清華大學

Empa
Materials Science and Technology

Lecture 04
Database, solubility,

Saturation indices

Barbara Lothenbach
Frank Winnefeld
Bin Ma
Zhenguo Shi

Software development/fitting tools/kinetic:

Dmitrii Kulik

Dan Miron

PAUL SCHERRER INSTITUT
PSI

Empa
Materials Science and Technology

Thermodynamic data

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

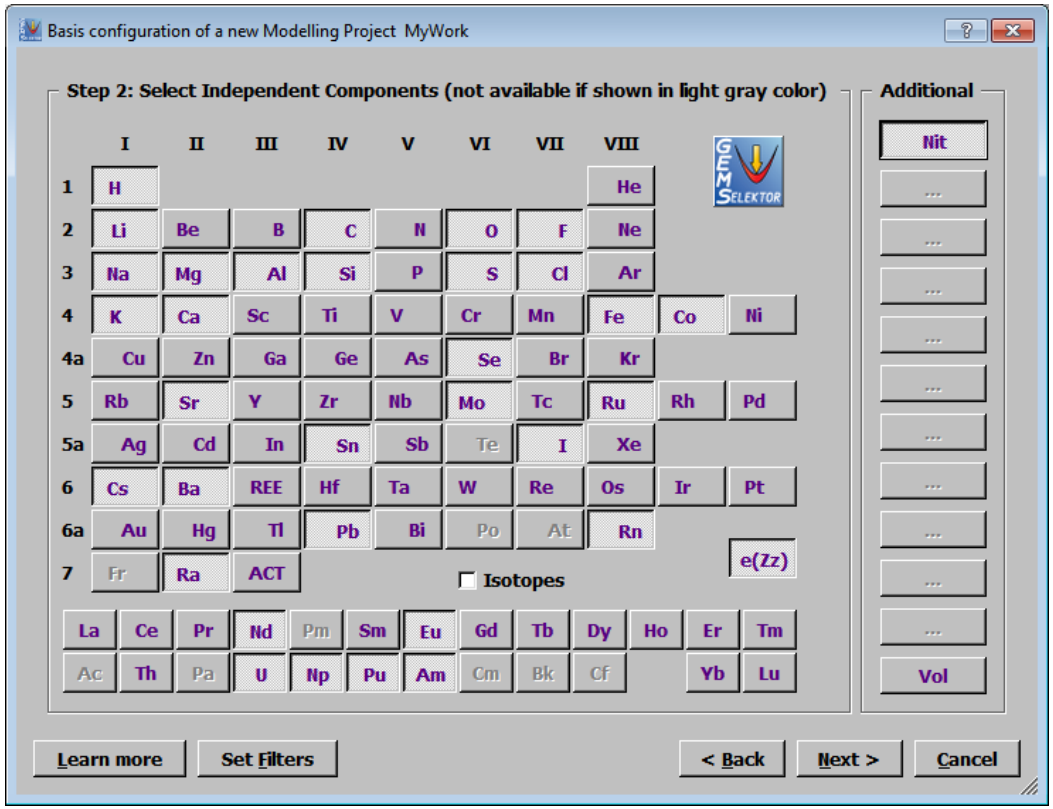
2. Solubility and speciation
3. Saturation indices
4. Hydrates in cement
5. Details on how to manage thermodynamic data in GEMS

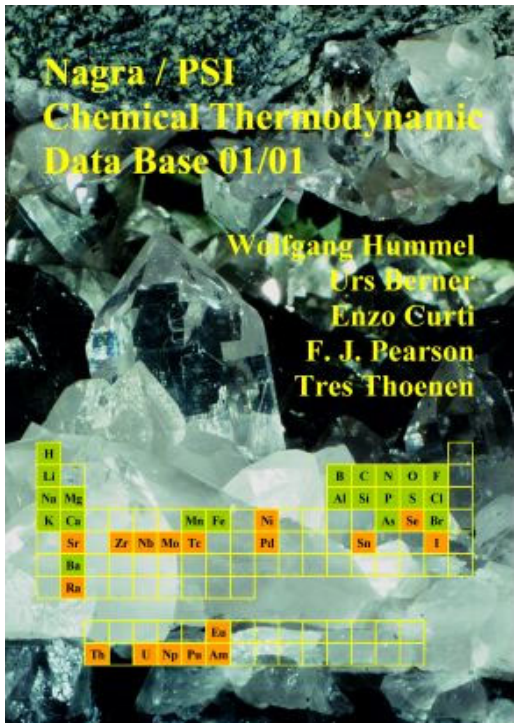
   => Self study

Default ThermoDynamic Databases

Empa
Materials Science and Technology

New modeling projects can easily be created using default TDBs. **PSI/Nagra 12/07 TDB [Thoenen ea]**





log*K* at 1 bar 25 C , enhanced with *T,P* corrections from SUPCRT

3rd-party: Cemdata'18

www.empa.ch/cemdata

3rd-party: HERACLES

www.psi.ch/heracles/heracles

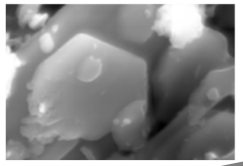
Complementary: SUPCRT (Slop98)

www.asu.edu/geopig

Thermodynamic databases

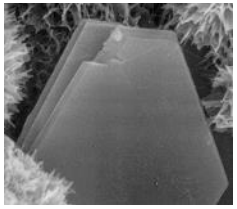
Empa
Materials Science and Technology

Generic data



general-TDB

- Aqueous phase (Ca^{2+}, $Ca(OH)^{+}$, …)
- Gaseous phase (e.g. CO_2 (g), ...)
- Minerals (calcite, gypsum, portlandite, …)



Cemdata 18

AFm

SO_4-AFm ⇕ solid solution OH-AFm

CO_3-AFm hemicarb. strätlingite

Al-AFm ⇕ solid solution Fe-AFm

AFt

SO_4-AFt ⇕ solid solution CO_3-AFt

thaumasite

Fe-AFt ⇕ solid solution Al-AFt

hydrogarnet

C_3AH_6

$C_3AS_{0.84}H_{4.32}$ ⇕ solid solution $C_3FS_{0.84}H_{4.32}$

C-S-HQ

$Ca_{0.67}SiH_{1.5}$

$C_{0.83}S_{0.67}H_{1.8}$

$C_{1.3}SH_{2.17}$

$C_{1.5}S_{0.67}H_{2.5}$

Cemdata18 additions:
Cl_2-, NO_3-, NO_2-AFm, relative humidity, M-S-H, zeolites, C-N-A-S-H, …

Data based on solubility measurements at different temperatures + solid phasec haracterisation

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.
  - **CEMDATA07**: Matschei et al. (2007) CCR, Lothenbach et al. (2008) CCR
  - Blanc et al. (2010) CCR 40, 851-866; 1360-1374
  - **CEMDATA18**: 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} *	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [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]
$C_6As_3H_{30}$[c]		-14728.1	-16950.2	1792.4	1452	2.156			708	[8]
$C_6As_3H_{13}$		-10540.6	-11530.3	1960.4	970.7	1.483			411	[8]
$C_6As_3H_9$		-9540.4	-10643.7	646.6	764.3	1.638			361	[8]
tricarboaluminate[a]	-46.5	-14565.64	-16792	1858	2042	0.559	$-7.78\cdot10^6$		650	[3, 4]
Fe-ettringite[b]	-44.0	-14282.36	-16600	1937	1922	0.855	$2.02\cdot10^6$		717	[3, 9]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	$-3.40\cdot10^6$		330	[10]
C_3AH_6[d]	-20.50	-5008.2	-5537.3	422	290	0.644	$-3.25\cdot10^6$		150	[11, 12]
$C_3AS_{0.41}H_{5.18}$[**d]	*-25.35*	*-5192.9*	*-5699*	*399*	*310*	*0.566*	*$-4.37\cdot10^6$*		*146*	*[12]*
$C_3AS_{0.84}H_{4.32}$[**e]	*-26.70*	*-5365.2*	*-5847*	*375*	*331*	*0.484*	*$-5.55\cdot10^6$*		*142*	*[12]*
C_3FH_6[f***]	*-26.30*	*-4122.8*	*-4518*	*870*	*330*	*1.237*	*$-4.74\cdot10^6$*		*155*	*[12]*
$C_3FS_{0.84}H_{4.32}$[e,f]	-32.50	-4479.9	-4823	840	371	0.478	$-7.03\cdot10^6$		149	[12]
$C_3A_{0.5}F_{0.5}S_{0.84}H_{4.32}$[e]	-30.20	-4926.0	-5335	619	367	0.471	$-8.10\cdot10^6$		146	[12]
$C_3FS_{1.34}H_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	$-8.39\cdot10^6$		145	[12]
C_4AH_{19}[g]	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	369	[11, 13]
C_4AH_{13}		-7325.7	-8262.4	831.5	208.3	3.13			274	[13]
C_4AH_{11}		-6841.4	-7656.6	772.7	0.0119	3.56	$1.34\cdot10^{-7}$		257	[13]
$C_2AH_{7.5}$	-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_4AsH_{16}		-8726.8	-9930.5	975.0	636	1.606			351	[13, 14]
C_4AsH_{14}[g]		-8252.9	-9321.8	960.9	1028.5				332	[13, 14]
C_4AsH_{12}[h]		-7778.4	-8758.6	791.6	175	2.594			310	[13, 14]
$C_4AsH_{10.5}$		-7414.9	-8311.9	721	172	2.402			282	[13, 14]
C_4AsH_9		-7047.6	-7845.5	703.6	169	2.211			275	[13, 14]
C_4AcH_{11}	-31.47	-7337.46	-8250	657	618	0.982	$-2.59\cdot10^6$		262	[3, 4]
C_4AcH_9		-6840.3	-7618.6	640.6	192.4	2.042			234	[13]
$C_4Ac_{0.5}H_{12}$	-29.13	-7335.97	-8270	713	664	1.014	$-1.30\cdot10^6$	-800	285	[3, 4]
$C_4Ac_{0.5}H_{10.5}$		-6970.3	-7813.3	668.3	0.0095	2.836	$1.07\cdot10^{-7}$		261	[13]
$C_4Ac_{0.5}H_9$		-6597.4	-7349.7	622.5	0.0088	2.635	$9.94\cdot10^{-8}$		249	[13]
C_4AcH_{13}[i]	-19.70	-5705.15	-6360	546	439	0.748	$-1.13\cdot10^6$	-800	316	[3, 4]

Database: Cemdata18

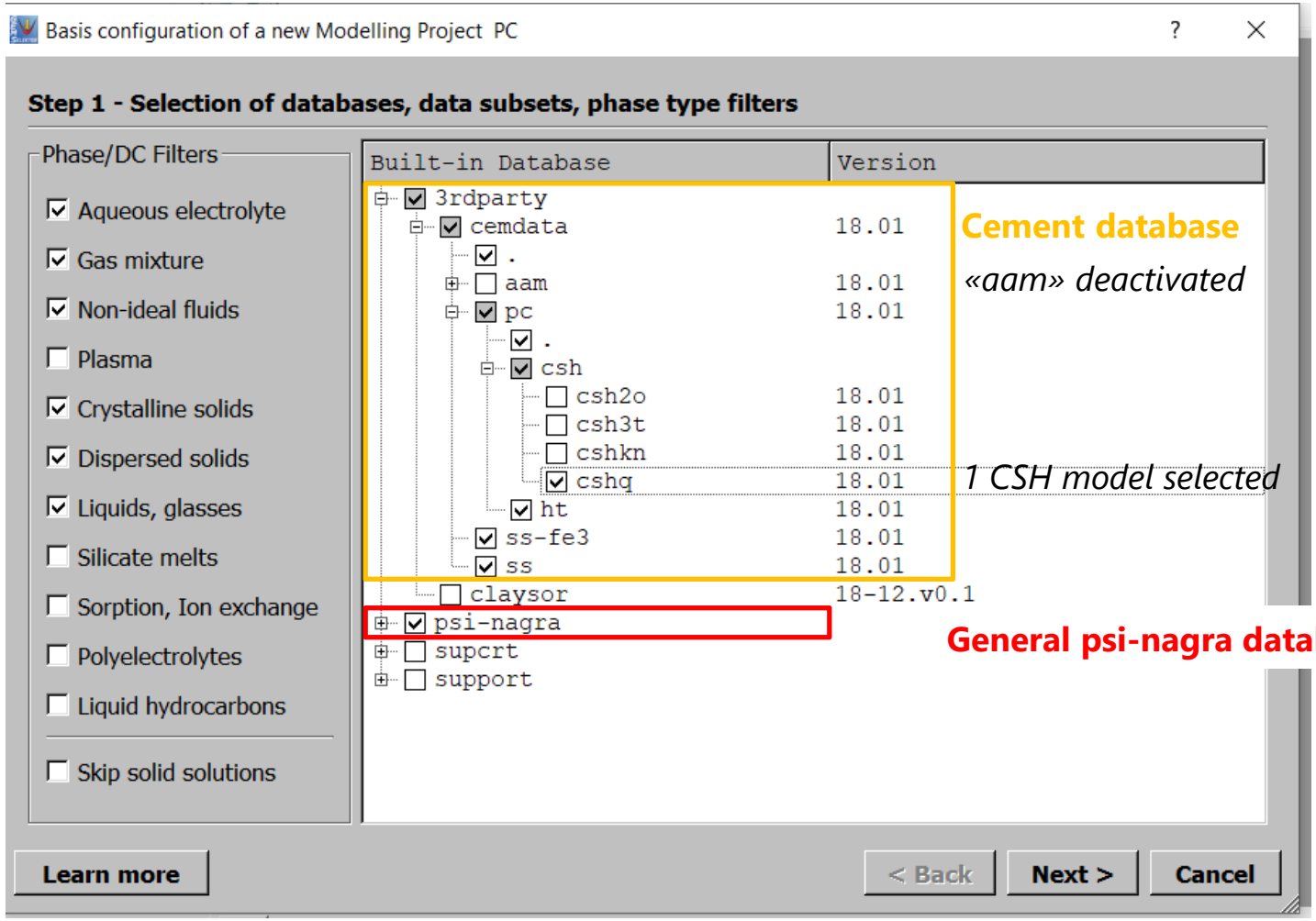
- **PC:**
  Focus on **Portland cements and Portland-blends**
  - CSHQ (Kulik): Ca/Si 0.67 – 2.2 (portlandite limits to Ca/Si **≈ 1.6**)
  - $(KOH)_{2.5}SiO_2H_2O$) and $(NaOH)_{2.5}SiO_2H_2O$) to **estimate** alkali uptake
  - Very stable hydrotalcite from Atkins: $Mg_4Al_2O_{10}$ $10H_2O$

- **AAM18**
  Focus on **alkali activated materials**
  - CSHT (Kulik) with Na uptake and Al-uptake (in bridging site) (Myers ea 2014)
    Ca/Si **0.67 – 1.5**
  - Less stable hydrotalcite, variable Mg/Al (Myers ea 2015)
    $Mg_4Al_2O_{10}$ $10H_2O$, $Mg_6Al_2O_{12}$ $12H_2O$, $Mg_8Al_2O_{14}$ $14H_2O$

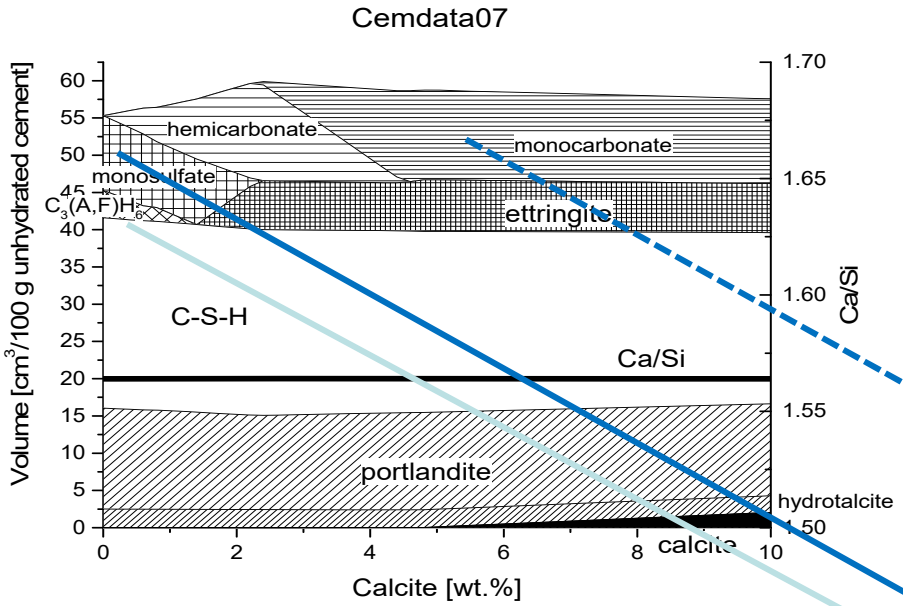
- **Cannot be used at the same time**
- Further CSH models can be activated by introducing additional solid solutions in «Phase»
  - Tob-jennite (Kulik and Kersten 2001, Lothenbach and Winnefeld 2006)
  - CSHT (Kulik 2011)

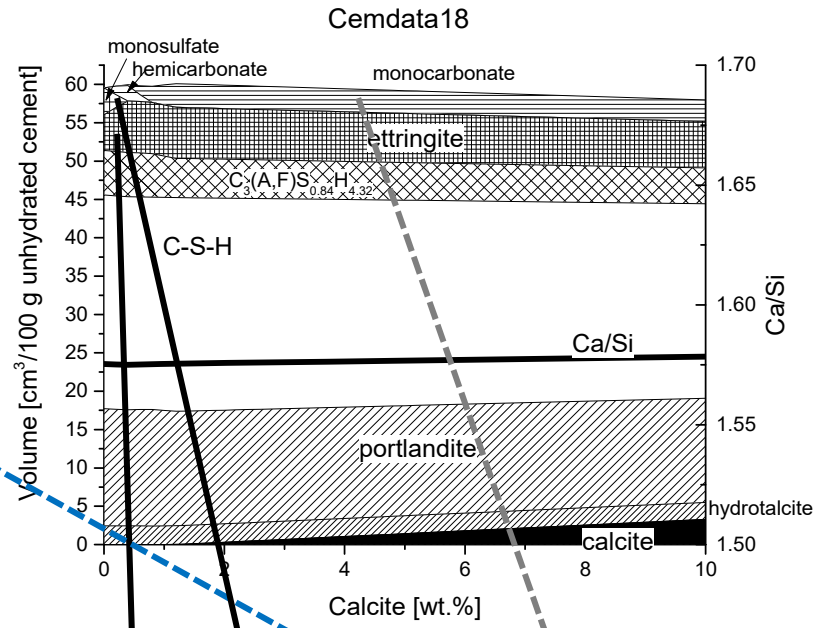
  All details in Lothenbach et al. (2019) CCR 115, 472-506

Recommended selection for PC and blended cements



What did change with cemdata18 ?



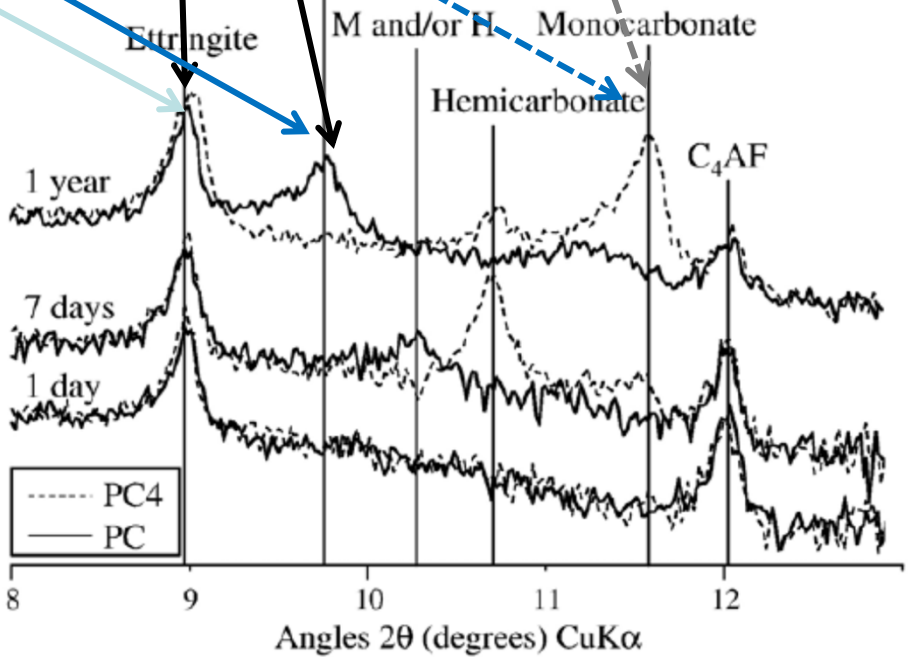


Lothenbach et al. 2008

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

=> Some **Al in Si-hydrogarnet**

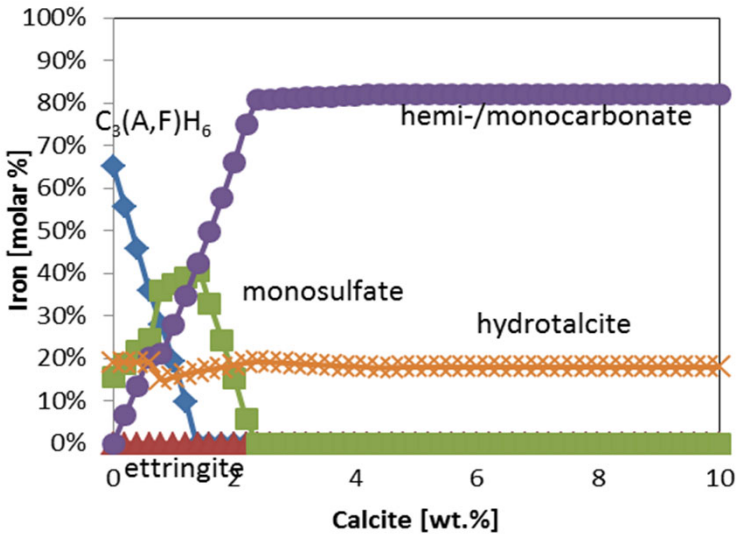
- No calcite: Ettringite, less monosulfate as all Fe and some Al in Si-hydrogarnet
- Calcite: less monocarbonate as some Al in Si-hydrogarnet, less strong volume effect of limestone



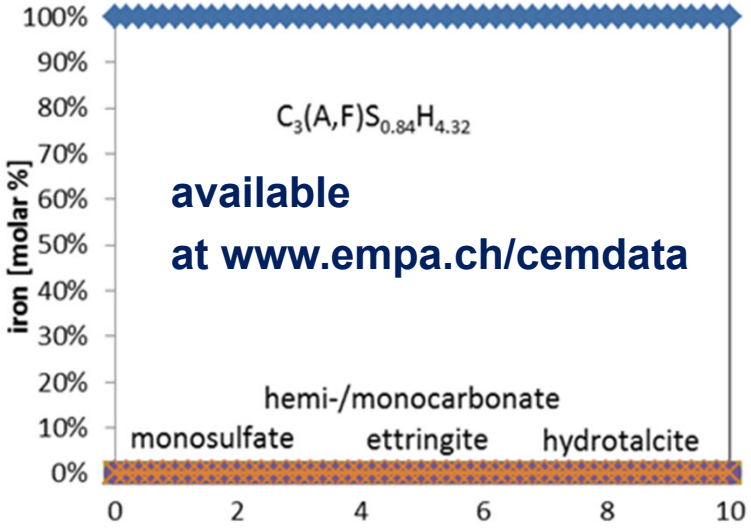
Cemdata07

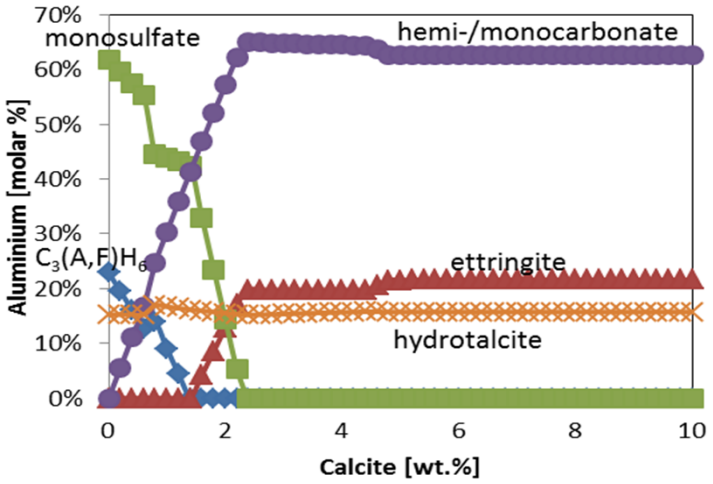
Cemdata18

main effect on Al and Fe distribution

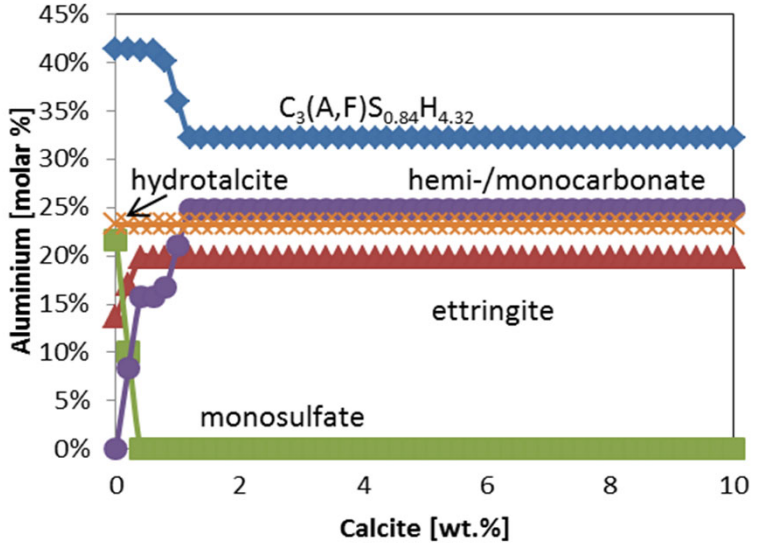


Fe





Al



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

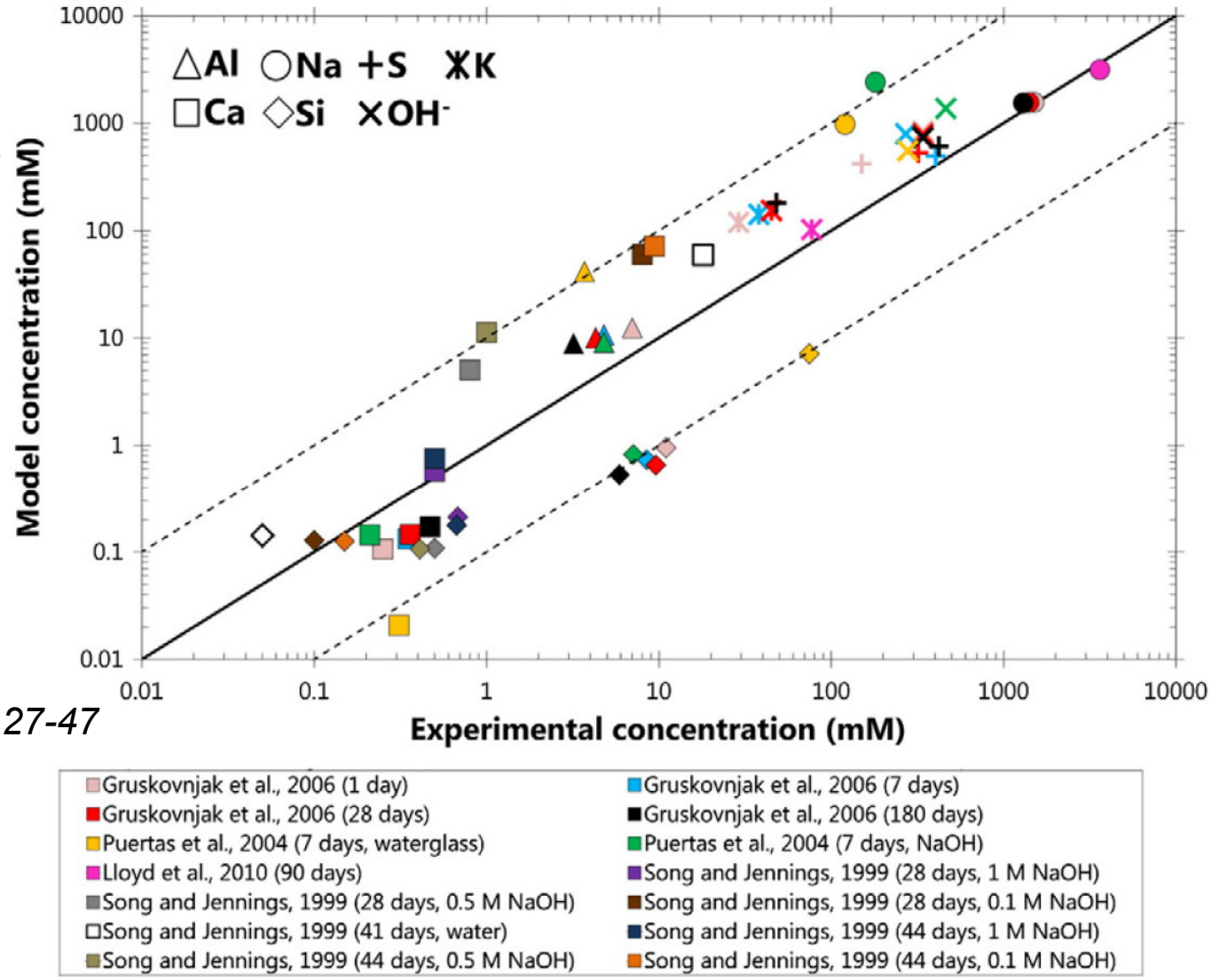
Calcite: less monocarbonate as some Al in Si-hydrogarnet

