA-INFCNA-INFCN-T2C-T5C-TobH_ss

Myers:2014:pap: all

0	I	r	s	CASH	5CA	...
1	I	r	s	CASH	INFCA	...
2	I	r	s	CNASH	5CNA	...
3	I	r	s	CNASH	INFCNA	...
4	I	r	s	CNSH	INFCN	...
5	I	d	s	CSH	T2C-CNASHss	...
6	I	d	s	CSH	T5C-CNASHss	...

Activate by: Phase : Record List : Restore : select "CNASH_ss Phase.txt"
Details in Myers ea 2104

C-S-H

Different models available
The user has to decide for 1 model
Do not use several at the same time

For PC

- CSHQ (incl. MCL)
- Or Tob-JEN

For alkali activated

- CSHT (incl. MCL)
- Or CNASH

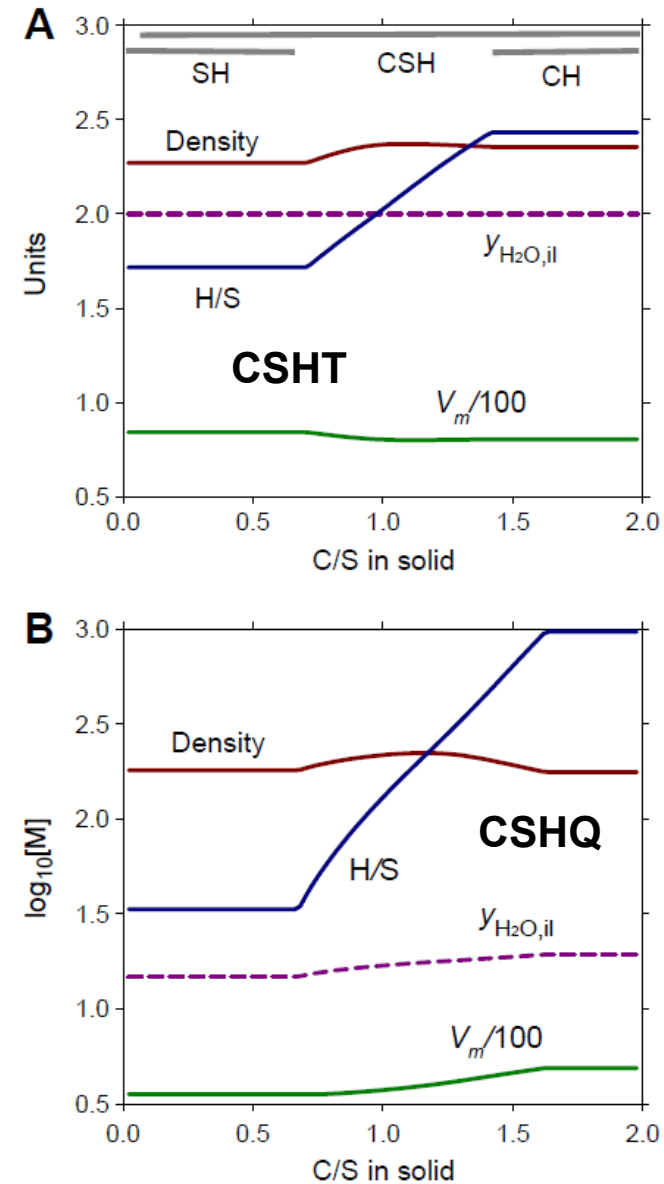


Fig. 8. Variations of density (in $g\ cm^{-3}$), volume V_m (in $cm^3\ mol^{-1}$), interlayer H_2O mole fraction $y_{H_2O,il}$, and H_2O/SiO_2 mole ratio H/S of the C-S-H phase, as predicted by the downscaled CSHT simple ideal model Table 5 (A) and by the downscaled CSHQ simple ideal model Table 6 (B).