Cemdata18 for AAM

For alkali activated materials

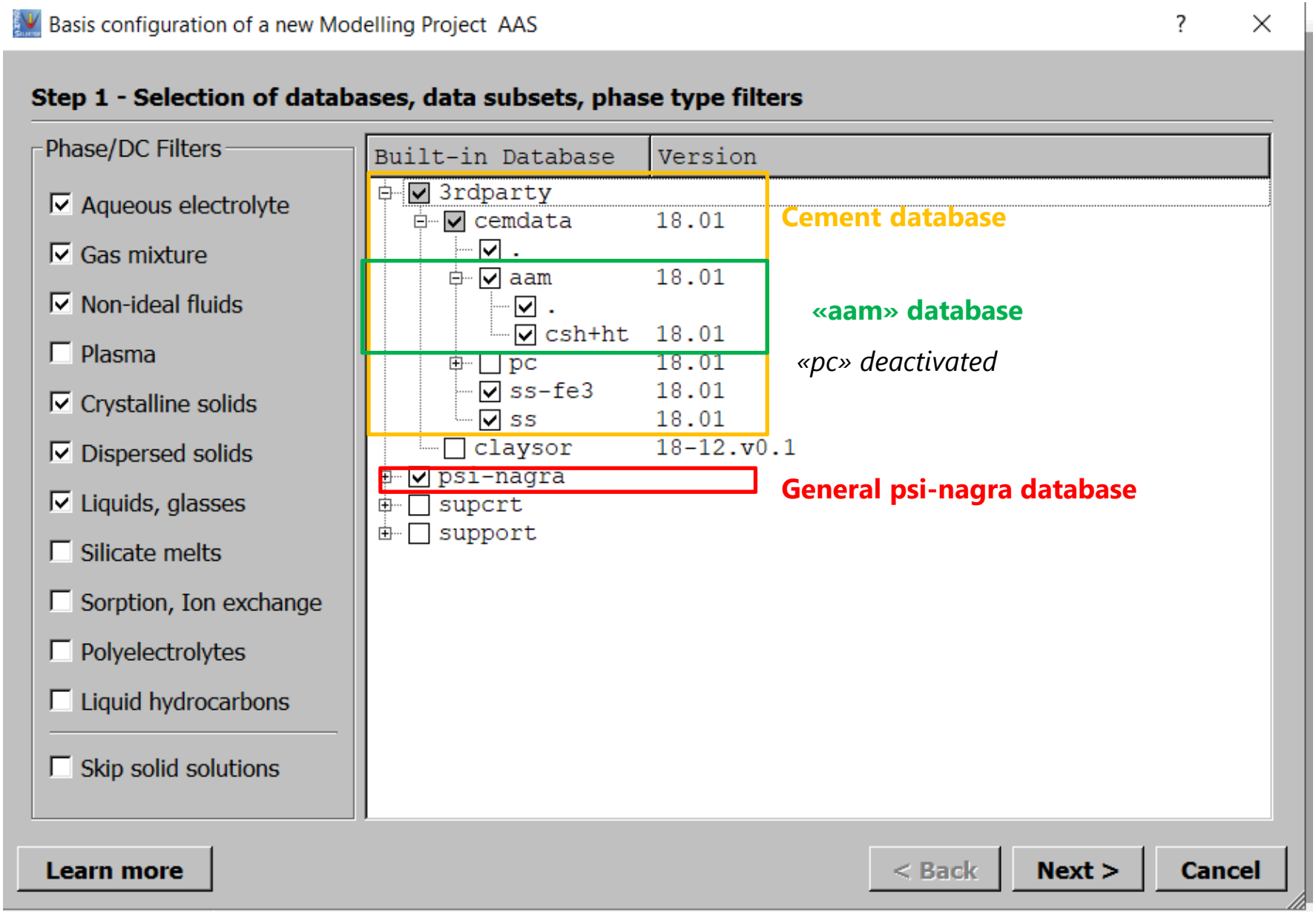
Same data as in Cemdata18 for PC with the following exceptions

CNASH model (Myers ea 2014): Ca/Si = 0.67 to 1.5; **uptake of Al and Na**



Myers ea (2014) CCR 66, 27-47

Recommended selection for alkali activated materials



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               Al02-     0.0      Al02     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

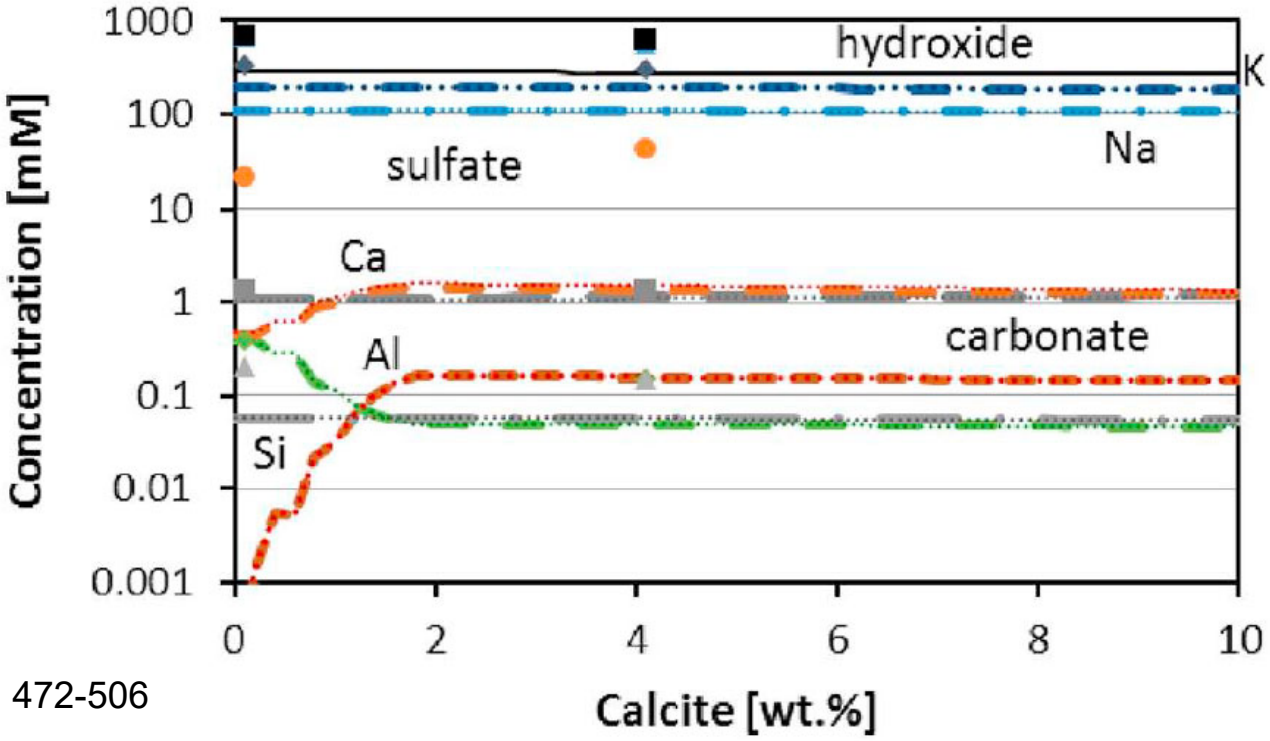
Cemdata18 also available in PHREEQC format *(uses log K instead of G°):*

```
C3AH6
        Ca3Al2O6(H2O)6 + 4H+ = 3Ca+2 + 2AlO2- + 8H2O
        -Vm     149.702
        -analytical_expression  6.92717 0 11498.865007 -4.036936 0 0 0
        -log_K  35.500282
```

Identical results

GEMS: dashed - - -

PHREEQC: dotted …
(ideal solid solution)



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

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, …)
  - $\Delta G_f°$ (Gibbs free energy of formation) (GEMS, MTDATA, …)
  - convertible: $K = e^{-\frac{\Delta G_r°}{RT}}$

$$\Delta G_r° = \sum_i \nu_i \Delta G_f°$$

Empa
Materials Science and Technology

Thermodynamic modelling: Limits

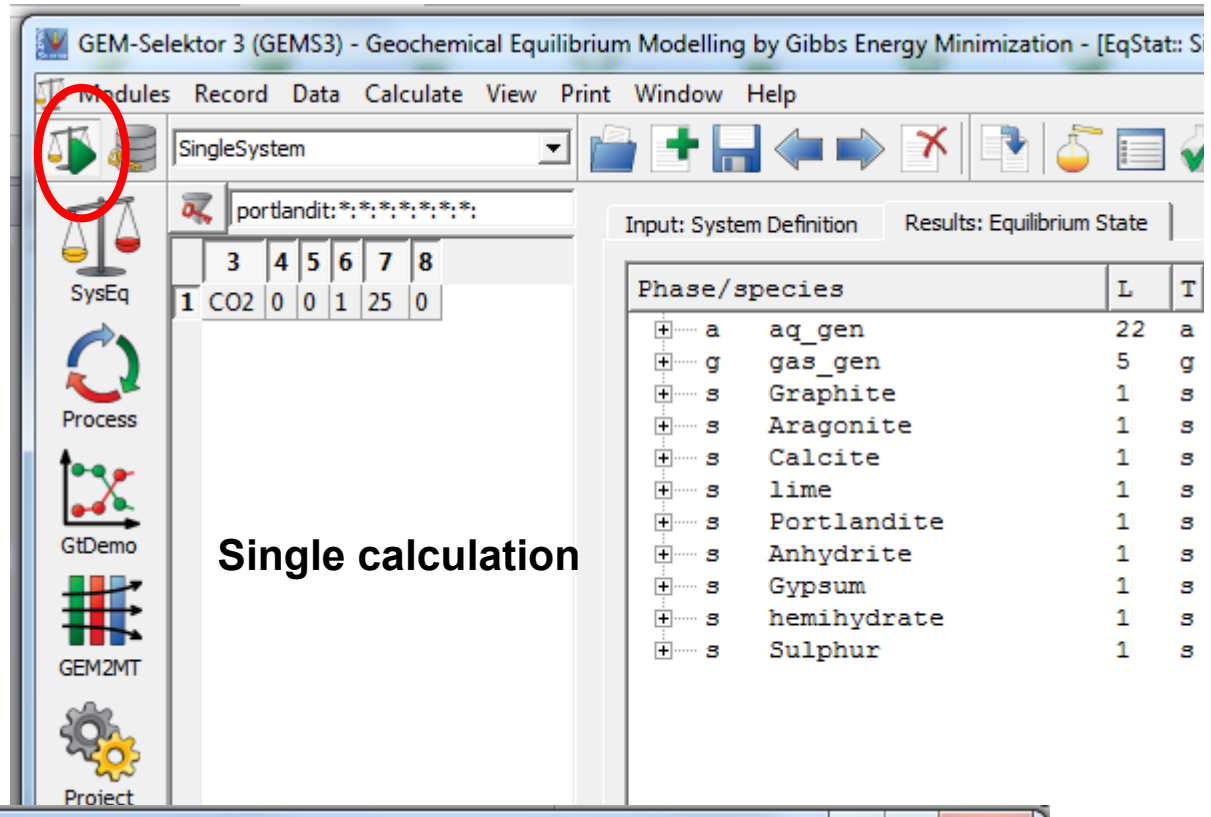
- **Thermodynamic data**
  - **Small differences in data -> other solids stable small errors can lead to wrong results**
  - **Gaps in database: Al-K-Na uptake in C-S-H, …**
- **Kinetics: some phases are metastable**
  - **C-S-H metastable (jennite, tobermorite, …)**
  - **Hydrated cement thermodynamically 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), ...**

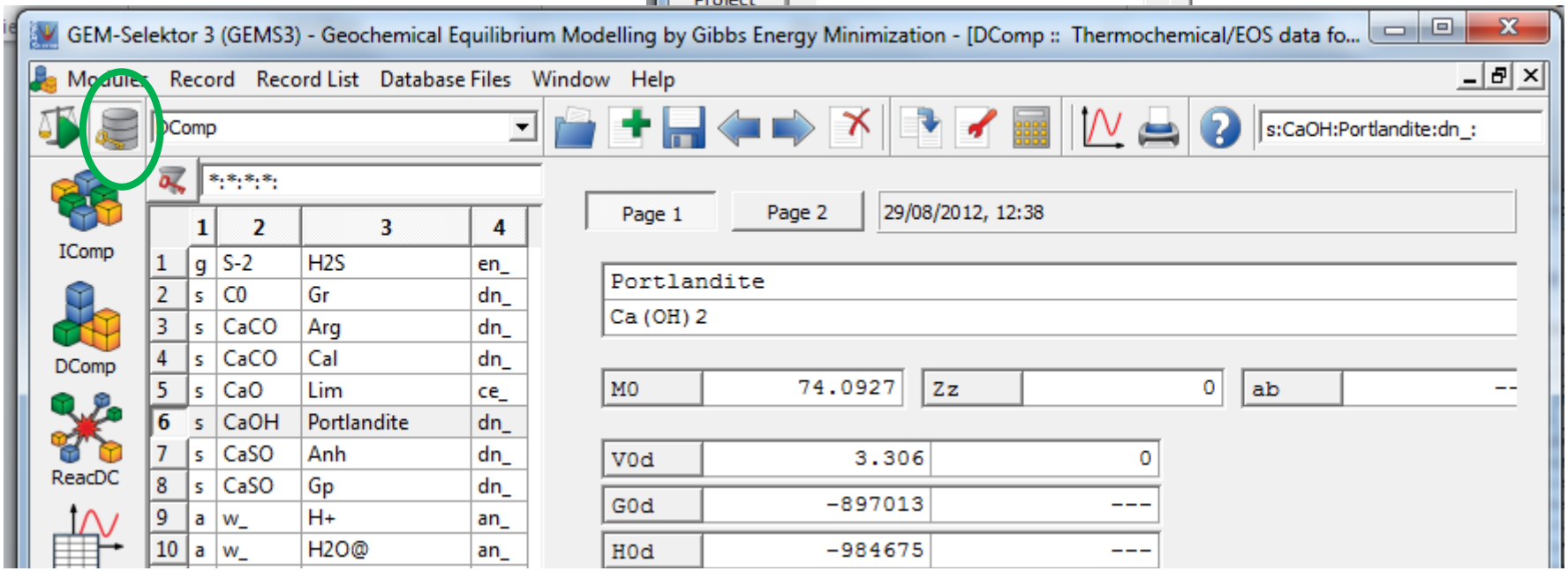
GEMS structure

calculations

Thermodynamic database

for experienced users





Thermodynamic database

Empa
Materials Science and Technology

Independent components (chemical elements: Ca)

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

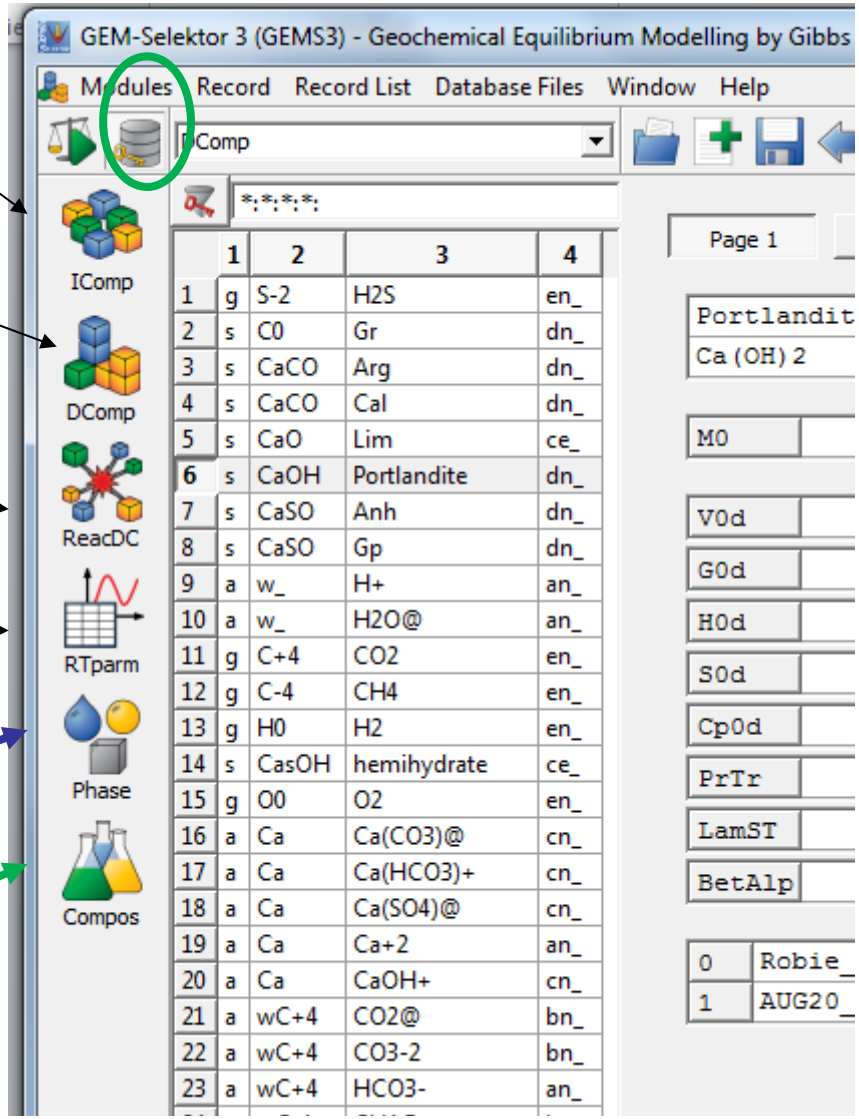
2 input options: both equally valid

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

Calculation and plotting of T/P dependency

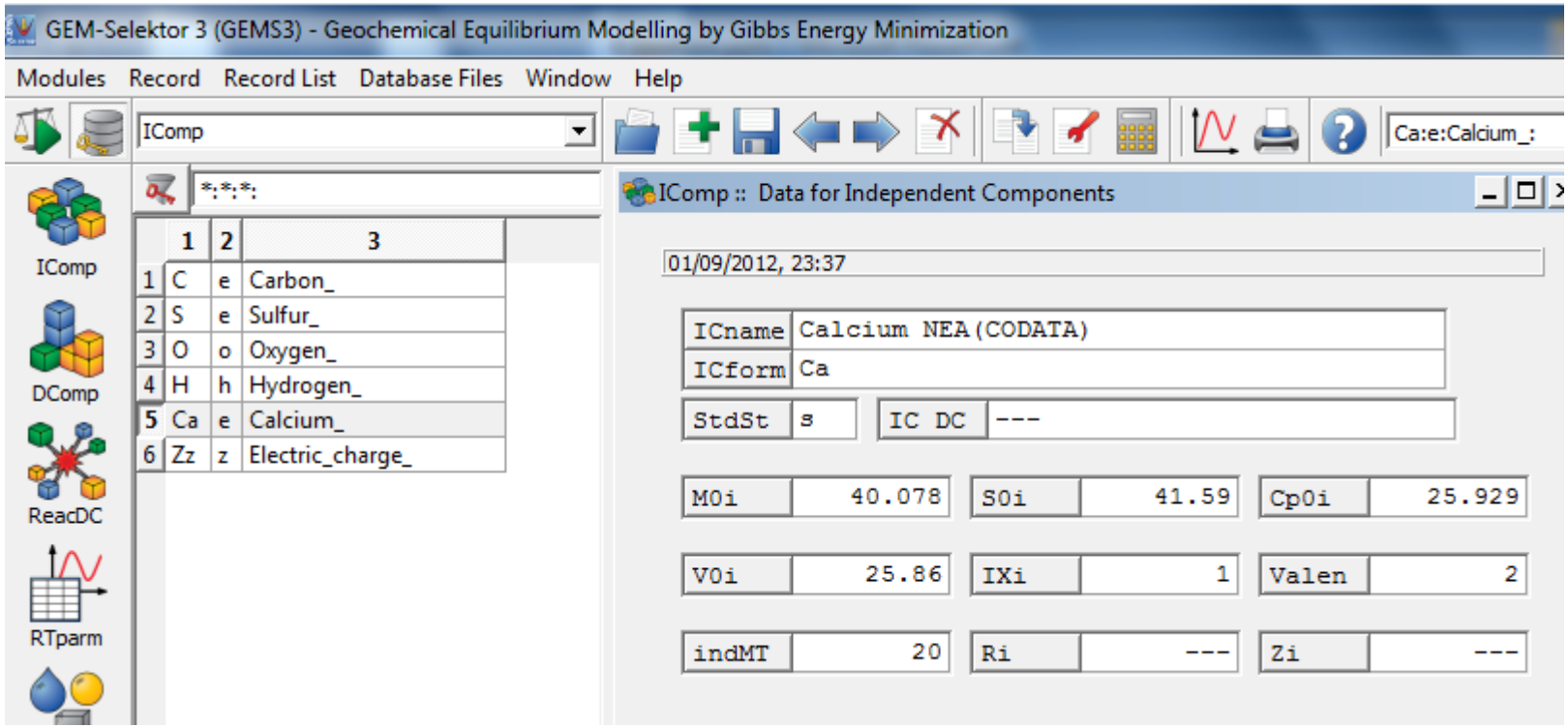
Solids phases single phases / solid solutions

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



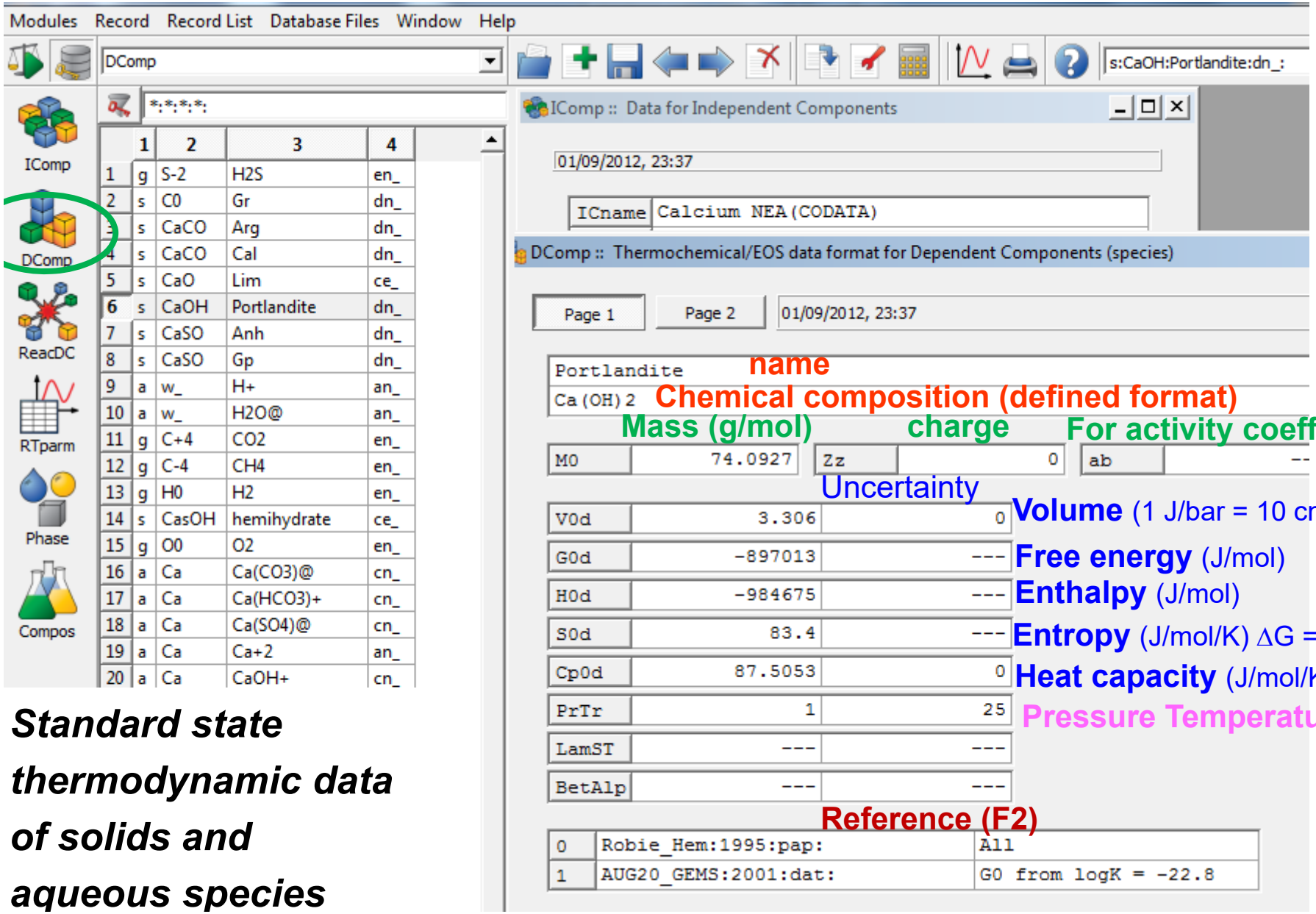
	1	2	3	4
1	g	S-2	H2S	en_
2	s	C0	Gr	dn_
3	s	CaCO	Arg	dn_
4	s	CaCO	Cal	dn_
5	s	CaO	Lim	ce_
6	s	CaOH	Portlandite	dn_
7	s	CaSO	Anh	dn_
8	s	CaSO	Gp	dn_
9	a	w_	H+	an_
10	a	w_	H2O@	an_
11	g	C+4	CO2	en_
12	g	C-4	CH4	en_
13	g	H0	H2	en_
14	s	CasOH	hemihydrate	ce_
15	g	O0	O2	en_
16	a	Ca	Ca(CO3)@	cn_
17	a	Ca	Ca(HCO3)+	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_

1) GEMS: independent components



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

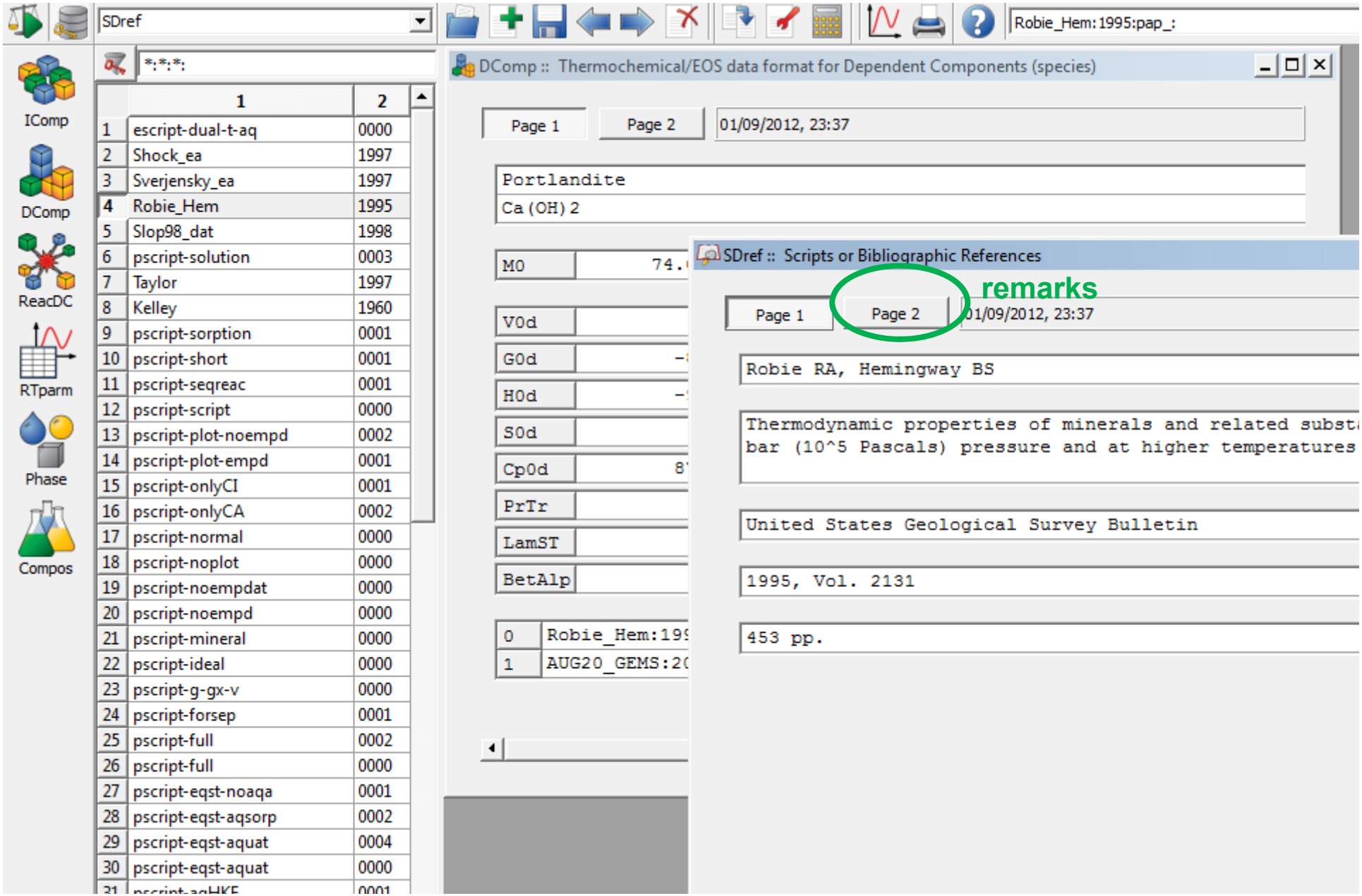
2) GEMS: dependent components (DComp)



	1	2	3	4
1	g	S-2	H2S	en_
2	s	C0	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_
11	g	C+4	CO2	en_
12	g	C-4	CH4	en_
13	g	H0	H2	en_
14	s	CasOH	hemihydrate	ce_
15	g	O0	O2	en_
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_

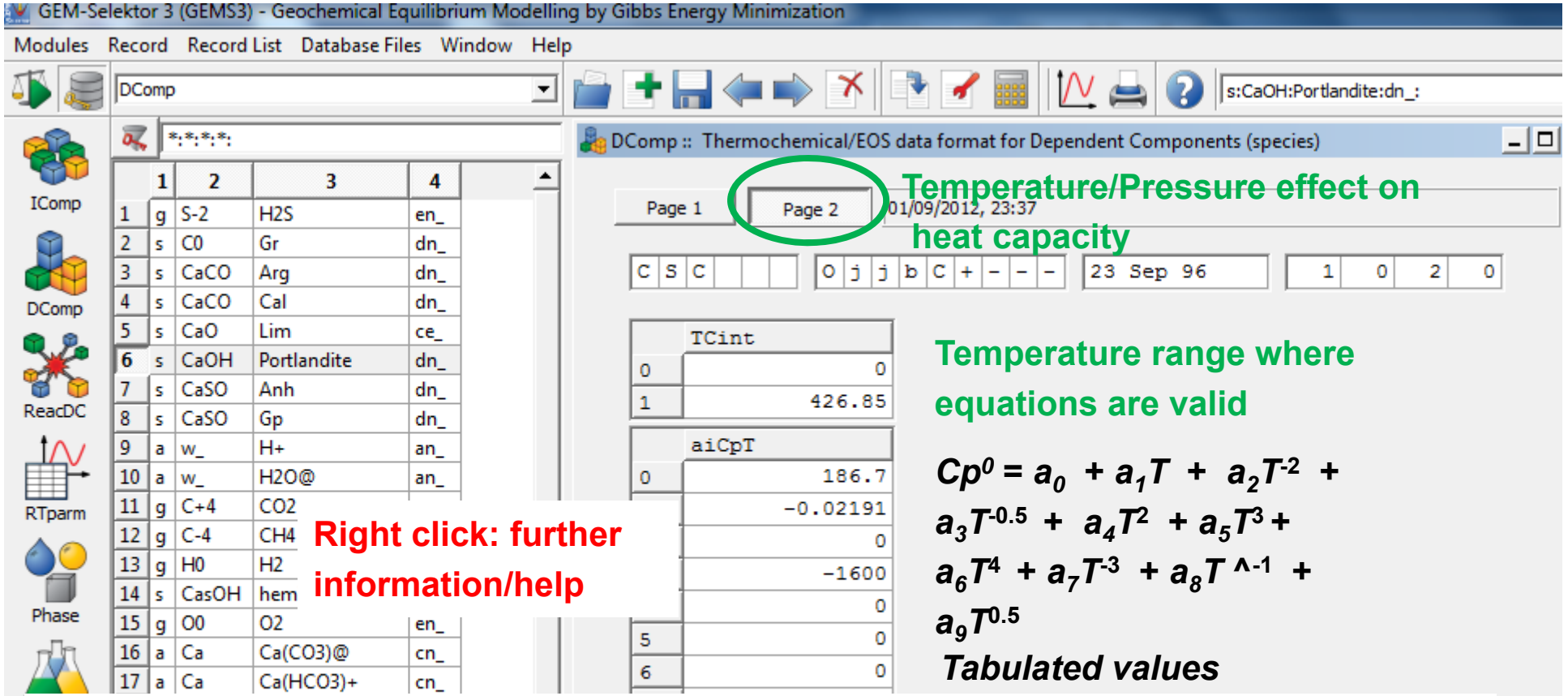
Standard state thermodynamic data of solids and aqueous species

GEMS: dependent components (DComp)



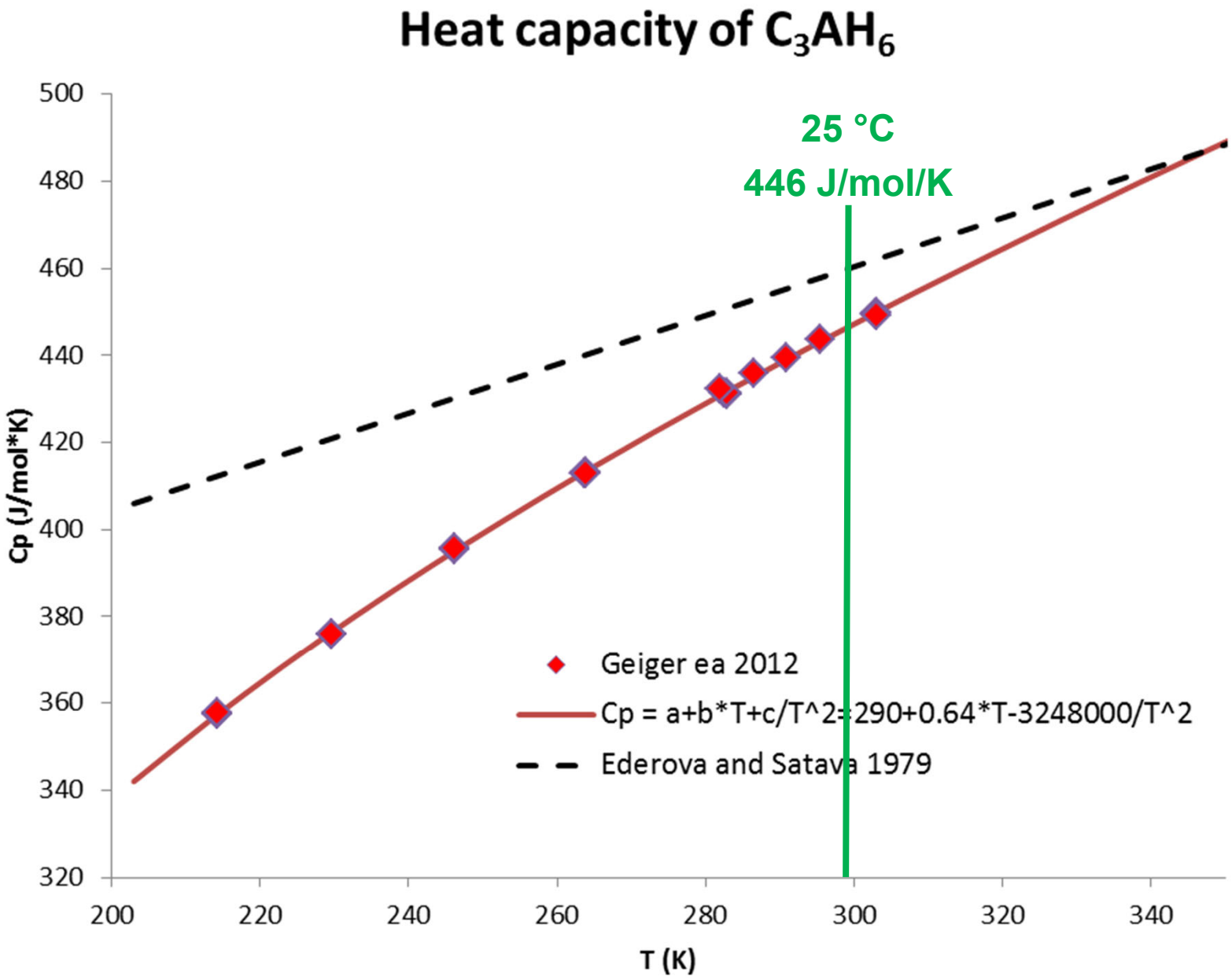
	1	2
1	escript-dual-t-aq	0000
2	Shock_ea	1997
3	Sverjensky_ea	1997
4	Robie_Hem	1995
5	Slop98_dat	1998
6	pscript-solution	0003
7	Taylor	1997
8	Kelley	1960
9	pscript-sorption	0001
10	pscript-short	0001
11	pscript-seqreac	0001
12	pscript-script	0000
13	pscript-plot-noempd	0002
14	pscript-plot-empd	0001
15	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-aqHKF	0001

GEMS: dependent components (DComp)

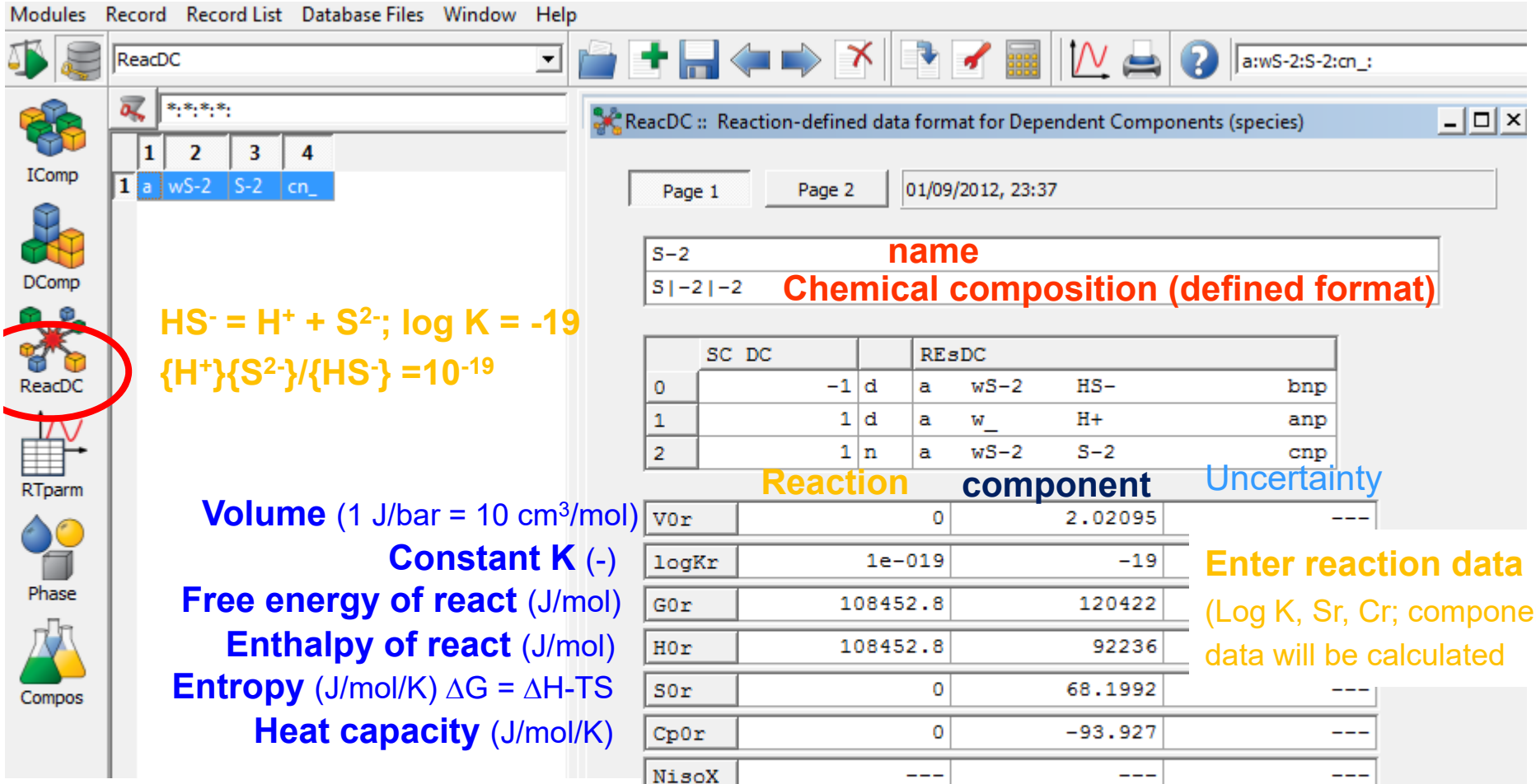


	log K_{S0} *	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/mol]	Ref
(Al-)ettringite[a,b,c]	-44.9	1939	0.789			707	[3, 4]
CH (portlandite)	-5.2	187	-0.022		-1600	33	[6, 7]
$SiO_{2,am}$	1.476	47	0.034	$-1.13 \cdot 10^6$		29	[3, 4]

GEMS: dependent components (DComp)



3) GEMS: reactions (ReacDC)



Volume (1 J/bar = 10 cm^3/mol)

Constant K (-)

Free energy of react (J/mol)

Enthalpy of react (J/mol)

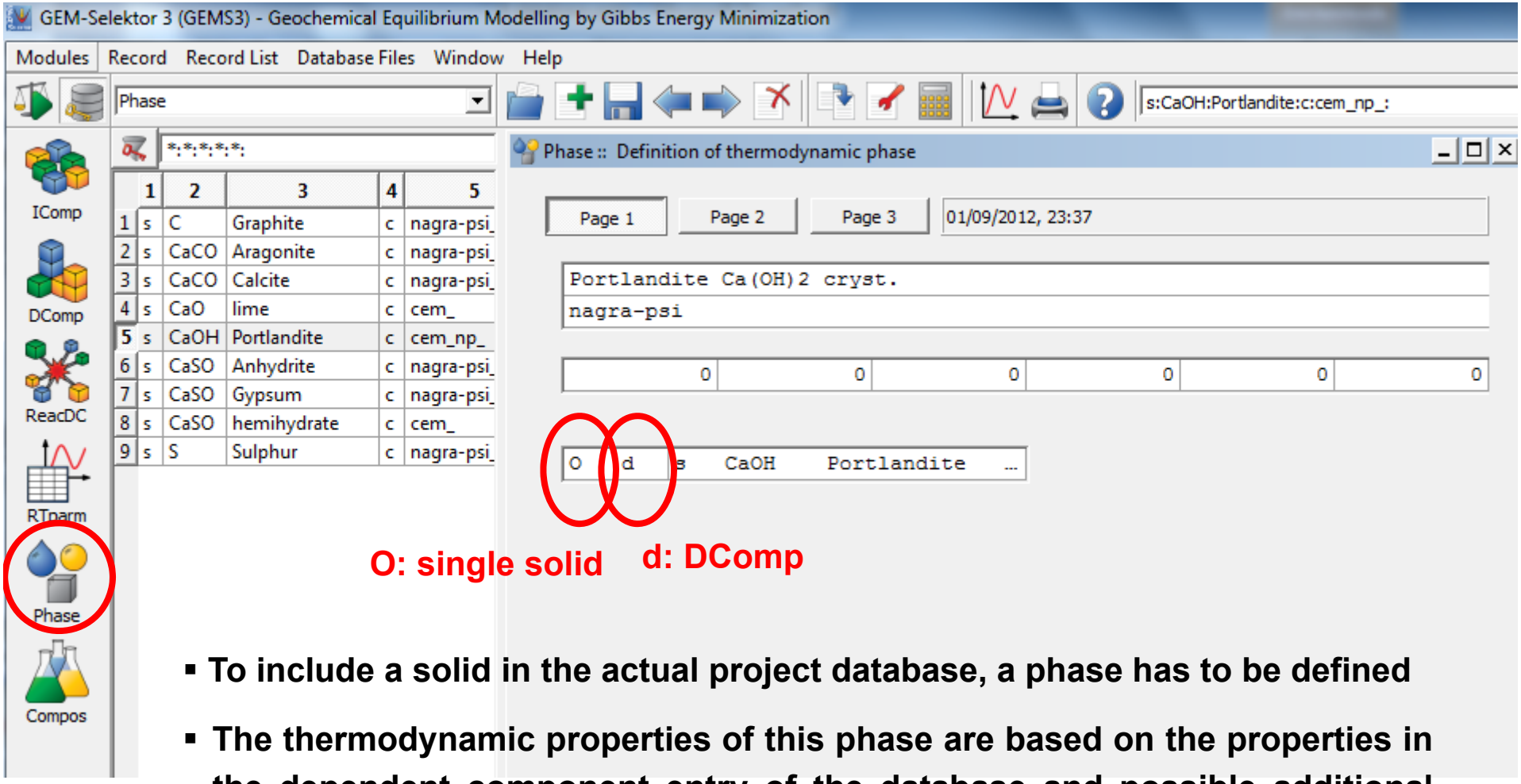
Entropy (J/mol/K) $\Delta G = \Delta H - TS$

Heat capacity (J/mol/K)

Standard state thermodynamic data of solids and aqueous species:

Reaction data are known

5.) Thermodynamic Phases

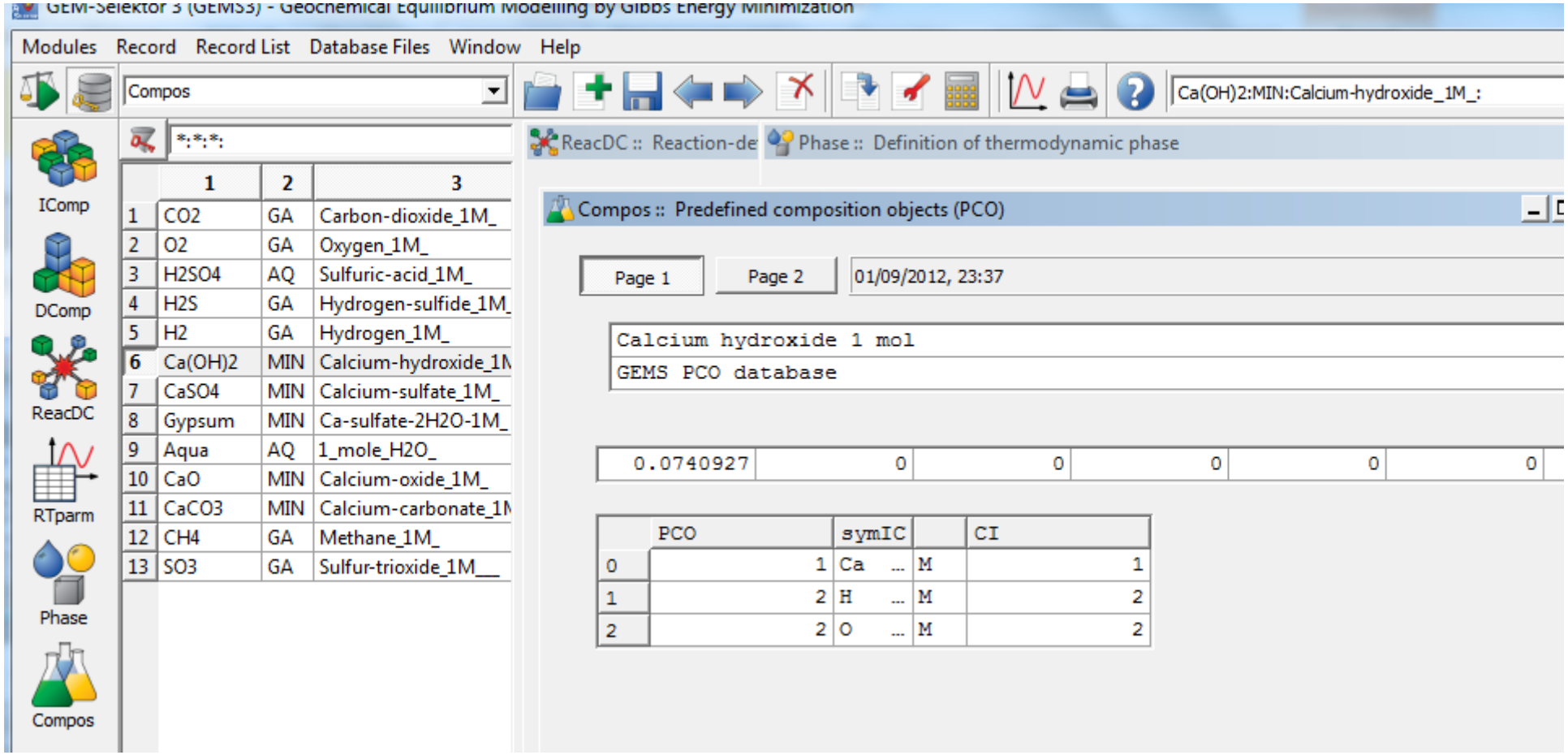


	1	2	3	4	5
1	s	C	Graphite	c	nagra-psi_
2	s	CaCO	Aragonite	c	nagra-psi_
3	s	CaCO	Calcite	c	nagra-psi_
4	s	CaO	lime	c	cem_
5	s	CaOH	Portlandite	c	cem_np_
6	s	CaSO	Anhydrite	c	nagra-psi_
7	s	CaSO	Gypsum	c	nagra-psi_
8	s	CaSO	hemihydrate	c	cem_
9	s	S	Sulphur	c	nagra-psi_

0	0	0	0	0	0

- 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



	1	2	3
1	CO2	GA	Carbon-dioxide_1M_
2	O2	GA	Oxygen_1M_
3	H2SO4	AQ	Sulfuric-acid_1M_
4	H2S	GA	Hydrogen-sulfide_1M_
5	H2	GA	Hydrogen_1M_
6	Ca(OH)2	MIN	Calcium-hydroxide_1M
7	CaSO4	MIN	Calcium-sulfate_1M_
8	Gypsum	MIN	Ca-sulfate-2H2O-1M_
9	Aqua	AQ	1_mole_H2O_
10	CaO	MIN	Calcium-oxide_1M_
11	CaCO3	MIN	Calcium-carbonate_1M
12	CH4	GA	Methane_1M_
13	SO3	GA	Sulfur-trioxide_1M___

Contains chemical compositions of input

(e.g. PC, slag, Ca(OH)2, HCl, …)

Alternative way of input, no thermodynamic properties needed

Empa
Materials Science and Technology

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

- $Ca(OH)_2$
  - $K_{s0,H+} = \frac{\{H^+\}^2\{Ca(OH)_2\}}{\{Ca^{2+}\}\{H_2O^0\}} = \frac{\{H^+\}^2\ 1}{\{Ca^{2+}\}\{H_2O^0\}} = 10^{-22.8}$
  - $K_{s0,OH-} = \frac{\{Ca(OH)_2\}}{\{Ca^{2+}\}\{OH^-\}^2} = \frac{1}{\{Ca^{2+}\}\{OH^-\}^2} = 10^{5.2}$

$\Delta = 1 / K_w^2$

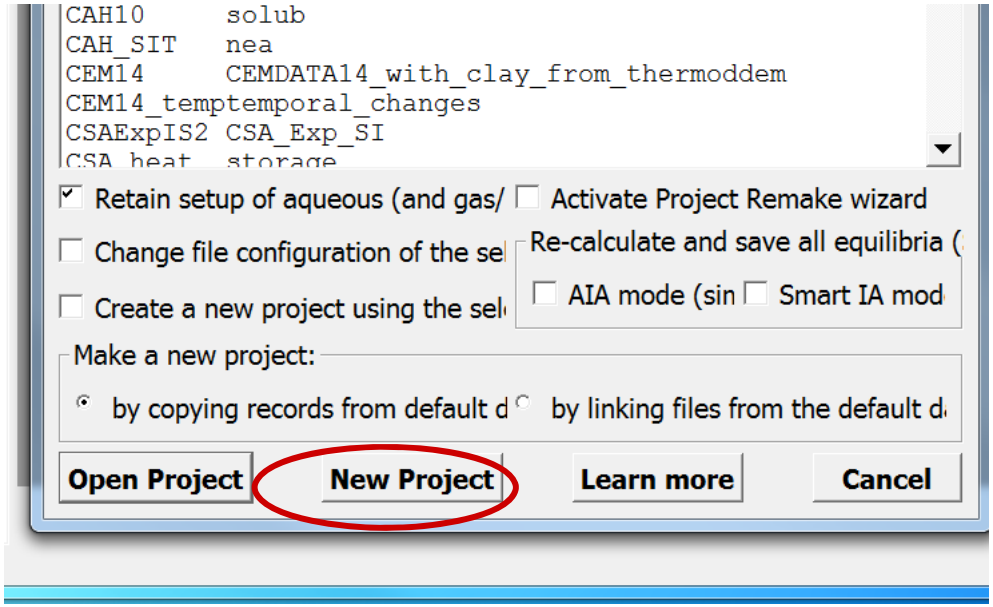
$\Delta = 1 / (10^{-14})^2$

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

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

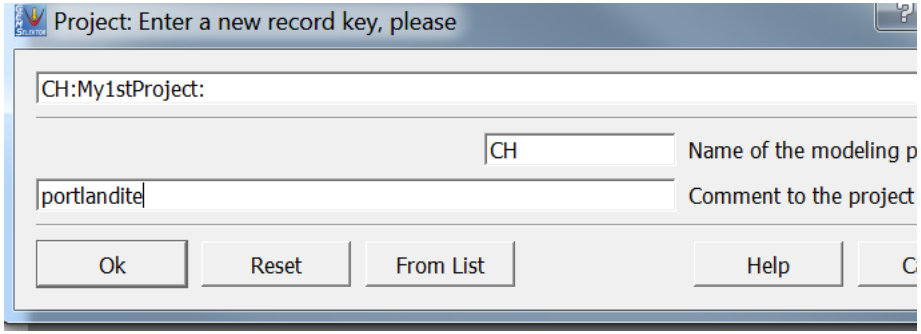
Portlandite						
Ca(OH)2						
M0	74.0927	Zz	0	ab	---	---
V0d	3.306	0				
G0d	ΔG_f° -897013	---				
H0d	ΔH_f° -984675	---				
S0d	83.4	---				
Cp0d	87.5053	0				
PrTr	1	25				
LamST	---	---				
BetAlp	---	---				

0	Robie_Hem:1995:pap:	All
1	AUG20_GEMS:2001:dat:	G0 from logK = -22.8

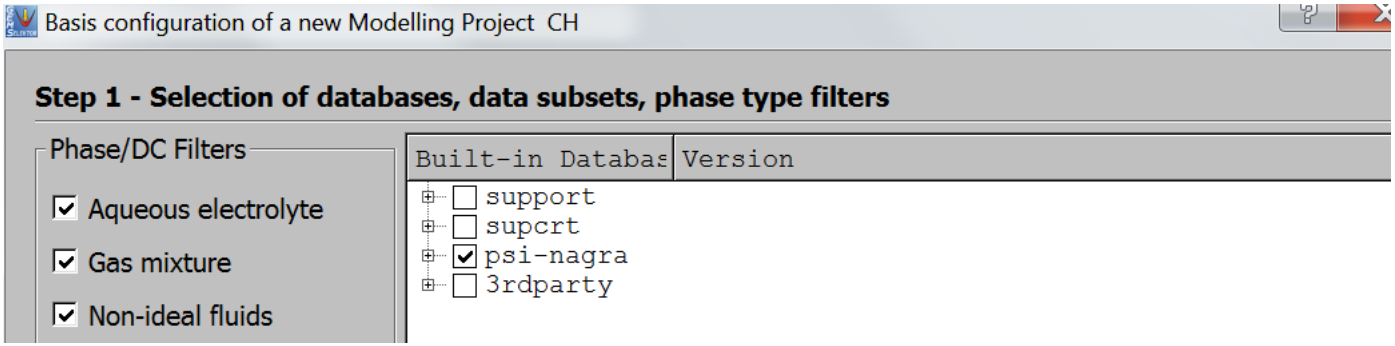


1. Select New project

2. Name it



3. Sufficient to select psi-nagra database only

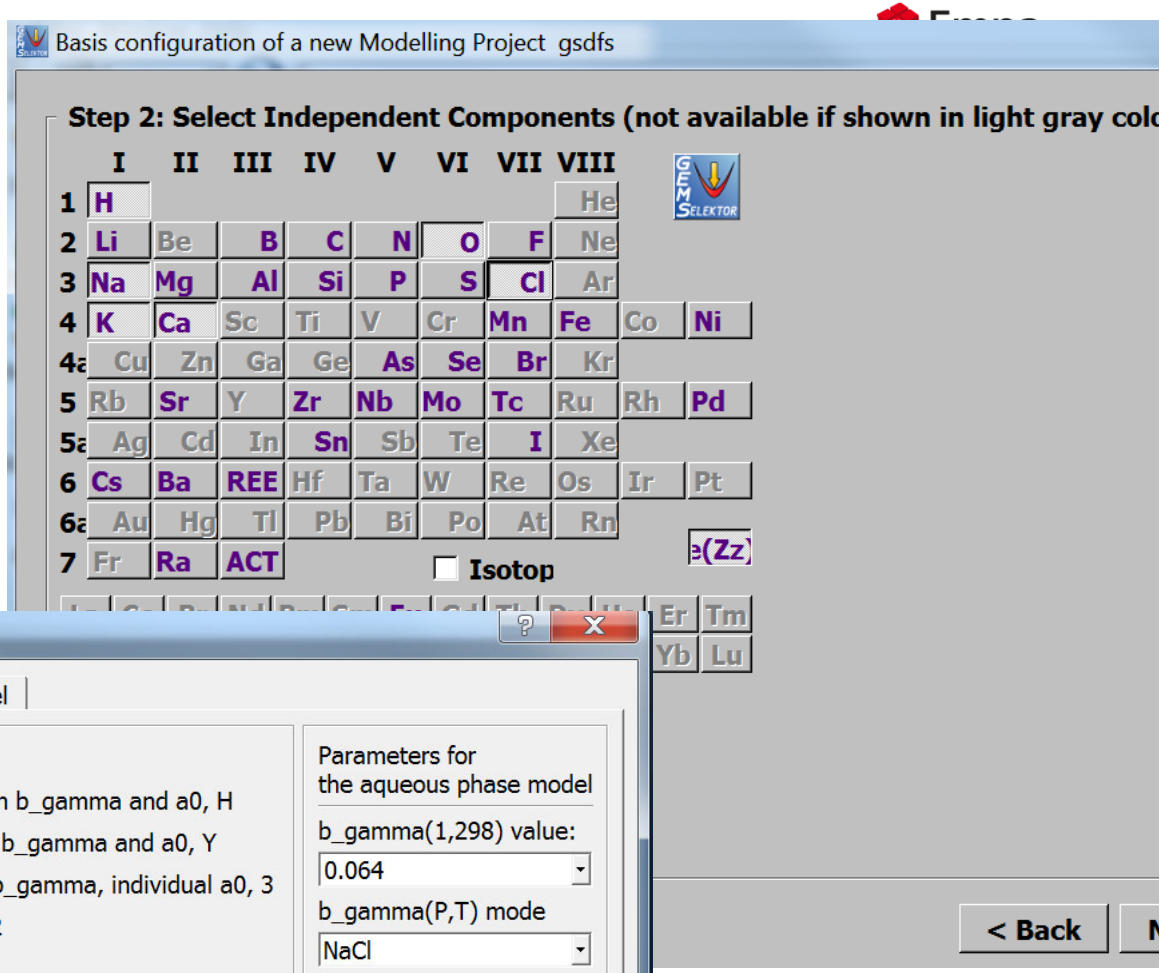


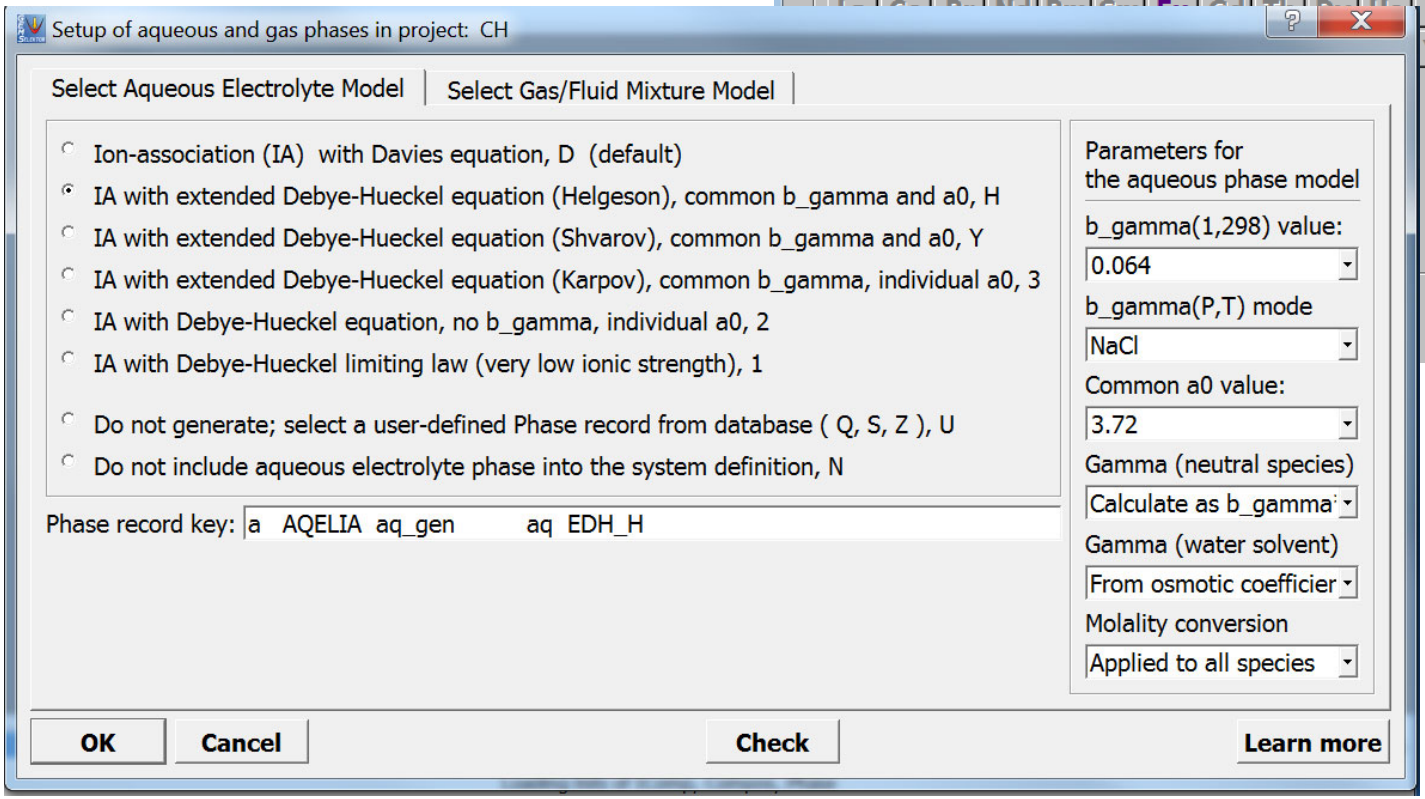
Portlandite

4. Select elements

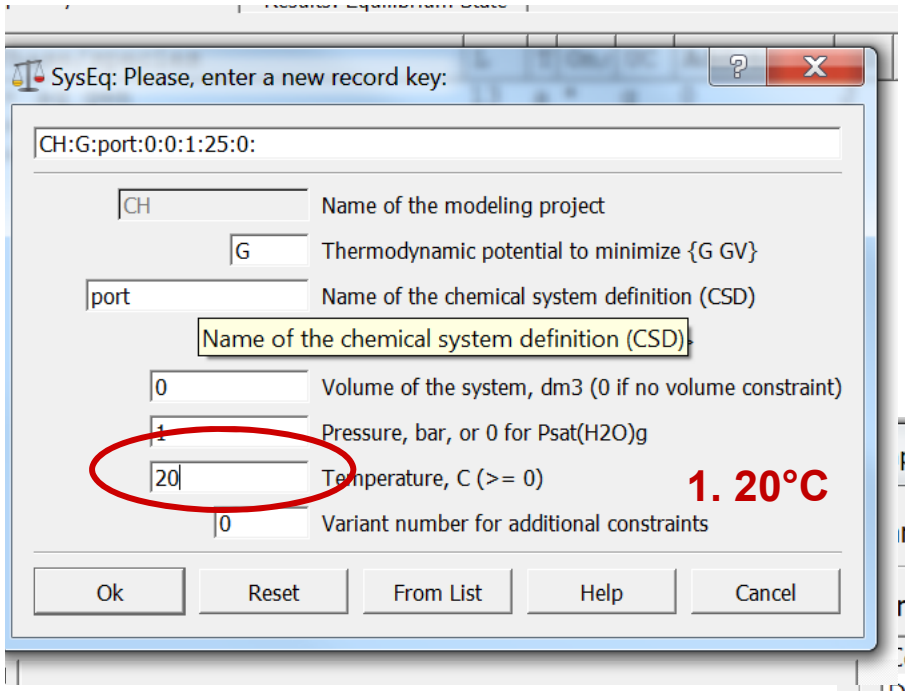
Ca, Na, Cl

5. Aqueous electrolyte model: Helgeson for NaCl

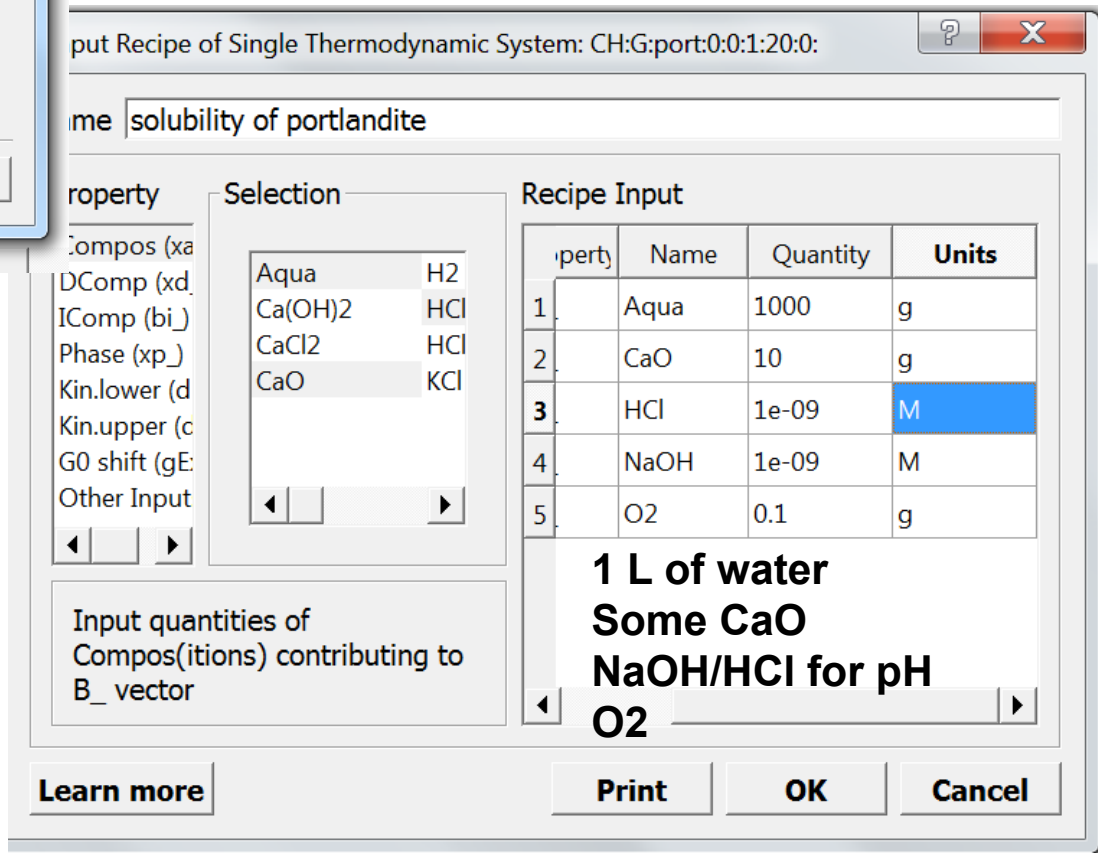




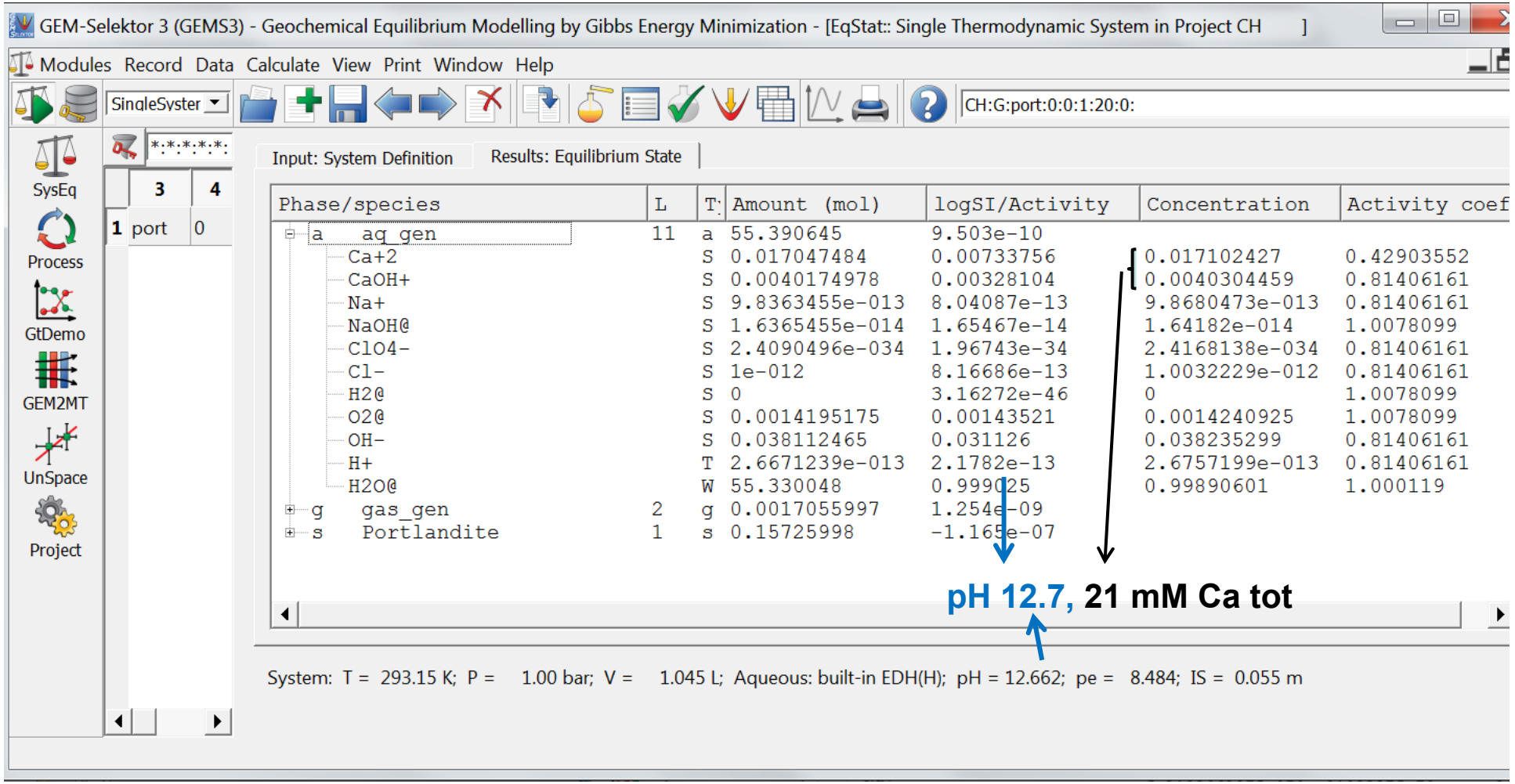
Portlandite



2. names

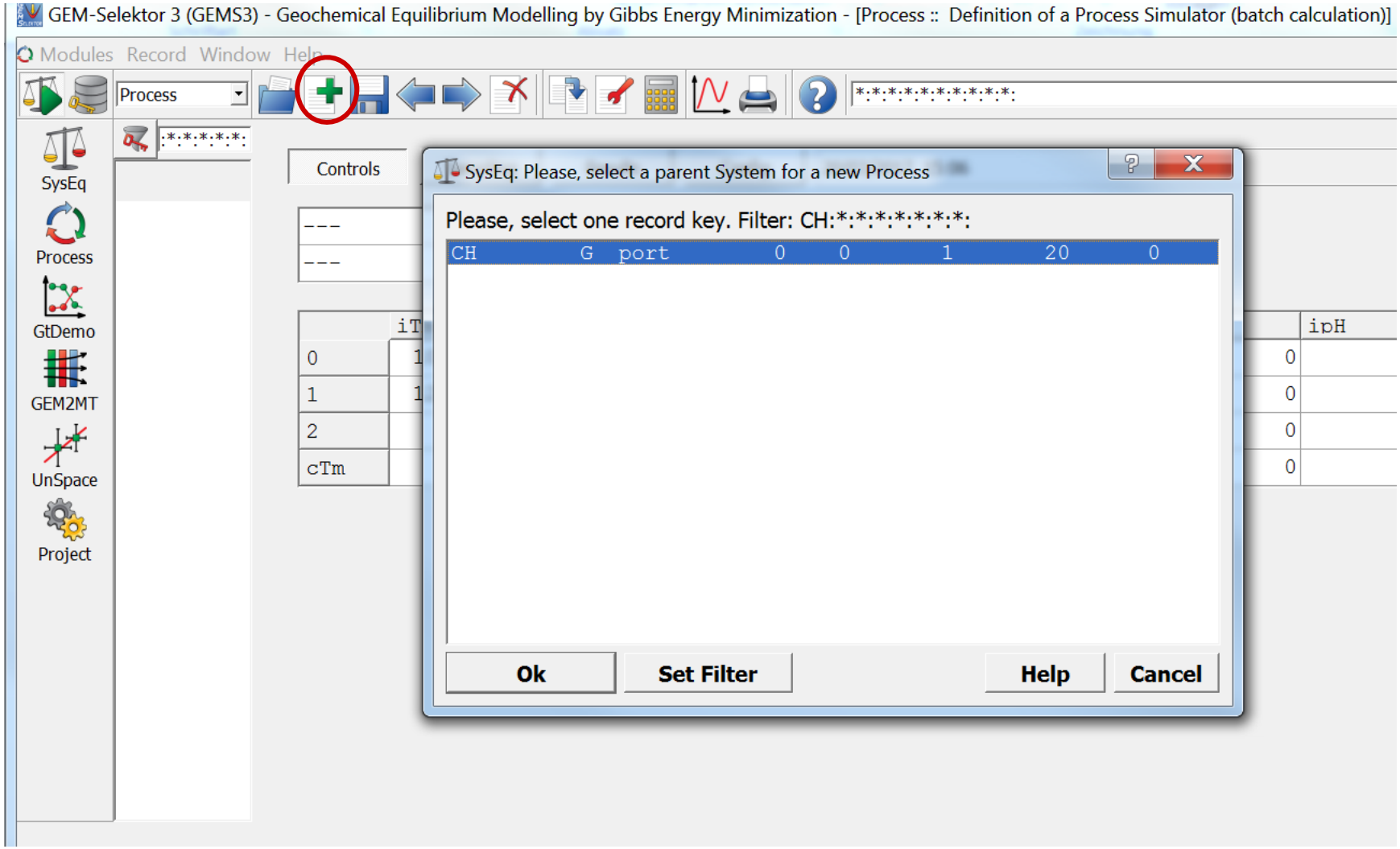


Portlandite solubility



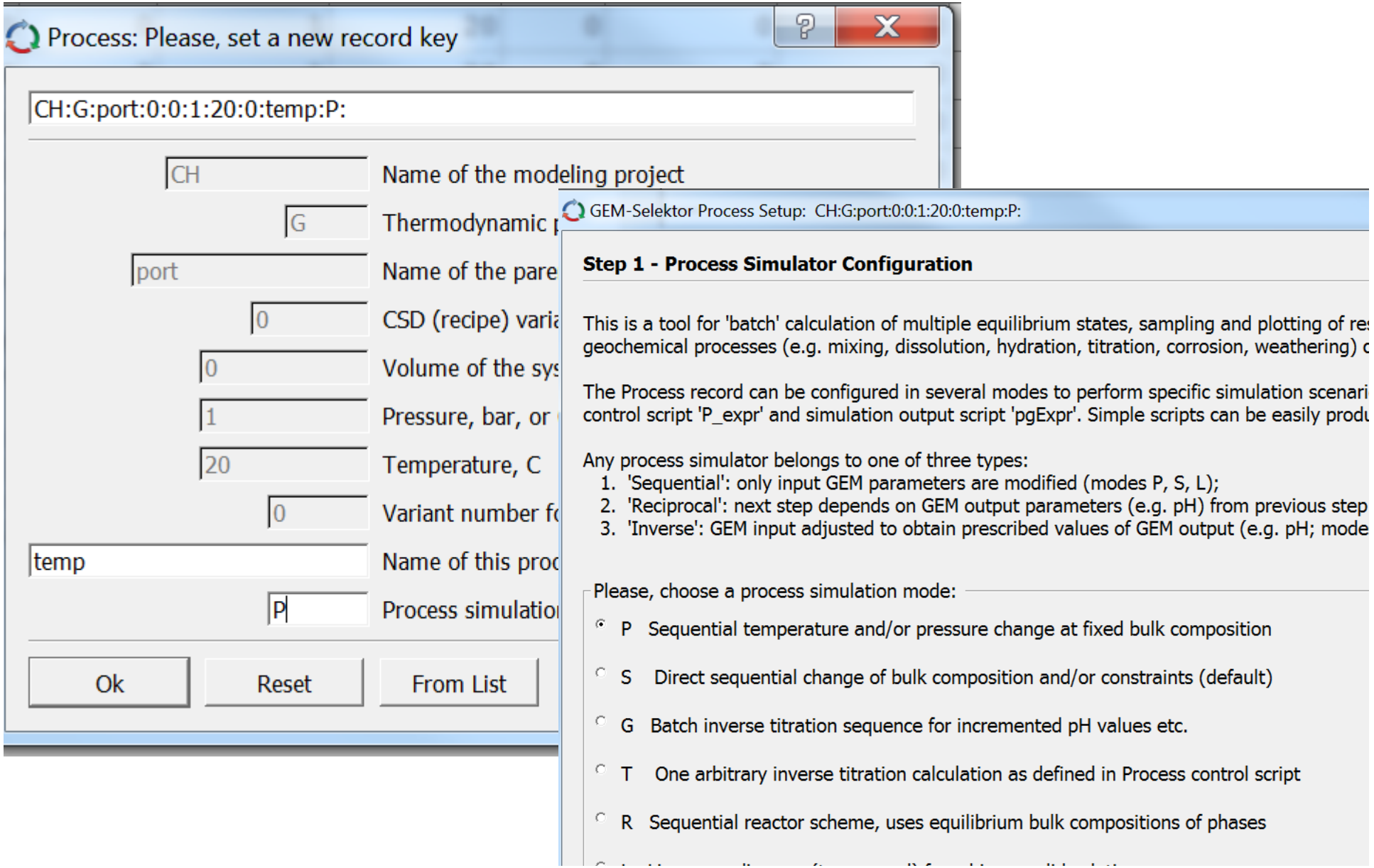
Portlandite: effect of temperature

1. Create new process



Portlandite

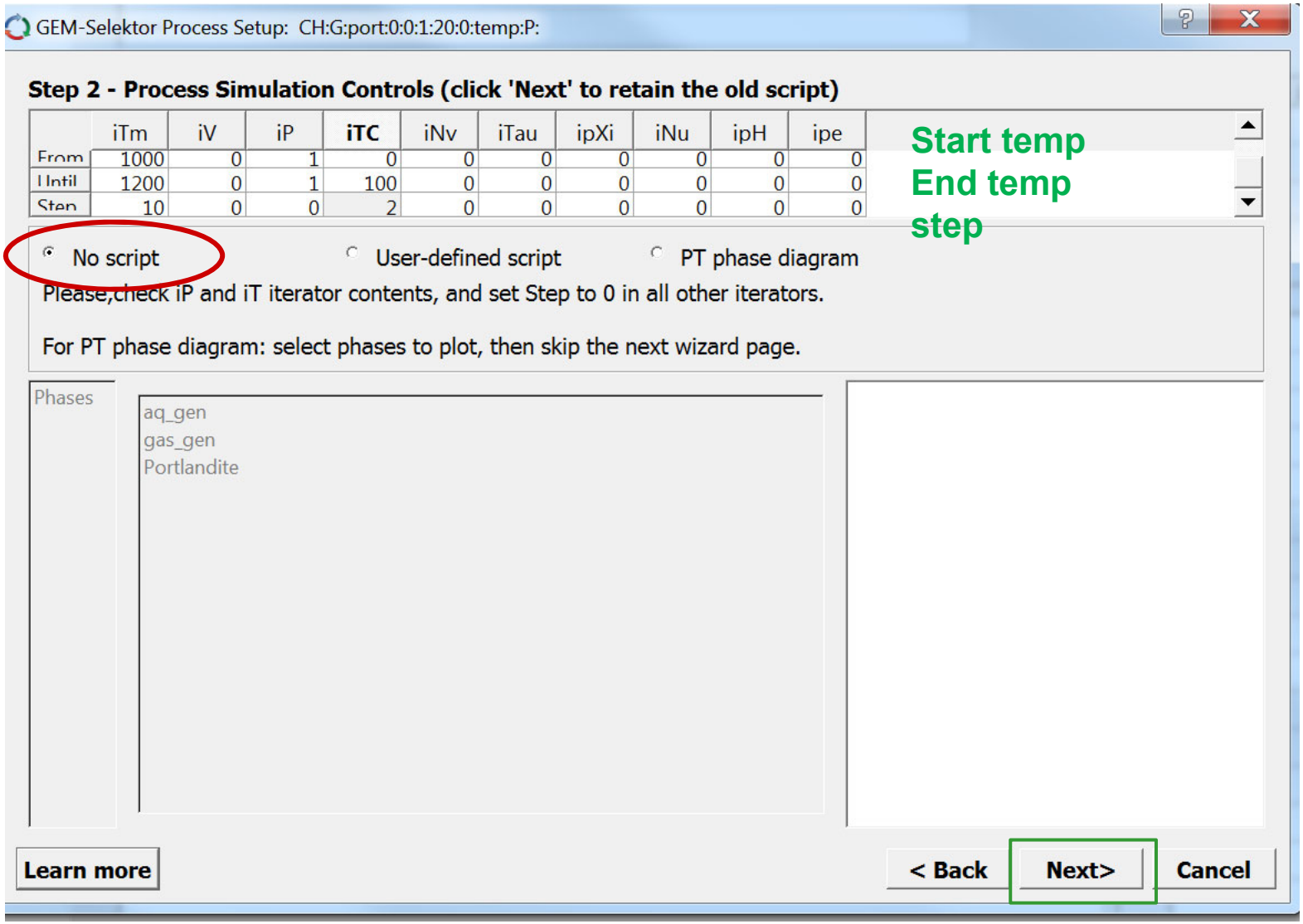
P: sequential change of temperature



Portlandite

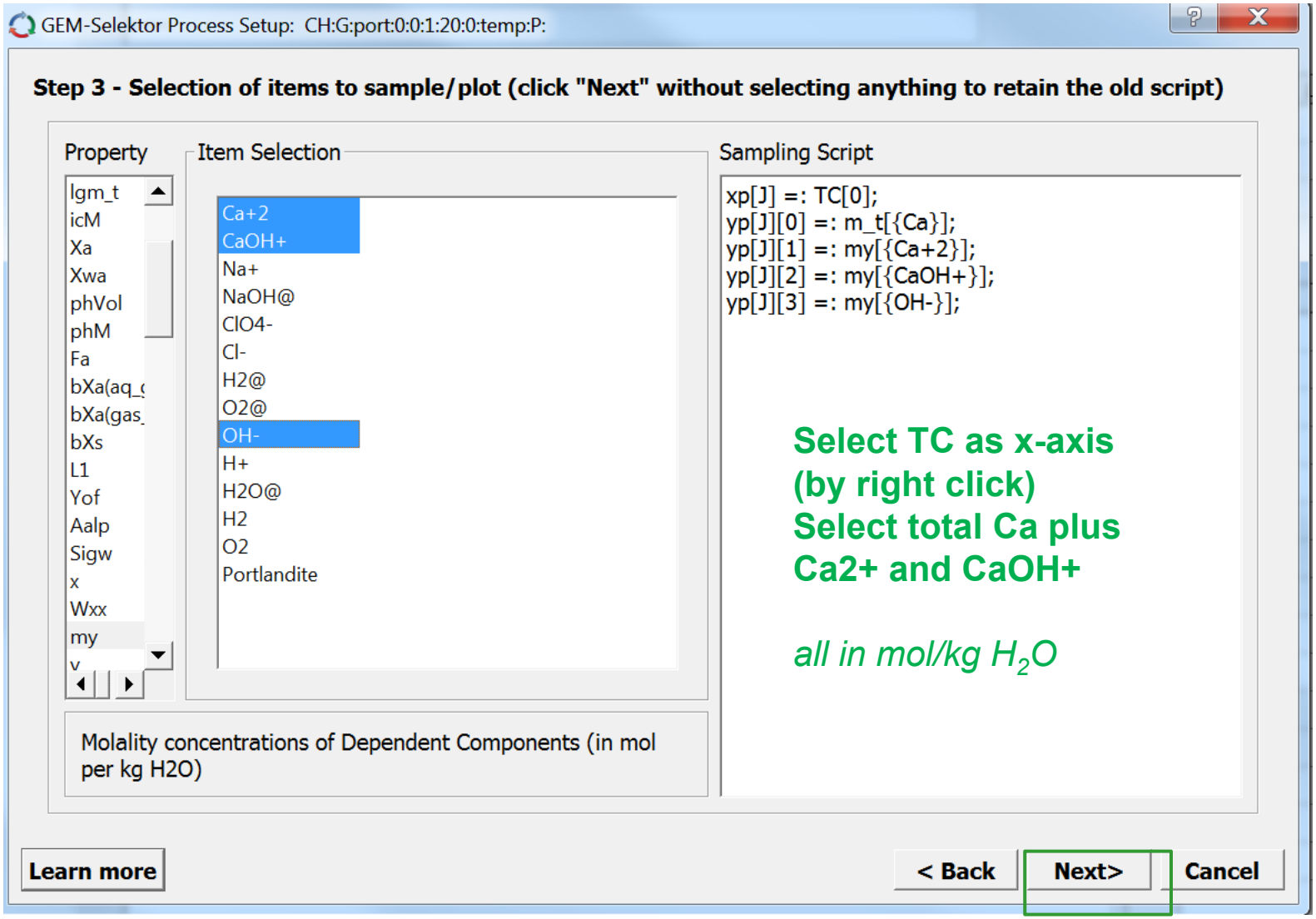
P: sequential change of temperature

Here: no additional input script needed



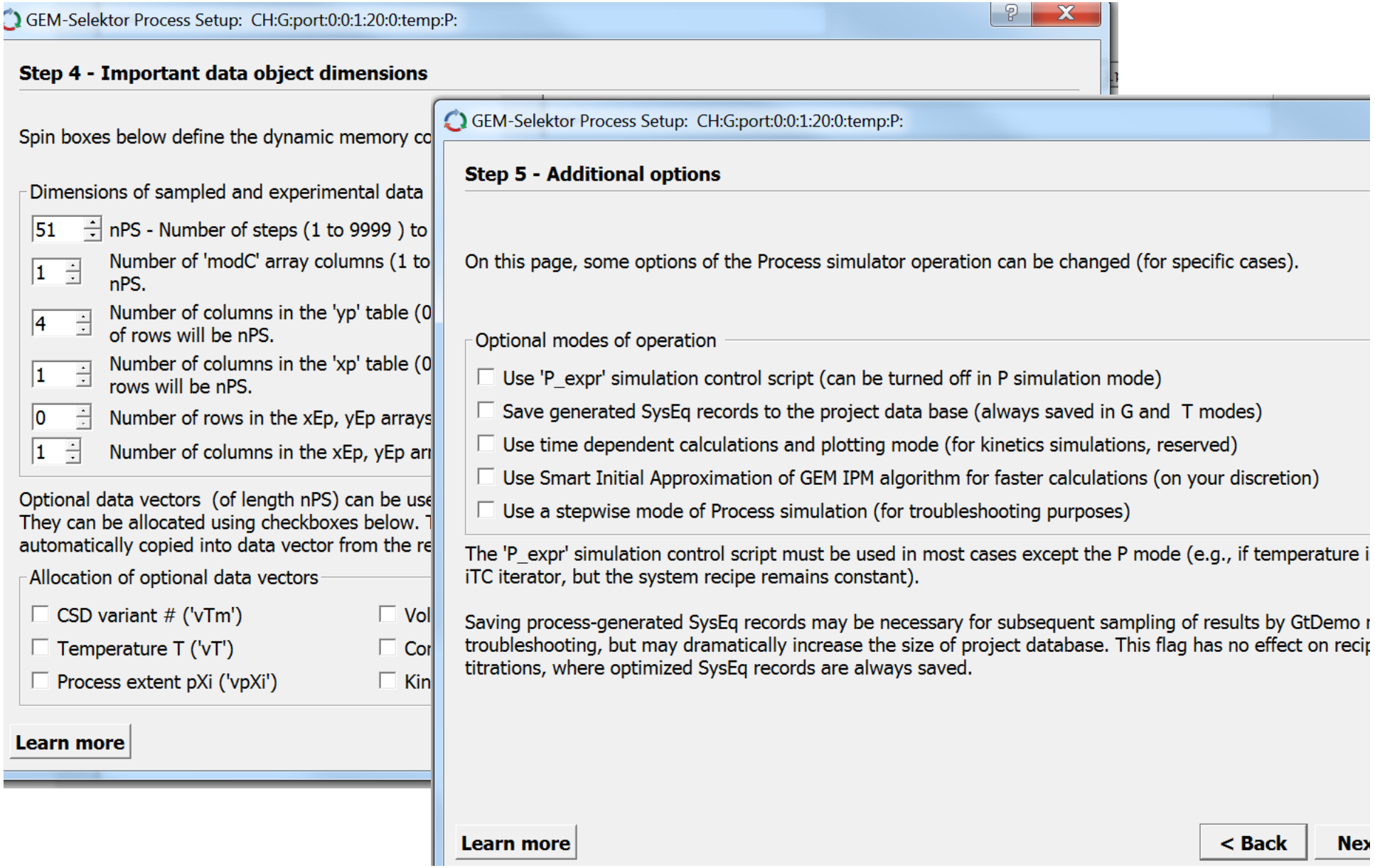
Portlandite

P: sequential change of temperature



Portlandite

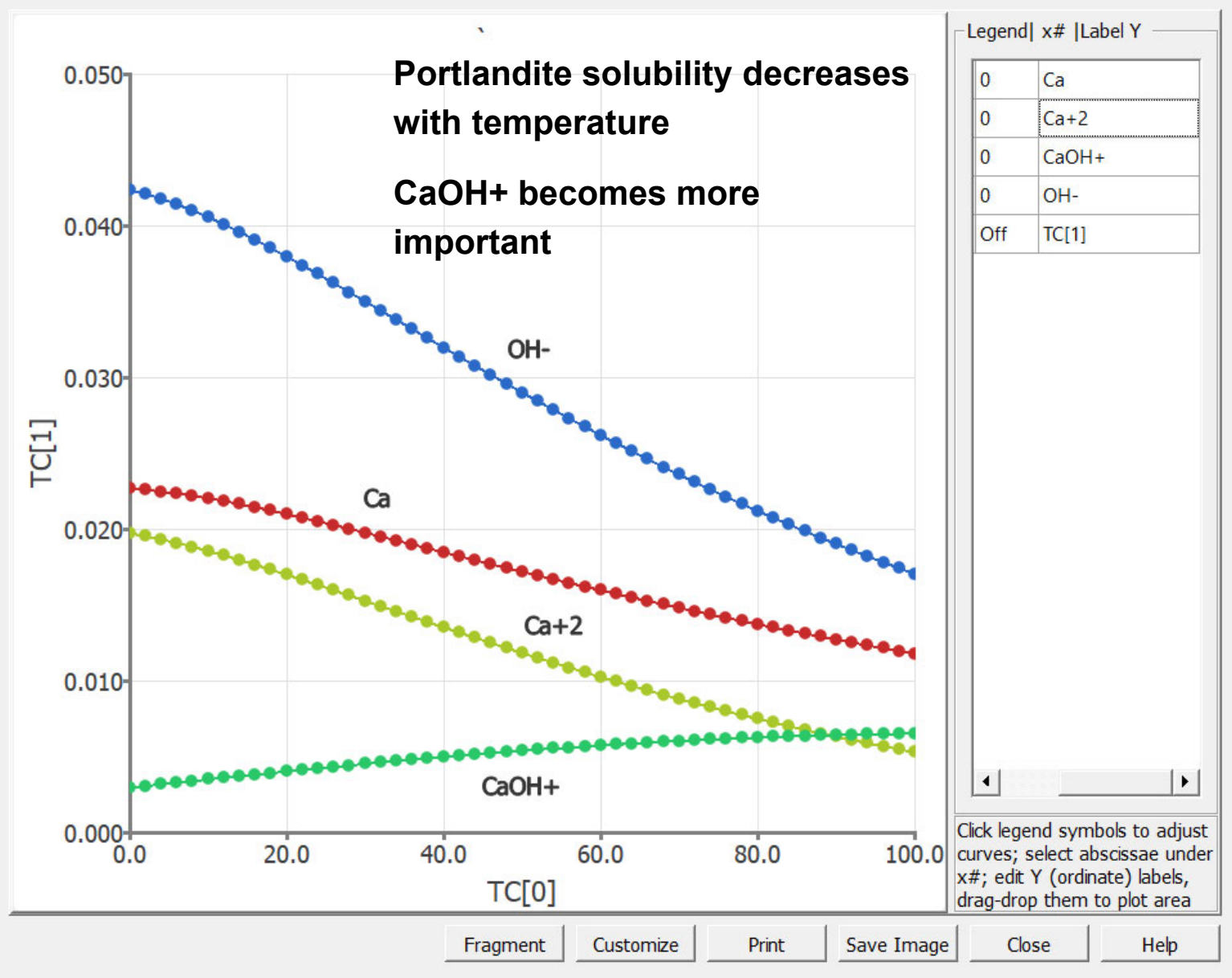
P: sequential change of temperature



Portlandite

Empa
Materials Science and Technology

P: sequential change of temperature



Portlandite

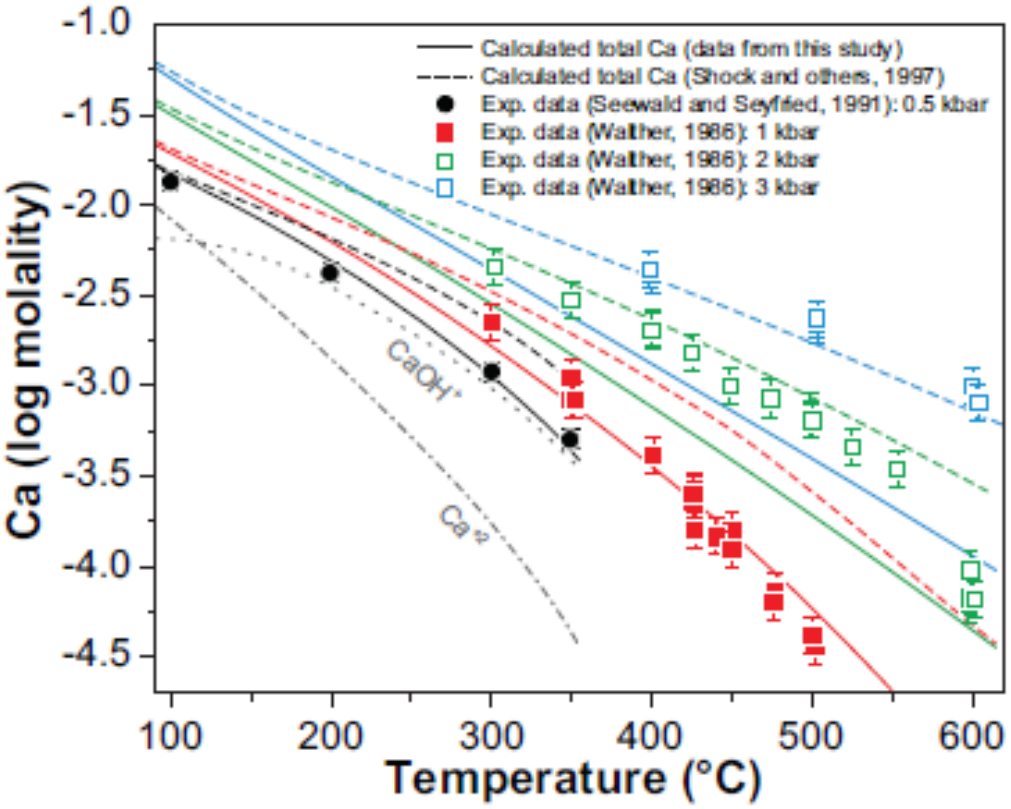


Fig. 16. Comparison between calculated and experimentally determined portlandite solubility in water (Walther, 1986; Seewald and Seyfried, 1991), expressed as total dissolved Ca as function of temperature at pressures of 0.5, 1.0, 2.0 and 3.0 kbar. Solid symbols represent experimental data points which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

Portlandite solubility decreases with temperature

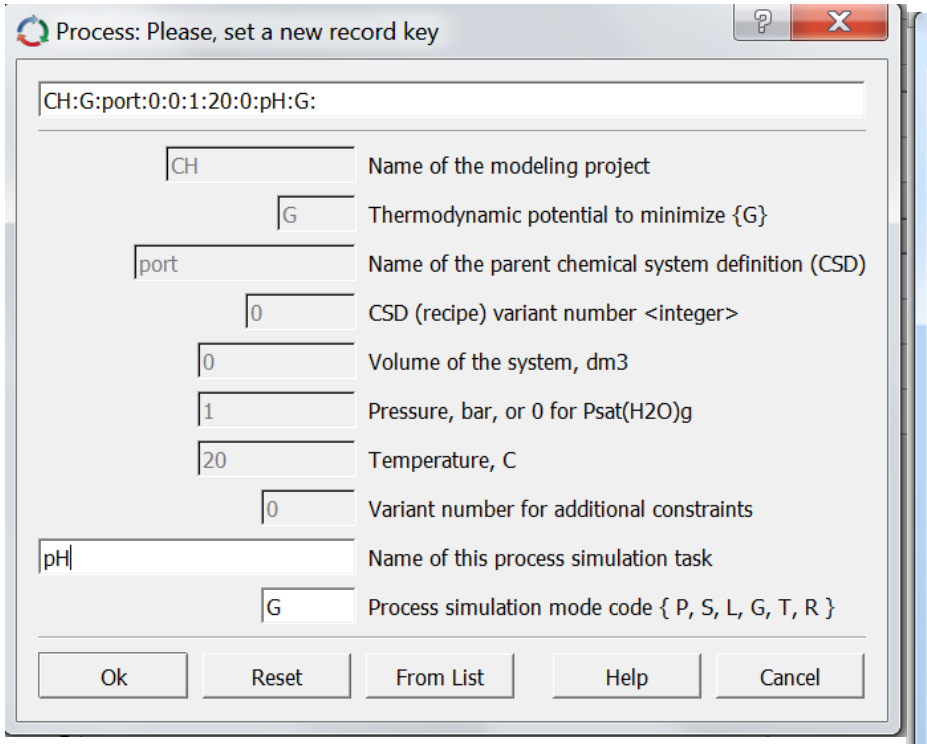
Agrees well with experimental trends

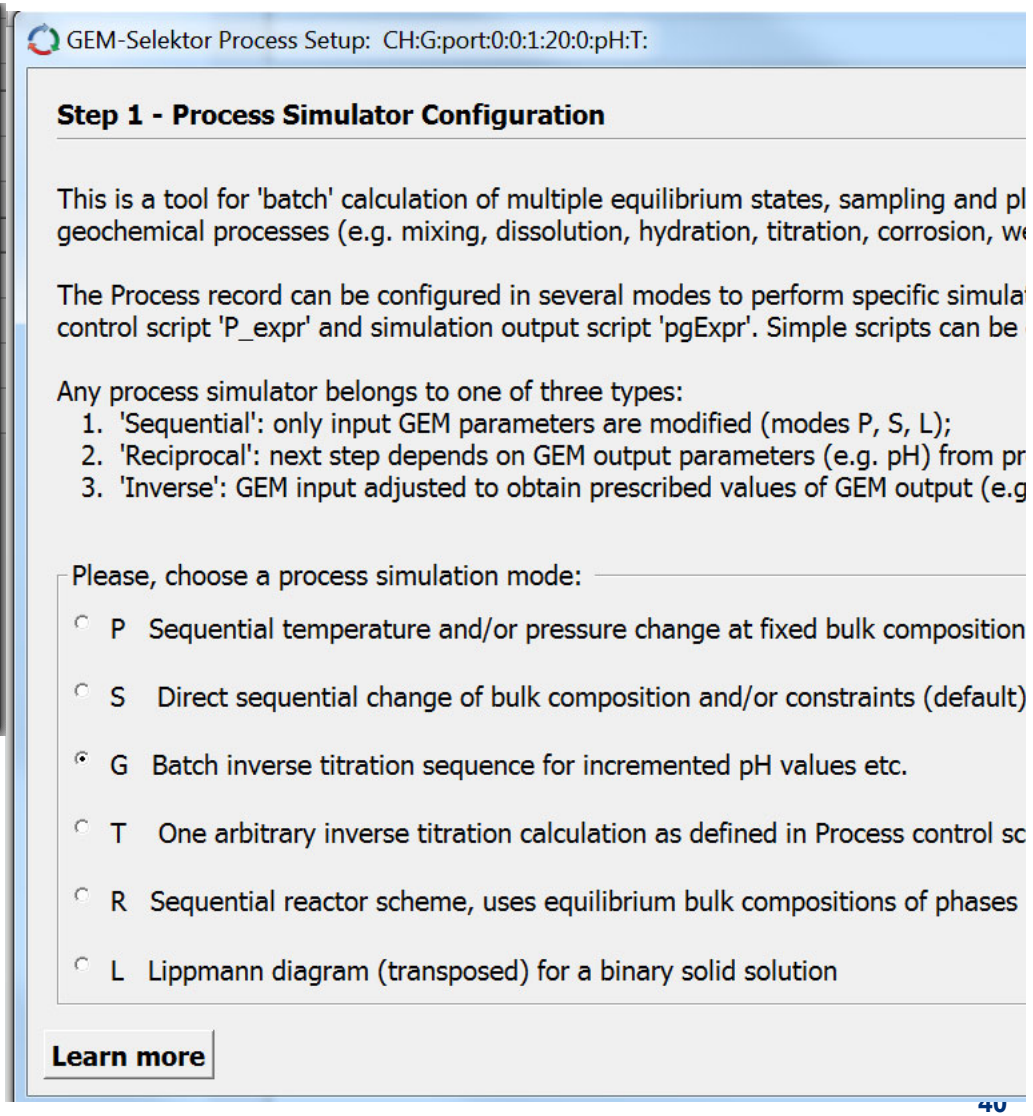
High pressures (kbar!) increases solubility
=> see group work

Miron ea (2017) *American Journal of Science*, 317(7), 755-806

Portlandite: effect of pH

1. Create new process

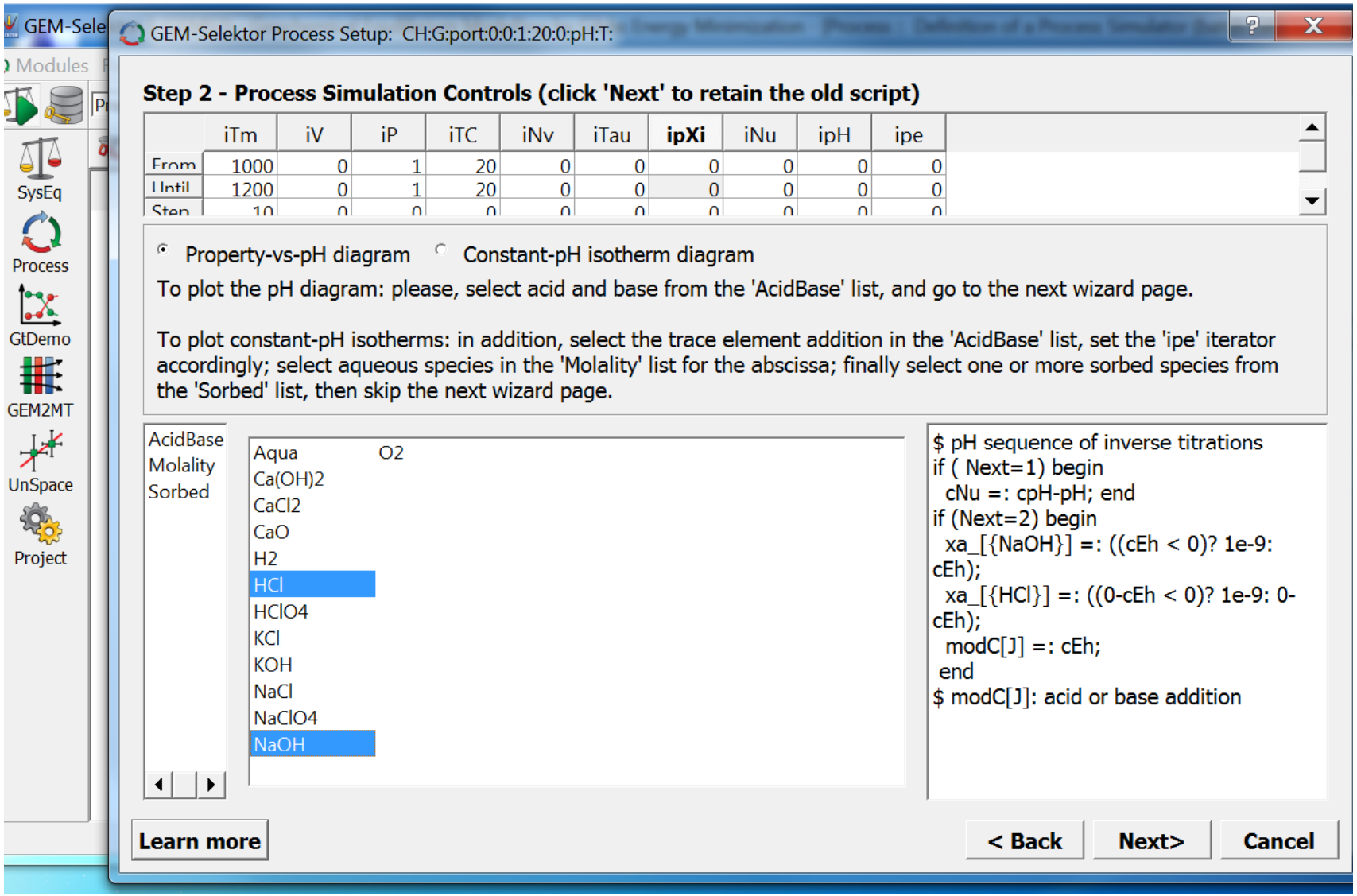




Portlandite

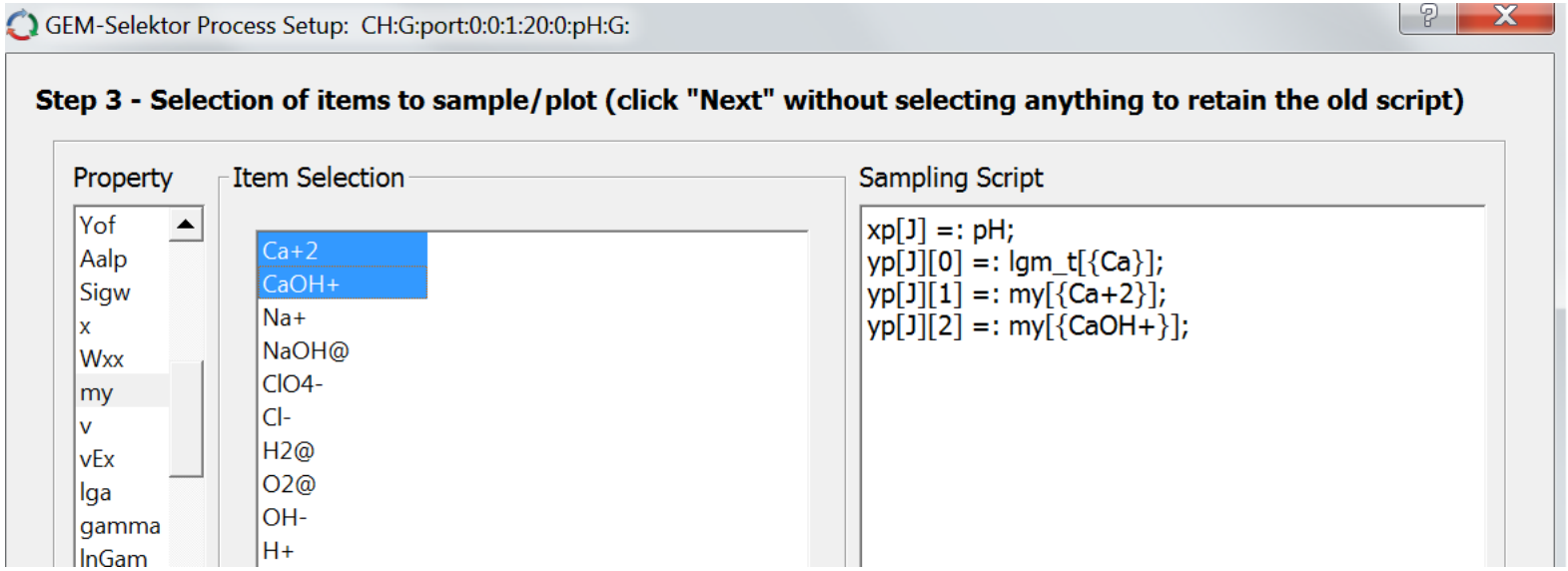
G: Batch inverse titration (Variation of pH)

Select HCl and NaOH



Portlandite

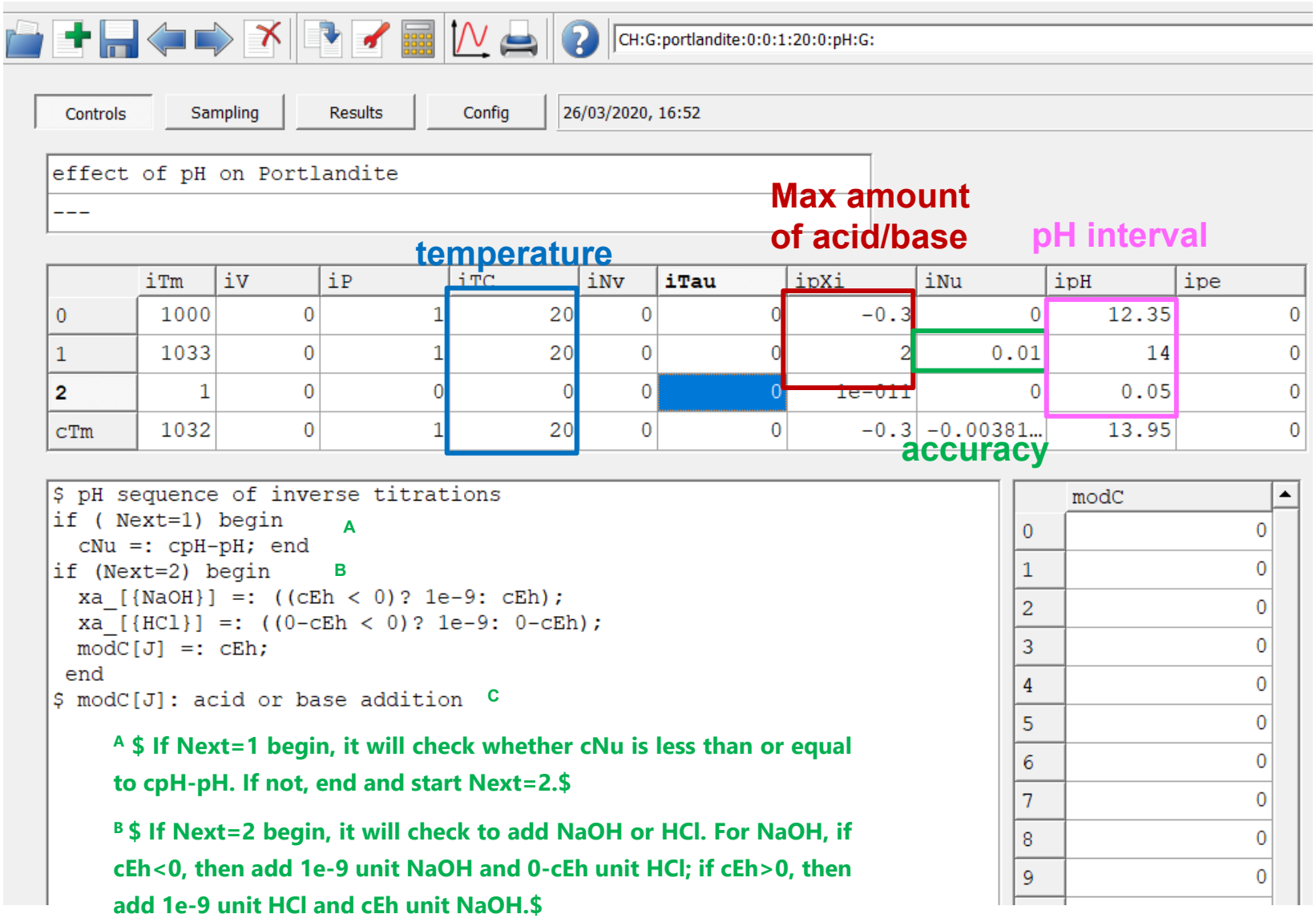
Output
pH as x-axis
log(Ca tot), Ca2+ and CaOH+



my[{Ca+2}] = Ca^{2+} concentration (in mol/kg H_2O)
m_t[{Ca}] = total concentration (in mol/kg H_2O) = Ca^{2+} + $CaOH^{+}$ + …

lgm_t[{Ca}] = log(10) of total concentration (in mol/kg H_2O) = Ca^{2+} + $CaOH^{+}$ + …)
lg(my[{Ca+2}]) = log(10) of Ca^{2+} concentration (in mol/kg H_2O)
(lg(…) has to be adapted afterwards)

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



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

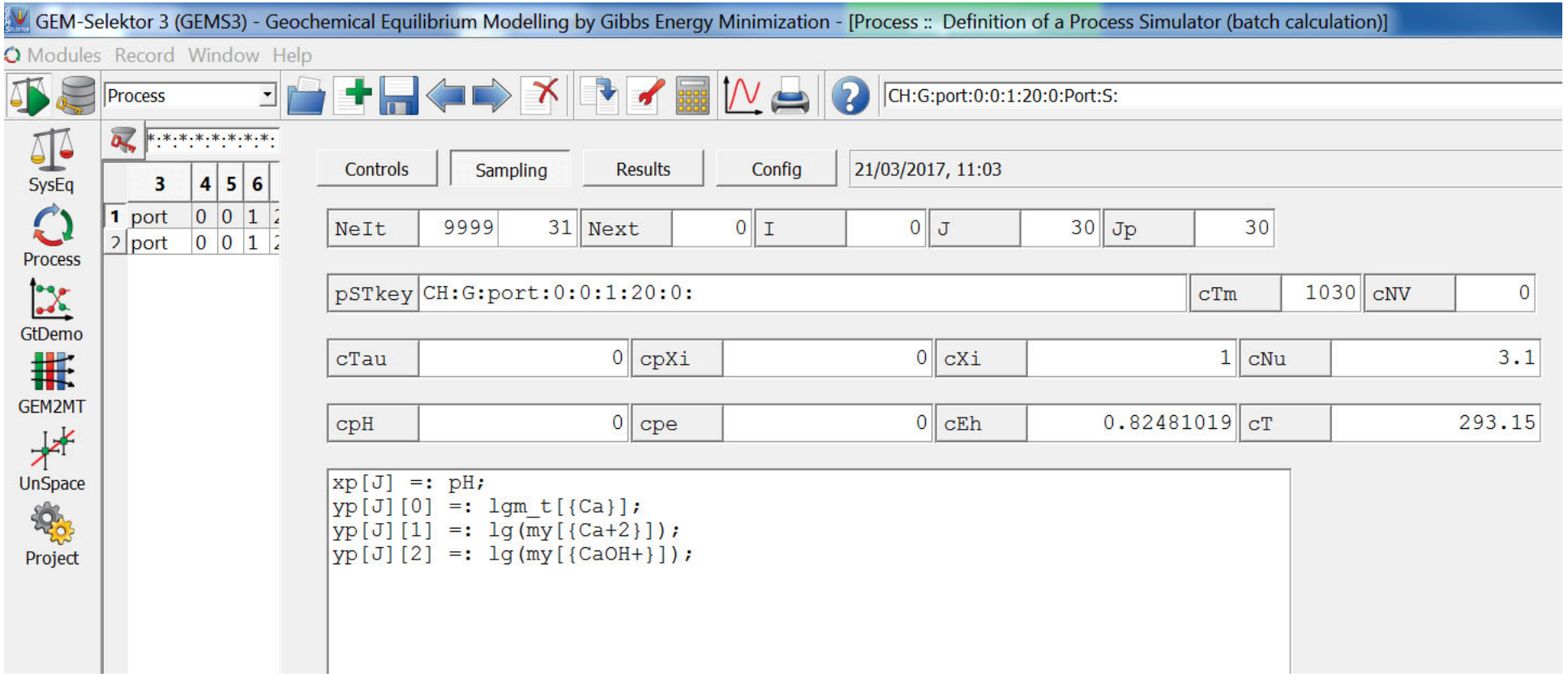
	modC
0	0
1	0
2	0
3	0
4	0
5	0
6	0
7	0
8	0
9	0

Collection of data

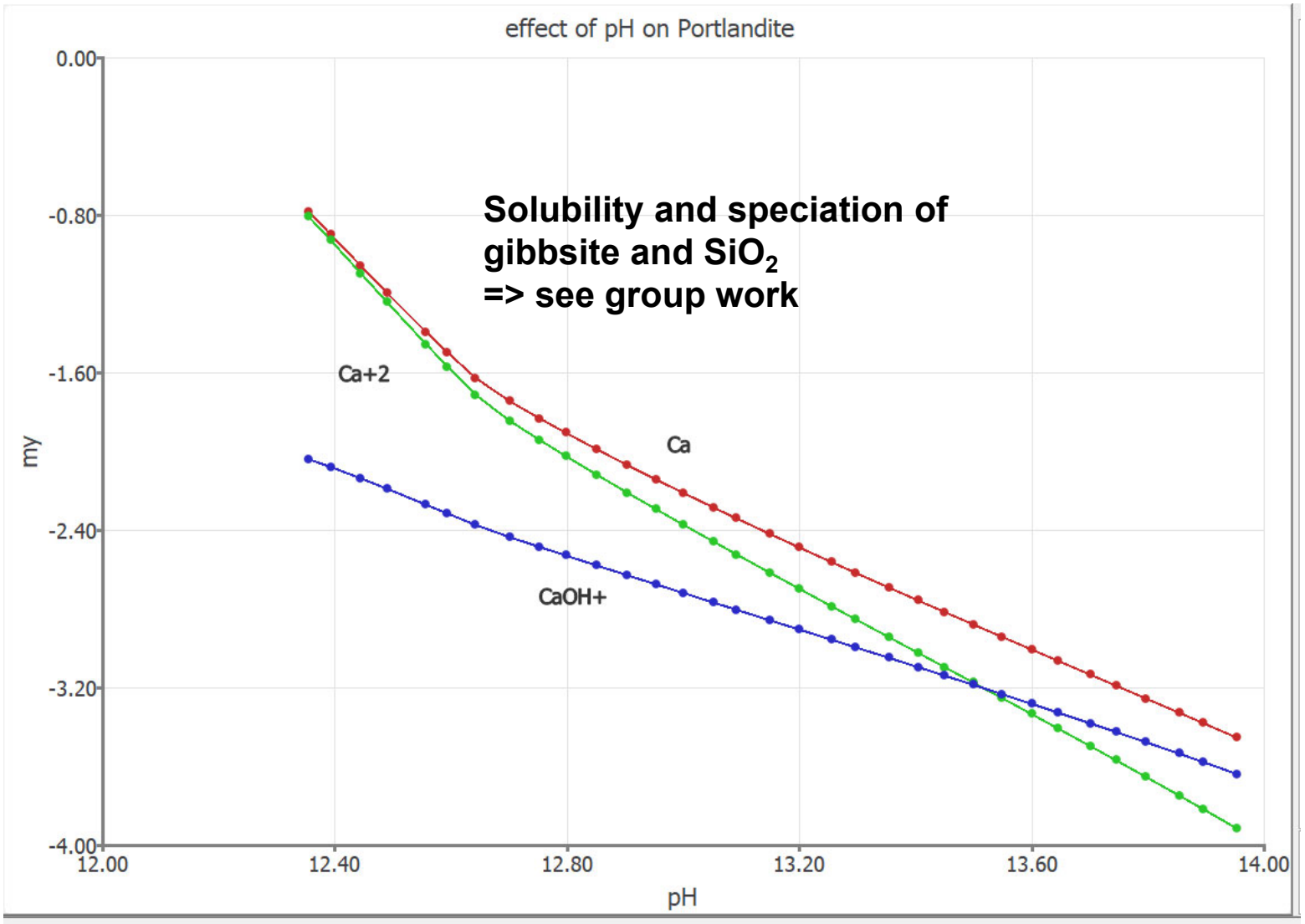
pH, total concentrations

concentrations of species

(use lg() = $\log_{10}$ for better readability)

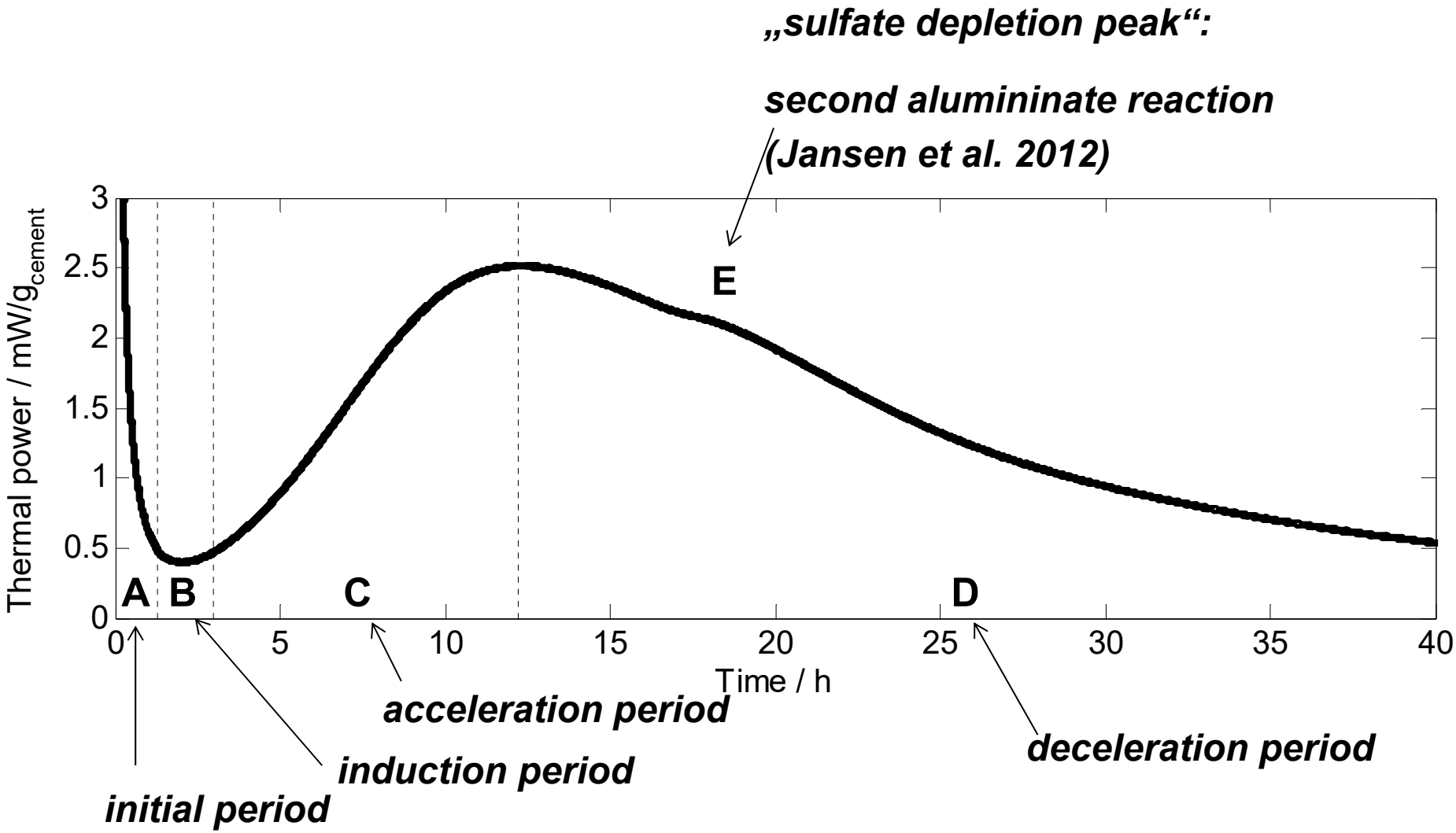


- Lower Ca concentrations at high pH
  - $\mathbf{K_{s0}} = \{Ca^{2+}\}\cdot\{OH^{-}\}^2$: pH↑ = OH^{-}↑ => Ca^{2+}↓
  - pH increase: more $CaOH^{+}$



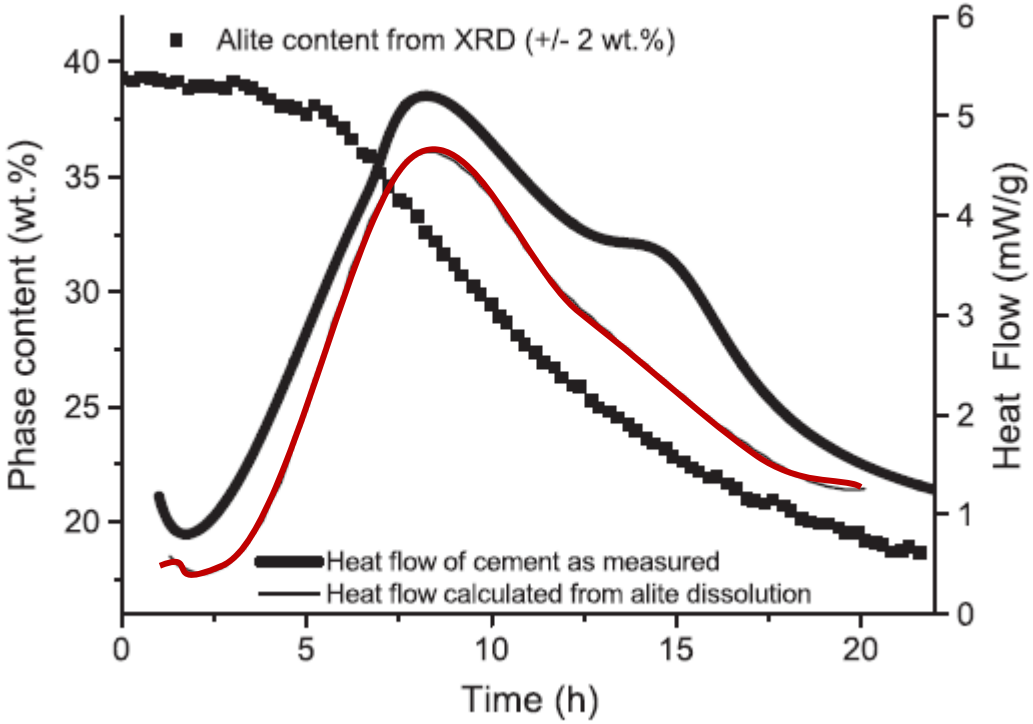
Cement hydration: calorimetry ⇔ enthalpy

Isothermal calorimetry



Heat of hydration (I)

Main early reaction: **C_3S(alite) + water → C-S-H + portlandite**



	ΔHf [kJ/Mol]	Mol weight [g/Mol]
Alite	-2929	228.2
H2O	-286	18
CSH	-2890	201.9
Portlandite	-986	73.97

Enthalpy of alite reaction

=-(-2929-3.9*286)+(-2890-1.3*986)

= -127 kJ/mol

=> -558 J/g Alite

23°C, w/c = 0.50

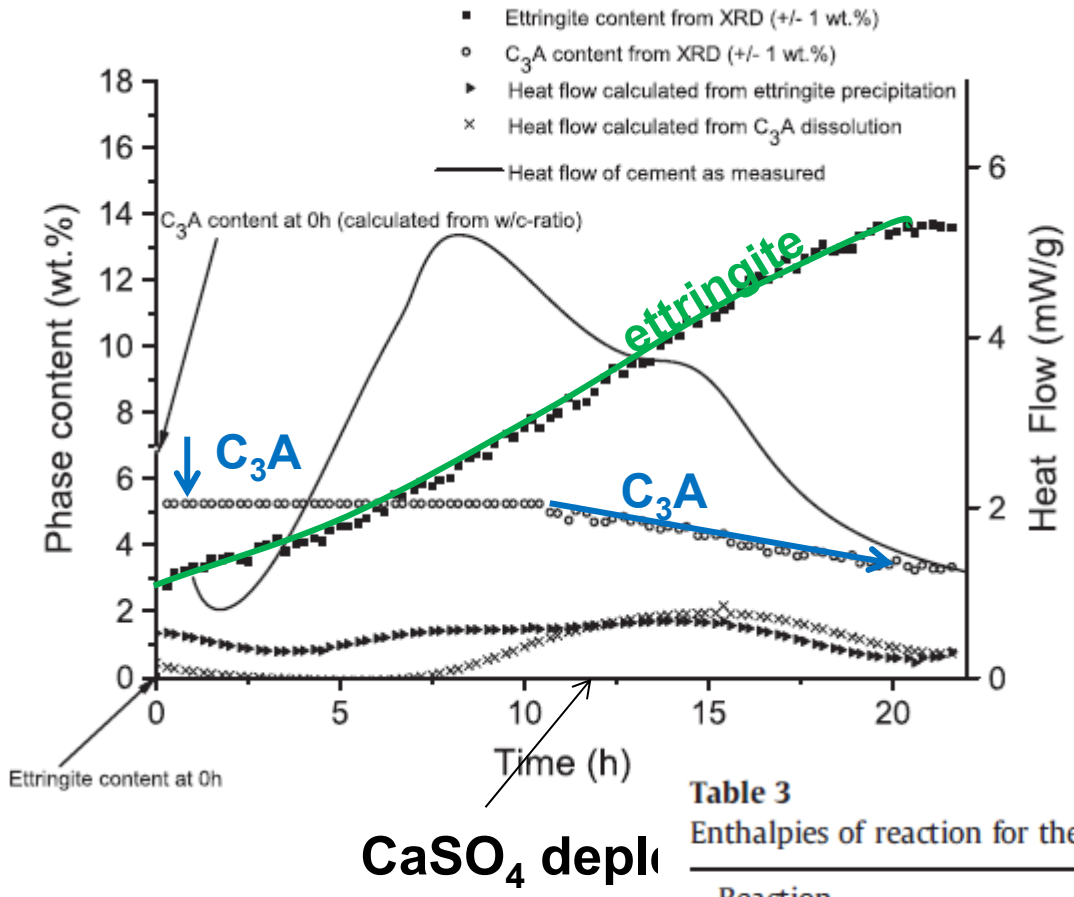
Jansen et al. 2012, CCR

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_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

Heat of hydration (II)

Main early reaction: **C_3S(alite) + water → C-S-H + portlandite**



C_3A + 3Cs + 32H → $C_6As_3H_{32}$

Main C_3A dissolution

- **1st minutes**
- **Depletion of CaSO4**

Ettringite forms continously

23°C, w/c = 0.50

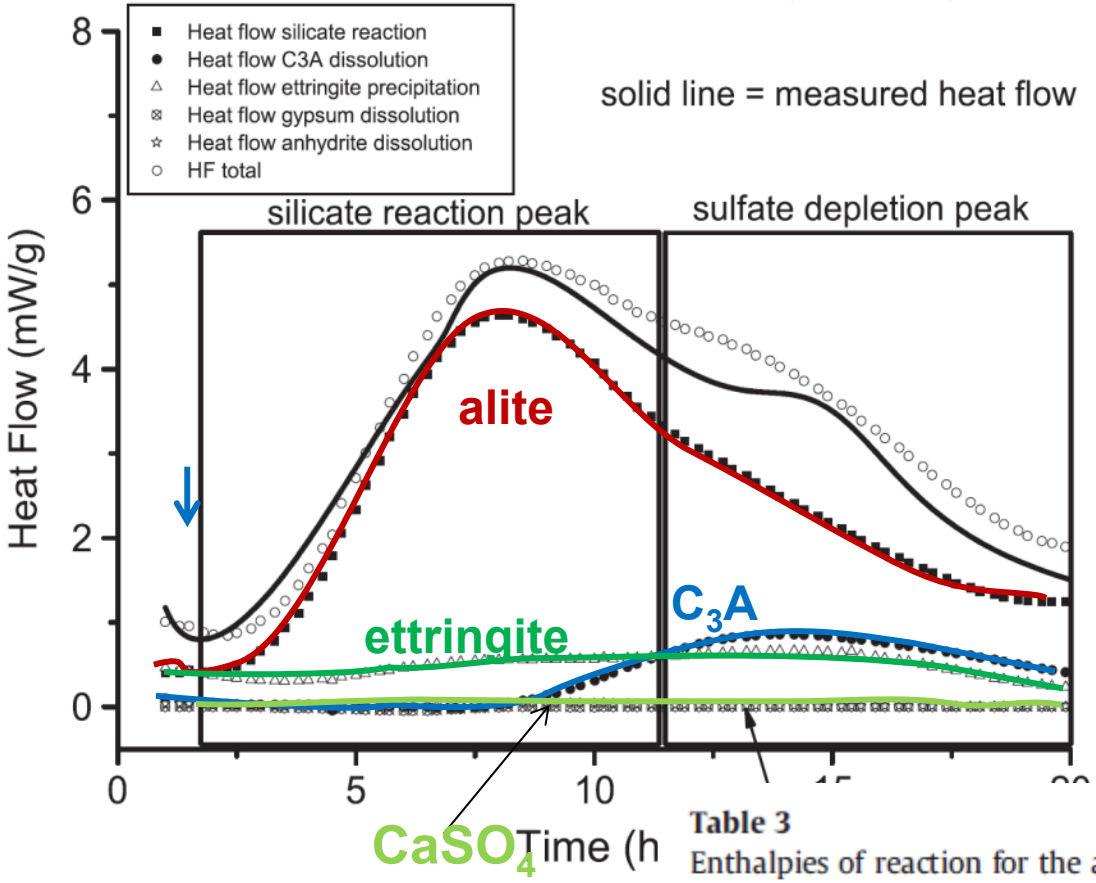
Jansen et al. 2012, CCR

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_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

Heat of hydration (III)

Main early reaction: **C_3S(alite) + water → C-S-H + portlandite**



C_3A + 3Cs + 32H → $C_6As_3H_{32}$

Main C_3A dissolution

- **1st minutes**
- **Depletion of $CaSO_4$**

Ettringite forms continously
Little effect of $CaSO_4$ dissolution

23°C, w/c = 0.50

Jansen et al. 2012, CCR

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_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

How to calculate heat

Empa
Materials Science and Technology

	log K_{S0}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [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]
$C_4As_3H_{30}$[q]		**-14728.1**	**-16950.2**	**1792.4**	**1452**	**2.156**			**708**	**[24]**
$C_4As_3H_{13}$		**-10540.6**	**-11530.3**	**1960.4**	**970.7**	**1.483**			**411**	**[24]**
$C_4As_3H_9$		**-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_3AH_6[c]	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
*$C_3AS_{0.41}H_{5.18}$[*c]*	*-25.35*	*-5192.9*	*-5699*	*399*	*310*	*0.566*	*-4.37e6*		*146*	*[11]*
*$C_3AS_{0.84}H_{4.32}$[*d]*	*-26.70*	*-5365.2*	*-5847*	*375*	*331*	*0.484*	*-5.55e6*		*142*	*[11]*
*C_3FH_6[e**]*	*-26.30*	*-4122.8*	*-4518*	*870*	*330*	*1.237*	*-4.74e6*		*155*	*[11]*
$C_3FS_{0.84}H_{4.32}$[d,e]	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
$C_3(A,F)S_{0.84}H_{4.32}$[d]	**-30.10**	**-4925.4**	**-5335**	**617**	**367**	**0.471**	**-8.10e6**		**146**	**[11]**
$C_3FS_{1.34}H_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	-8.39e6		145	[11]
C_4AH_{19}[f]	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	**369**	[10,23]
C_4AH_{13}		**-7325.7**	**-8262.4**	**831.5**	**208.3**	**3.13**			**274**	**[23]**
C_4AH_{11}		**-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 !
  $\Delta_f H°$ (H_2O) = -285.88 kJ/mol

How to calculate heat

	log K_{S0}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [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*v	-1436.34*v	-1575.3*v	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum

1) 1M $CaSO_4$ (= 136.14 g) + 2 M H_2O (36.03 g) => 1M $CaSO_4$ $2H_2O$

-2'023'361 -(-1'434'601 +2*(-285'881)) = -16'998 J/mol = **-17.0 kJ/mol**

=> -125 J/g anhydrite or -98.7 J/g gypsum

$$\Delta_r H° = \Delta_f H°_{\text{gypsum}} - \Delta_f H°_{\text{anhydrite}} - 2\,\Delta_f H°_{\text{water}}$$
$$= -2022.63 - (-1434.11) - 2\,(-285.830)$$
$$= -16.86\,\text{kJ mol}^{-1}$$

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}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [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*v	-1436.34*v	-1575.3*v	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum

1) 1M $CaSO_4$ (= 136.14 g) + 2 M H_2O (36.03 g) => 1M $CaSO_4$ $2H_2O$
   -2'023'361 -(-1'434'601 +2*(-285'881)) = -16'998 J/mol **= -17.0 kJ/mol**
   => -125 J/g anhydrite or -98.7 J/g gypsum

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

Input	M	g/mol	H (J/mol)	g/L	J/g CaSO4
CaSO4	0.0073	136	-1434601	1	-10537
output					
Ca2+	0.0055	40	-543069	0.22105834	-2995
SO4-2	0.0055	96	-909697	0.5298638	-5018
CaSO4 aq	0.0018	136	-1448430	0.2490777	-2650
Dissolution					**-126**

Empa
Materials Science and Technology

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

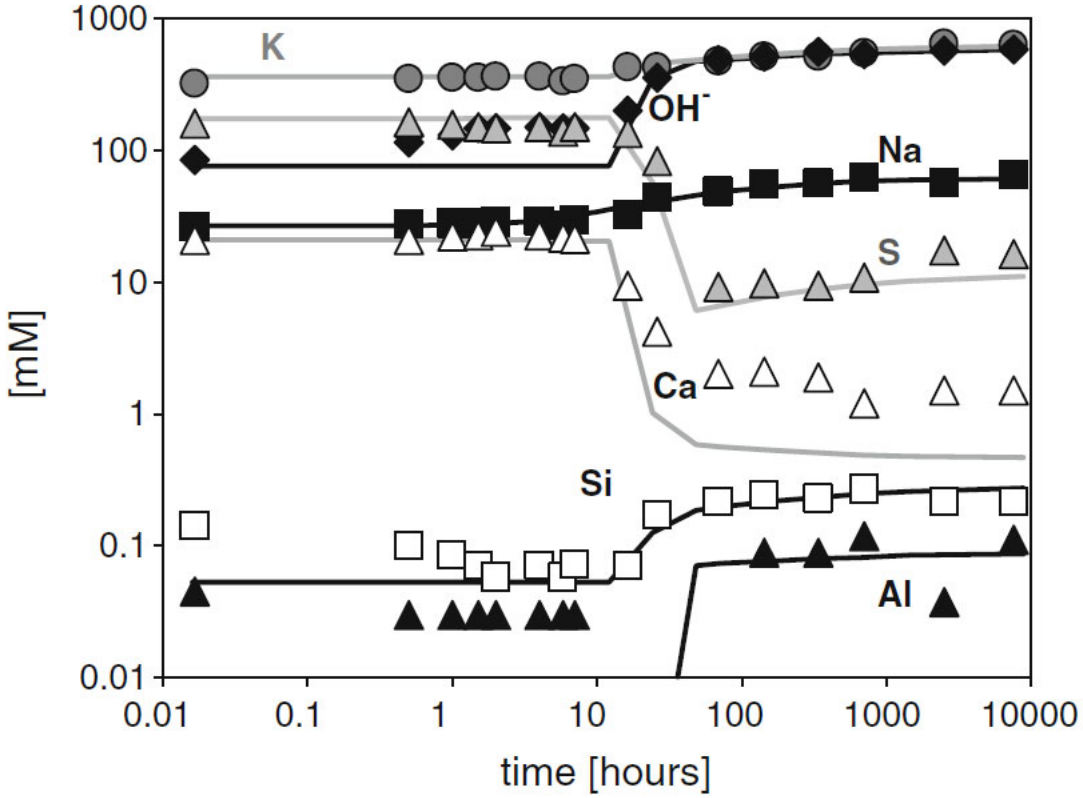


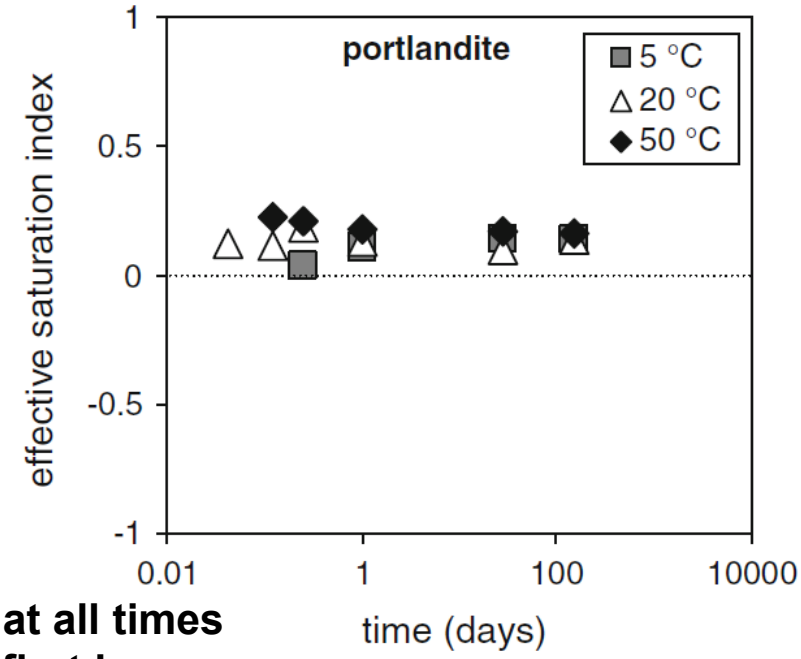
Fig. 1 Evolution of the pore solution during the hydration of OPC. *Symbols* refer to measured concentrations, *lines* to modeled concentrations. Adapted from [17]

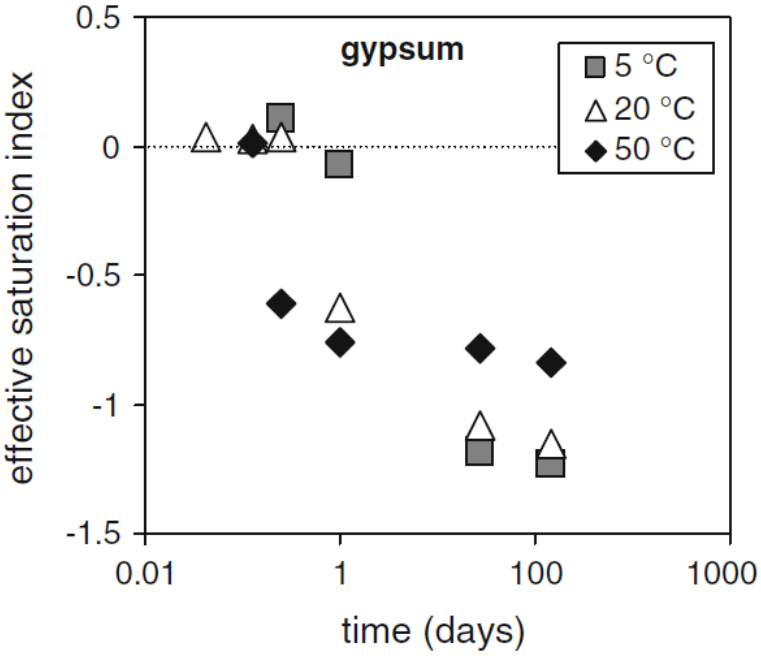
Lothenbach (2010) Materials and Structures 43, 1413-1433

Composition changes during cement reaction

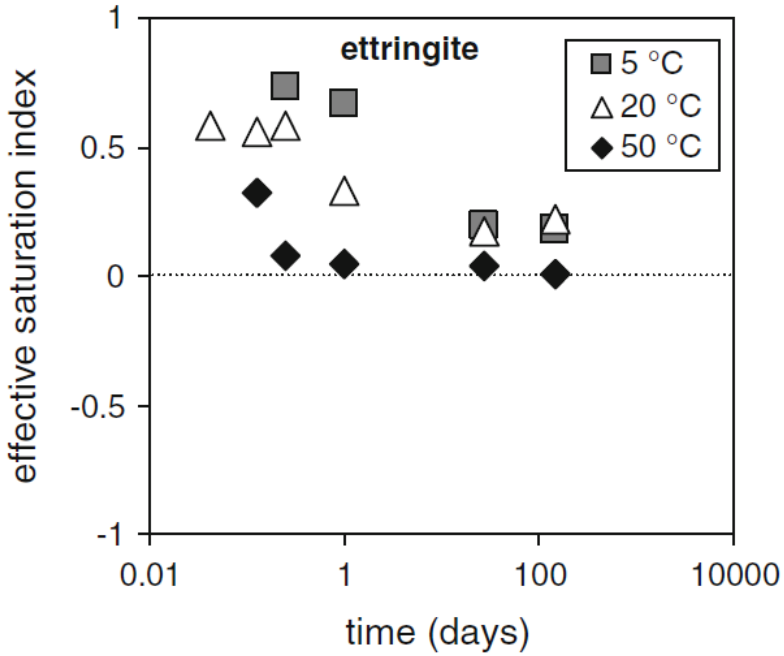
In particular for calcium and sulfate:

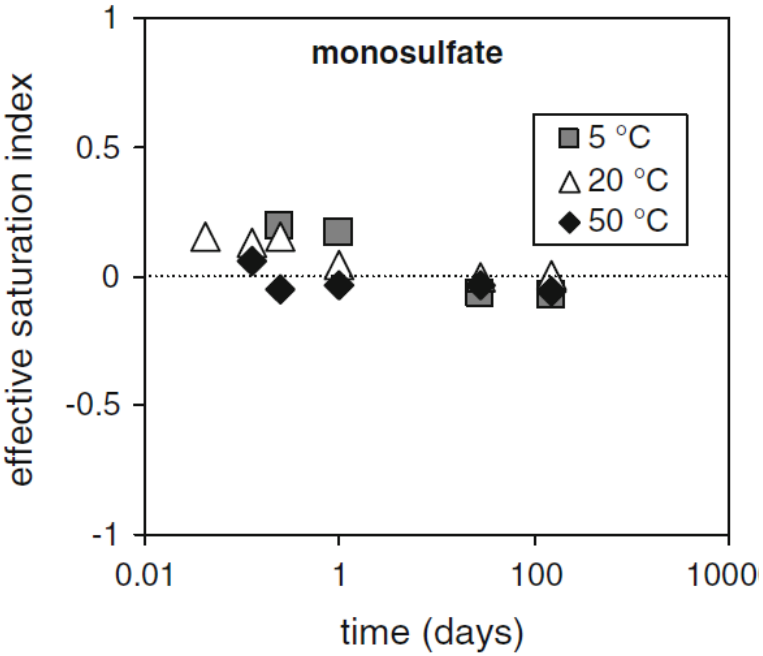
Calculation of saturation indices
=> indicate changes in solid phases





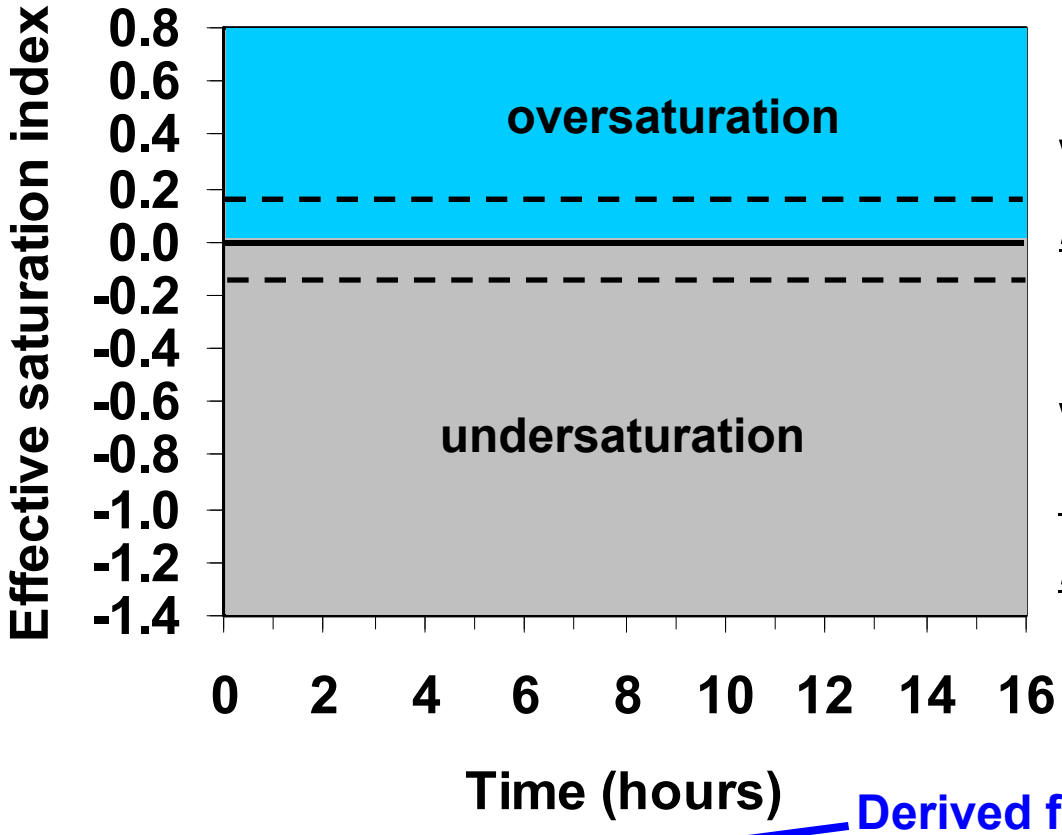
CH, AFt, AFm at all times
Gypsum only first hours





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

Calculation of saturation indices



Phase in equilibrium with pore solution
Might **form**

Phase not in equilibrium with pore solution
Cannot **form**
Dissolves

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

$$IAP = ion\ activity\ product = measured\ concentrations$$

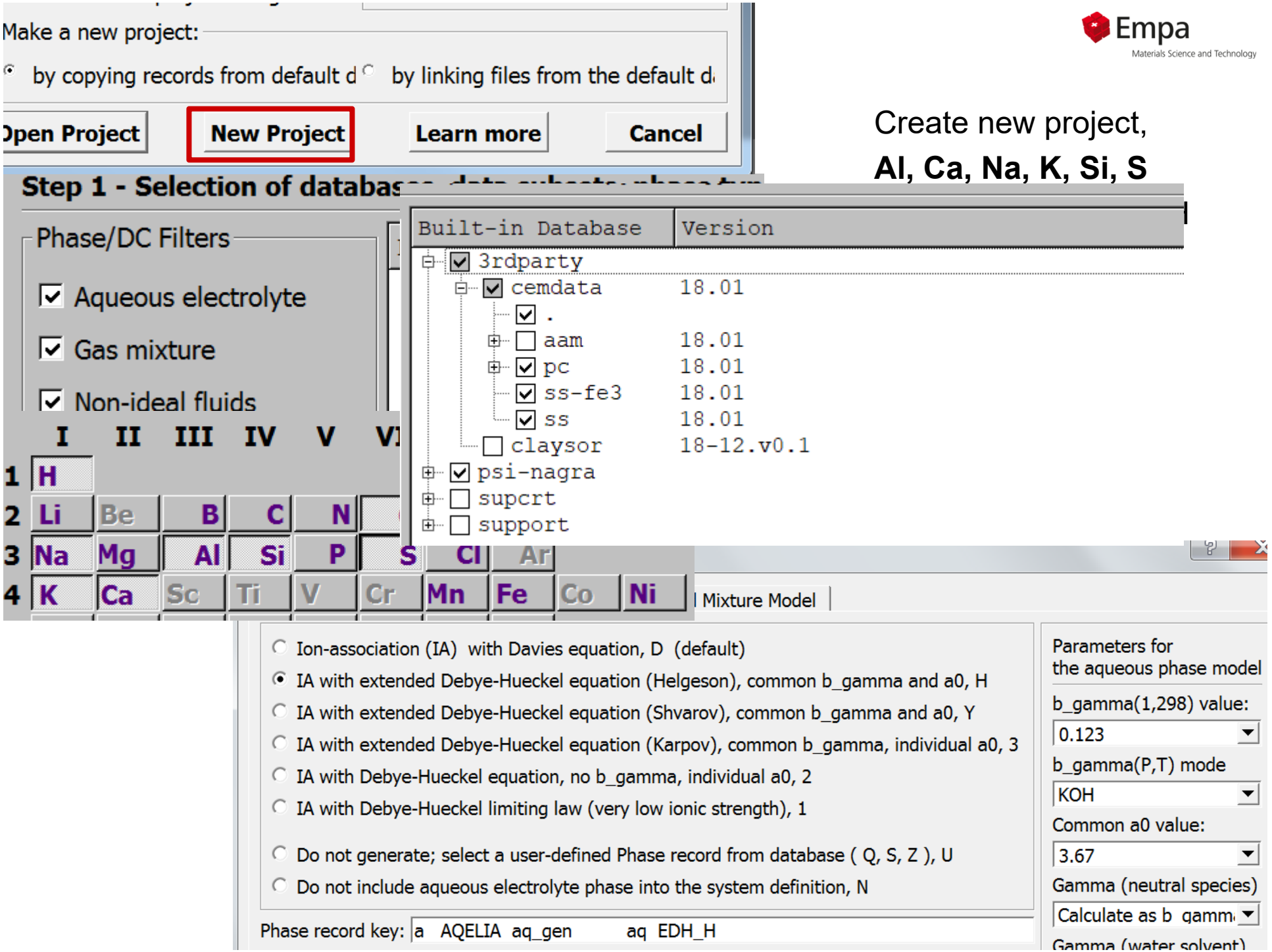
GEMS used to calculalate $\{Ca^{2+}\}$ from Ca_{tot}

Saturation indices: measured conc.

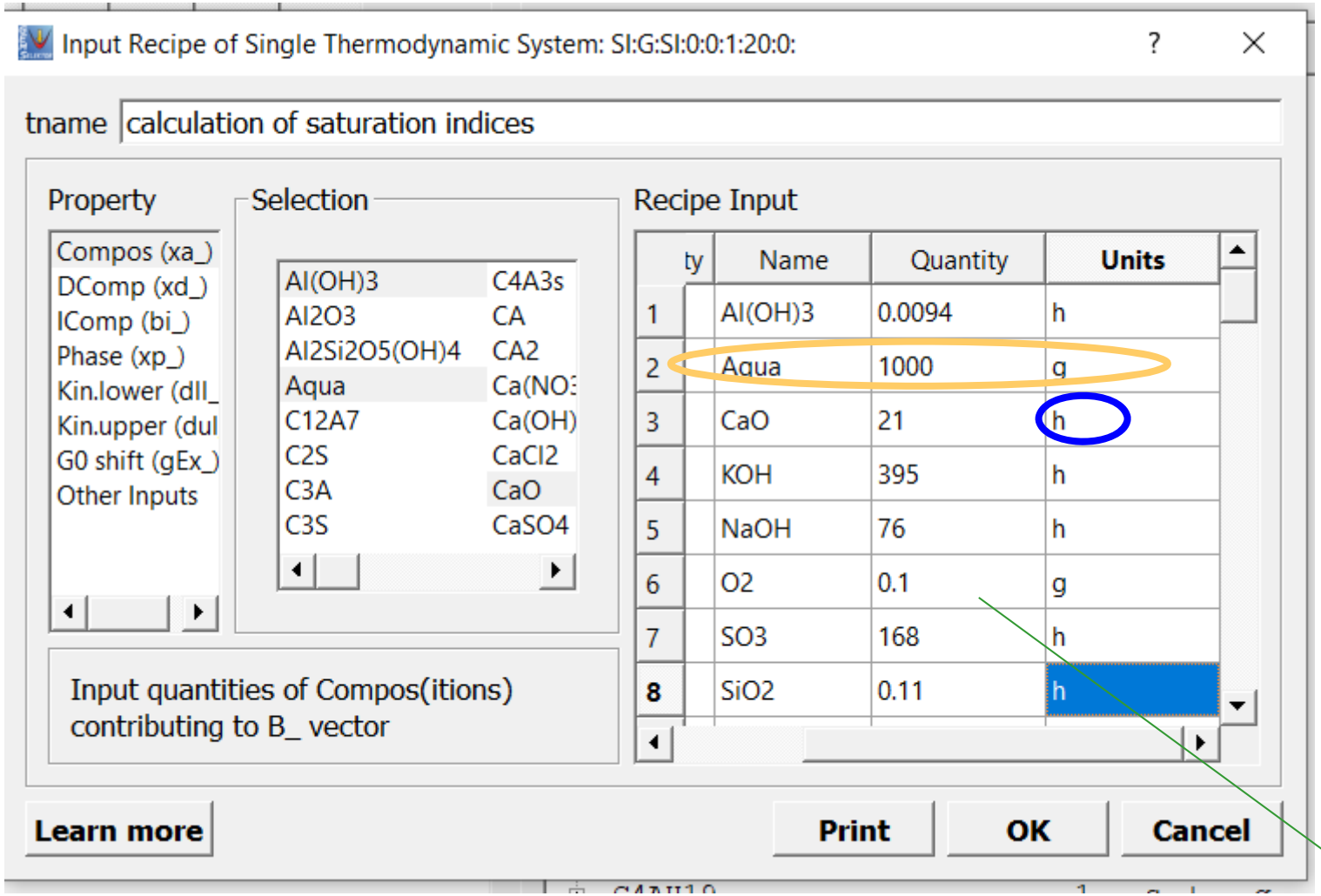
time days	Al	Ca	S	K	Na	Si	OH-	pH
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	
0.04	0.0094	21	168	395	76	0.11	170	13.2
0.08	0.0043	21	175	404	77	0.13	164	13.2
0.17	0.0074	21	176	401	78	0.13	164	13.2
0.25	0.032	18	180	408	83	0.17	164	13.2
1	0.216	2.5	2.6	447	106	0.31	472	13.6
7	0.621	1.5	3.4	556	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

Empa
Materials Science and Technology

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



Calculation of saturation inidices

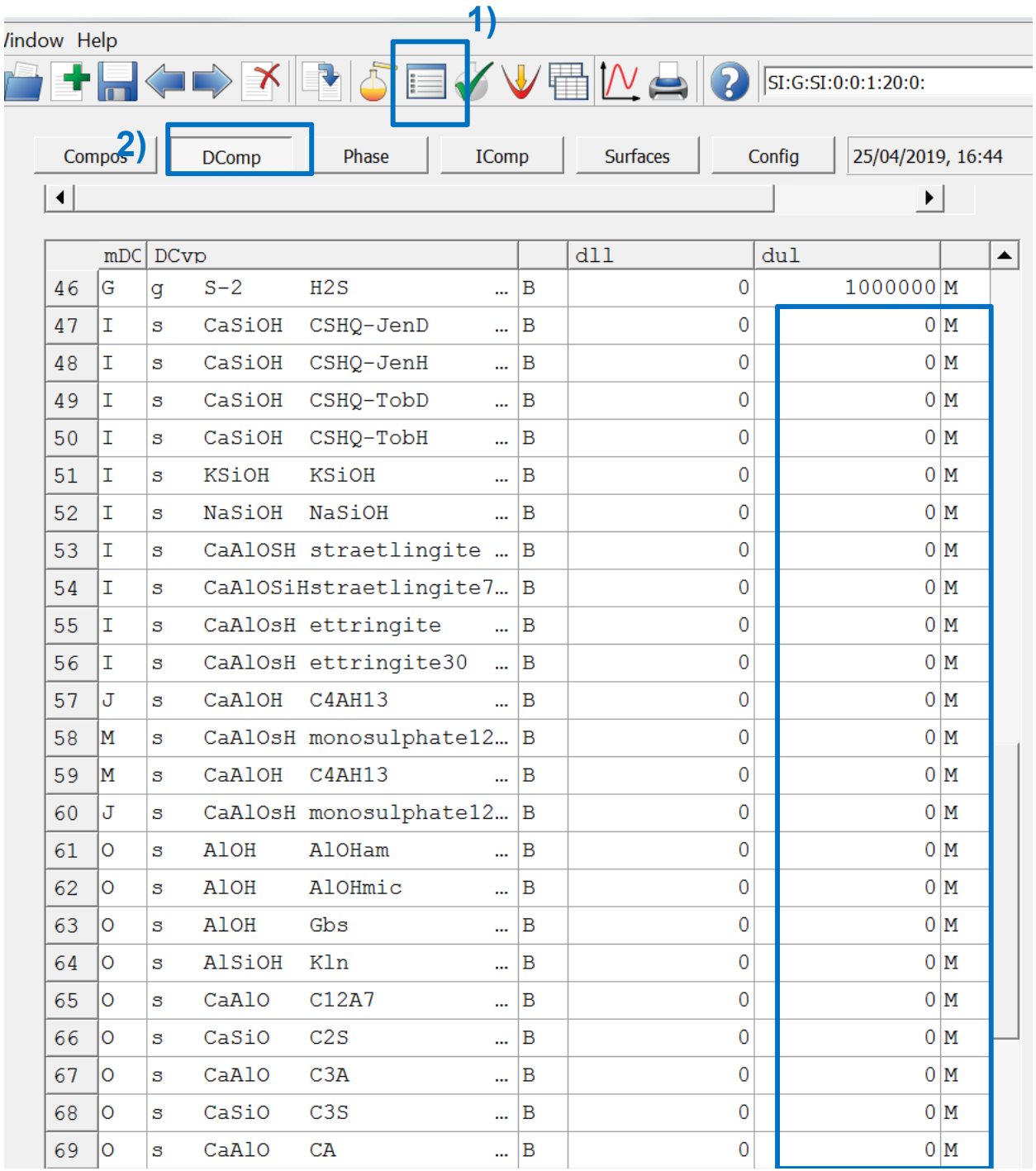


1 kg of water
=> mmol/l

h: mmol

O_2 =>
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



	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	CaAlOSiH	straetlingite7	...	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

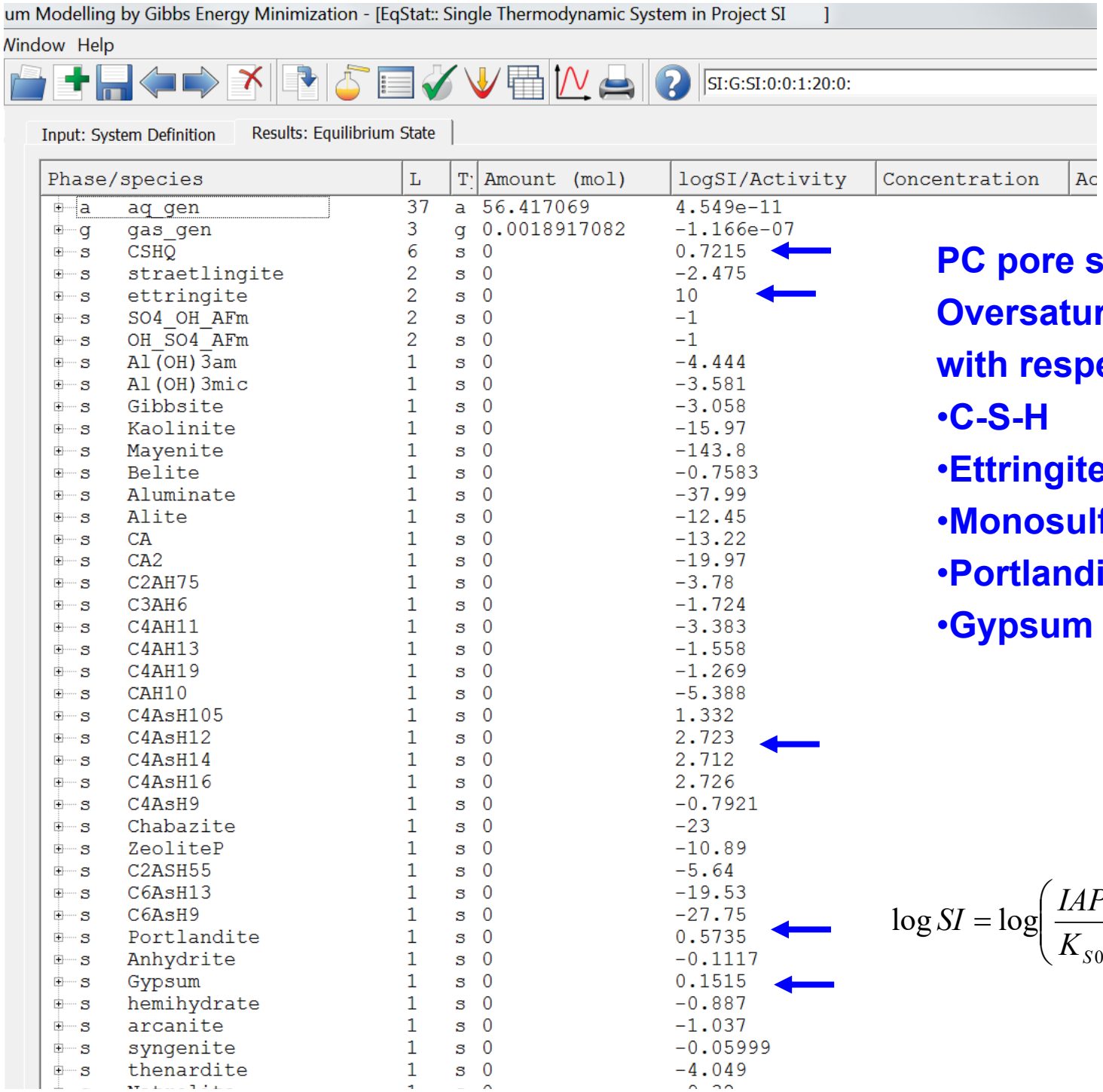
3) Scroll down to 2nd table

4) Select all dul of solids

5) Press F8,
0, Ok-do it

dul = upper limit
dul = 0
Solid cannot form

dll = lower limit



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 Aluminate	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**

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

Thermodynamic data

1. Databases
2. Solubility and speciation
3. Saturation indices

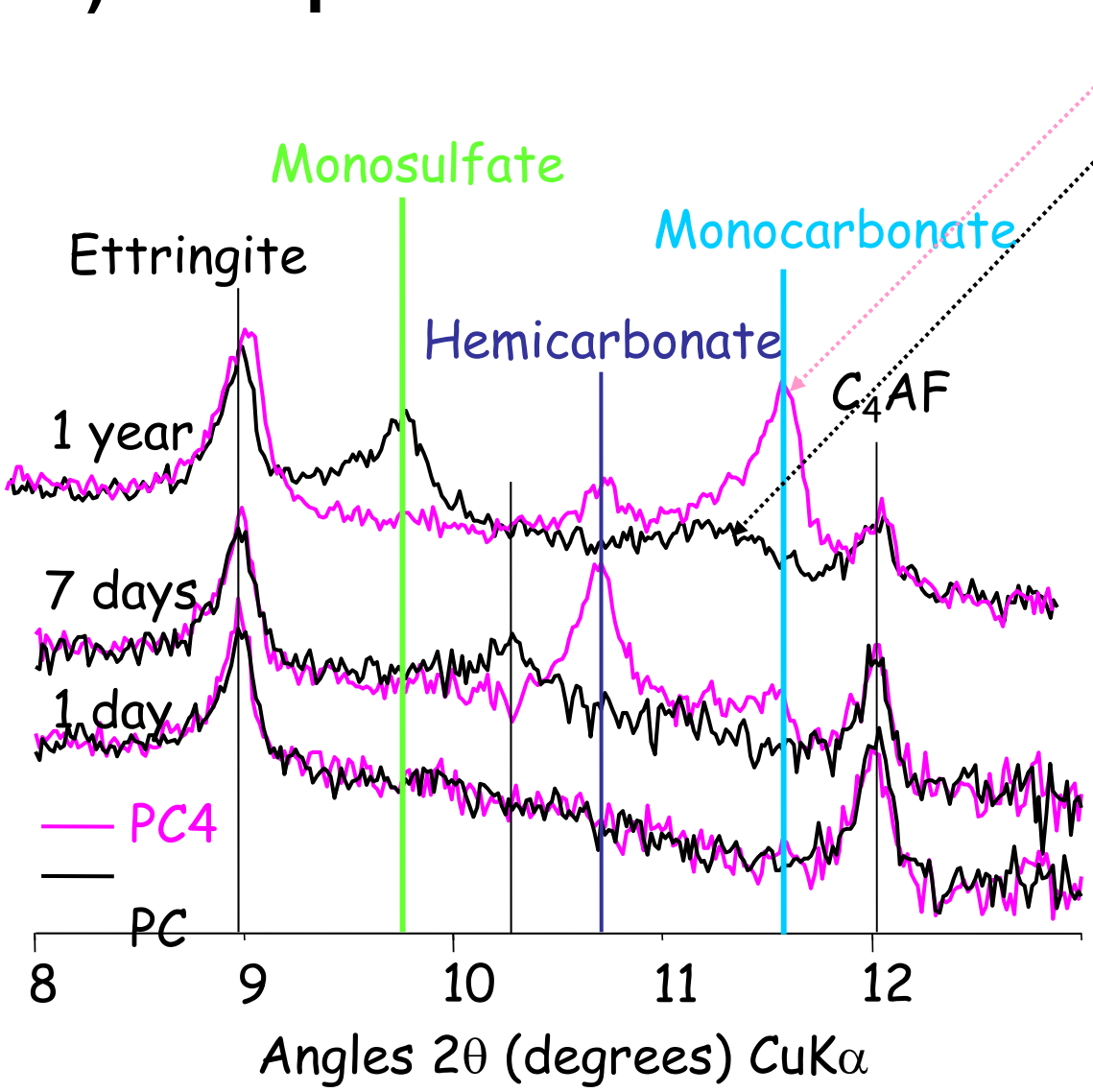
4. **Hydrates in cements**

5. Details on how to manage thermodynamic data in GEMS

   => Self study

Empa
Materials Science and Technology

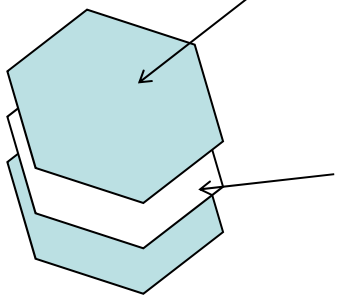
1) AFm phases



Main difference:

AFm phases

$[Ca_2(Al, Fe)(OH)_6]_2^{2+}$



Monosulfate

$[SO_4, 6H_2O]^{2-}$

Monocarbonate

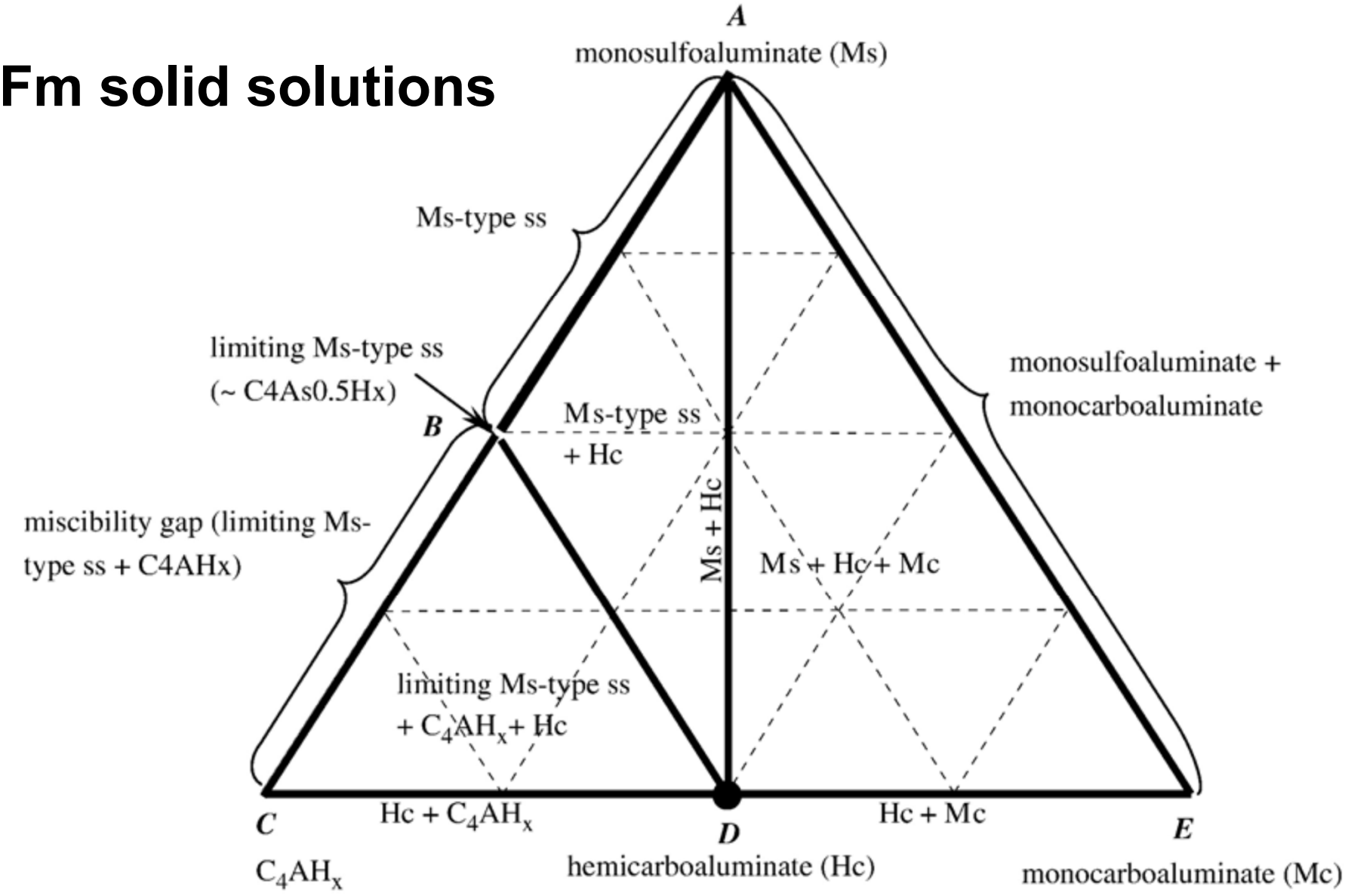
$[CO_3, 5H_2O]^{2-}$

Hemicarbonate

$[0.5CO_3, OH, 5.5H_2O]^{2-}$

63

AFm solid solutions



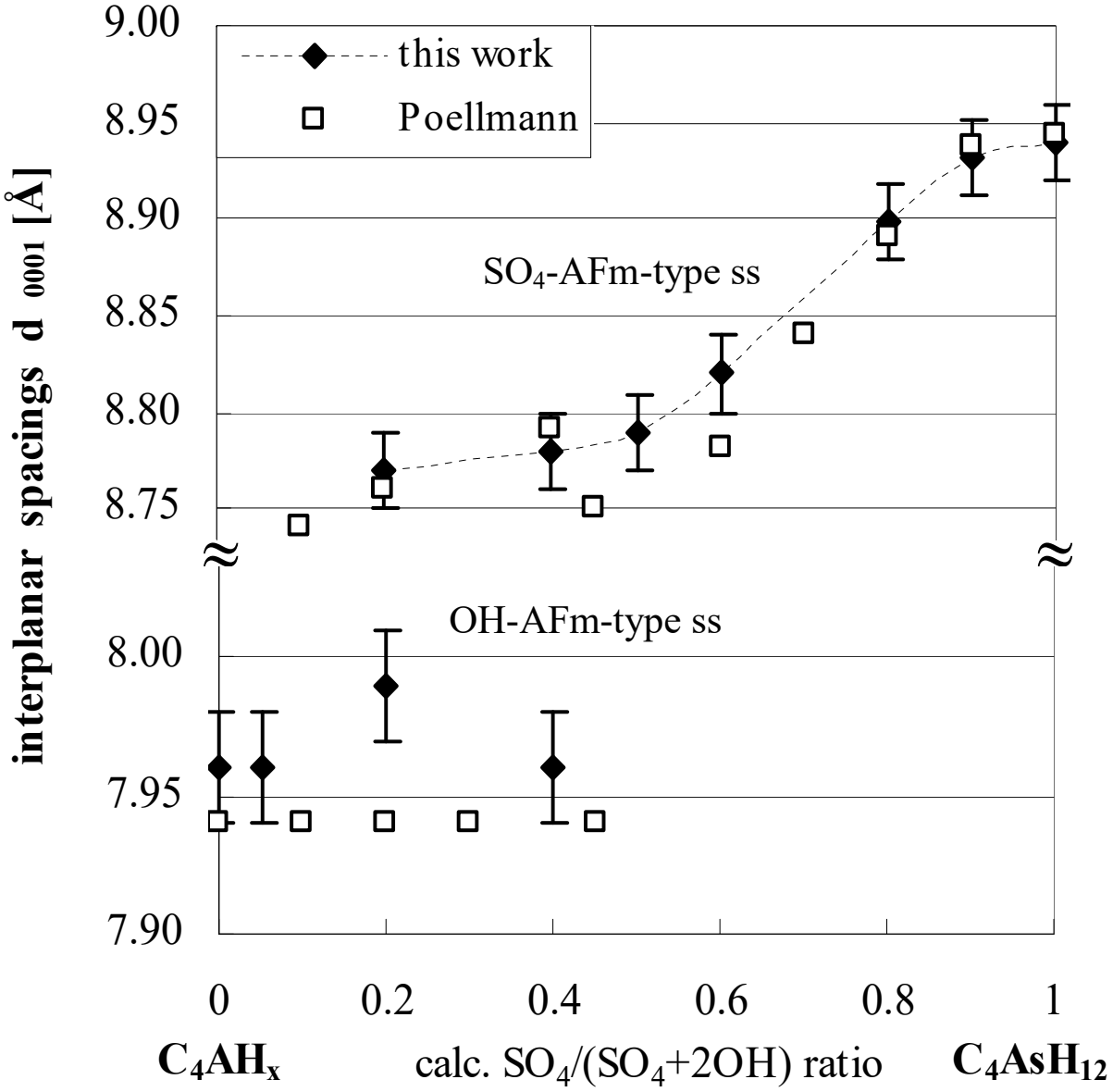
Matschei ea 2007

1) AFm phases

Characteristics solid solutions:

- XRD peak shift

- change of concentrations



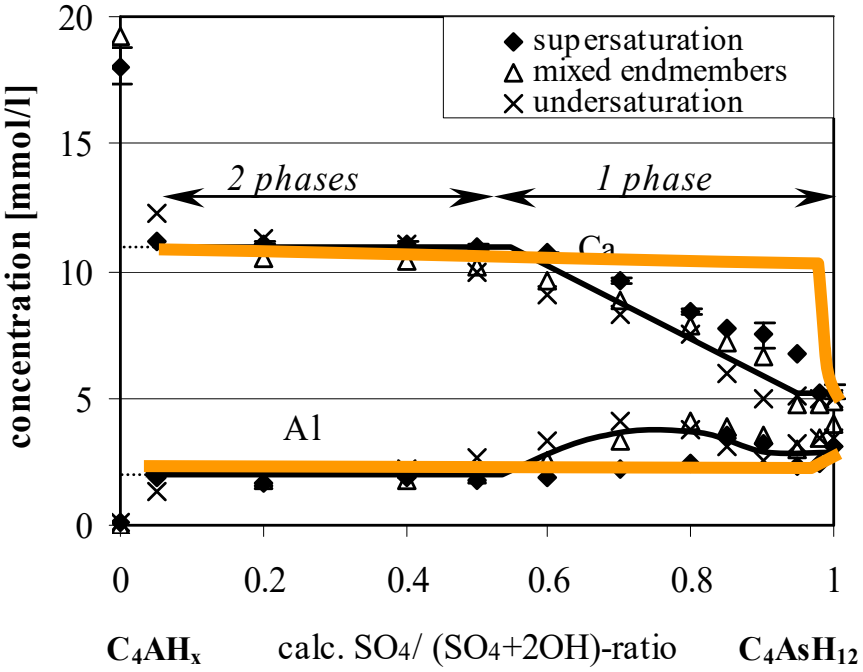
C_4AH_{13} – monosulfate: solid solution

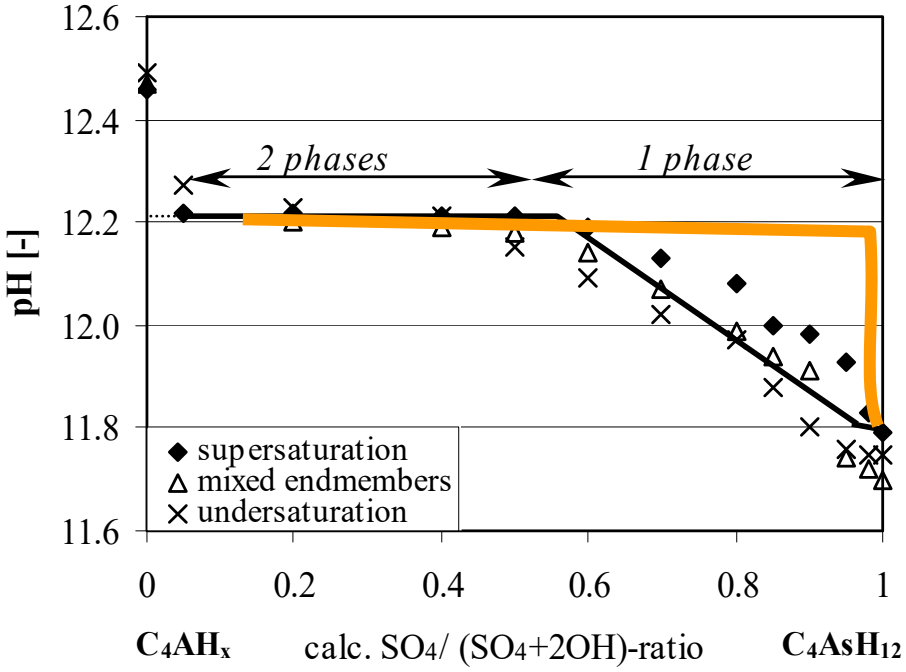
Matschei et al (2007) CCR 37, 118-130

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

- miscibility gap 0.03-0.5
- no solid solution

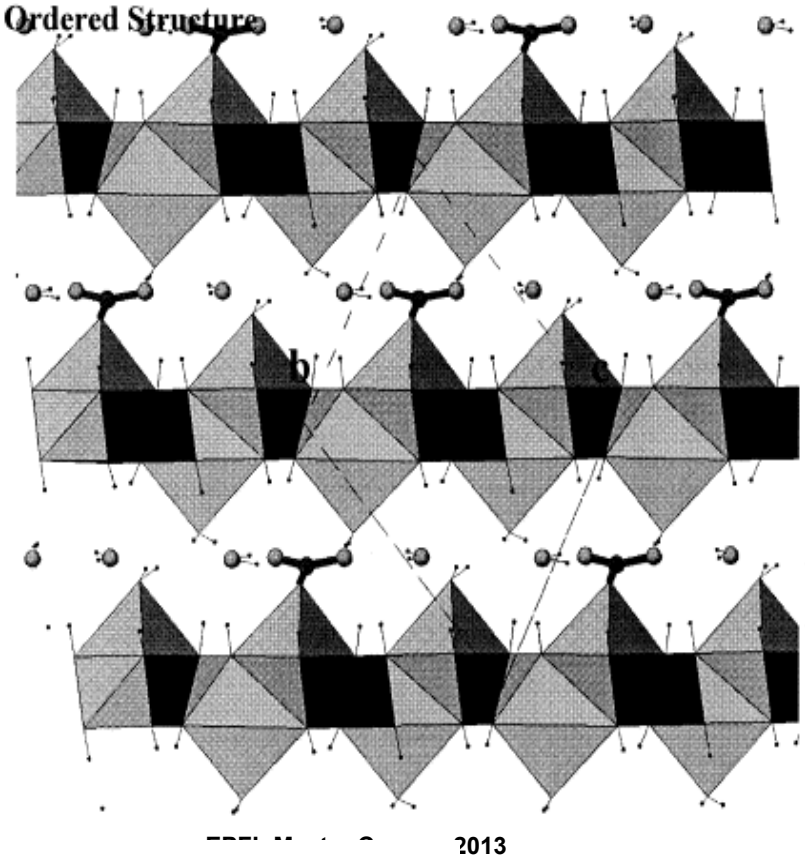
66

Solid solutions probable

- Similar charge
- Similar structure
- Similar size

AFm: $4CaO \cdot Al_2O_3 \cdot CaX \cdot nH_2O$

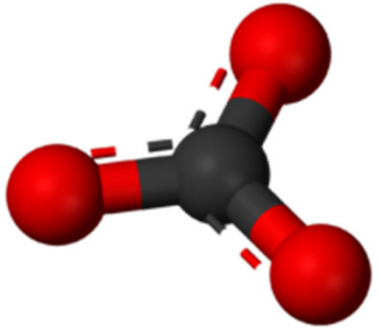
CO_3^{2-} H_2O



$[Ca_4Al_2(OH)_{12}]^{2+}$ Renaudin 1999

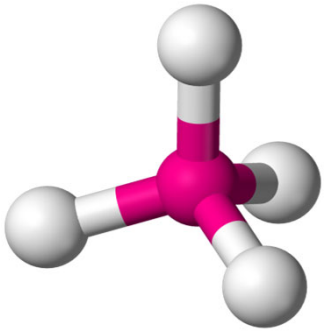
Monocarbonate: $4CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$

CO_3^{2-}

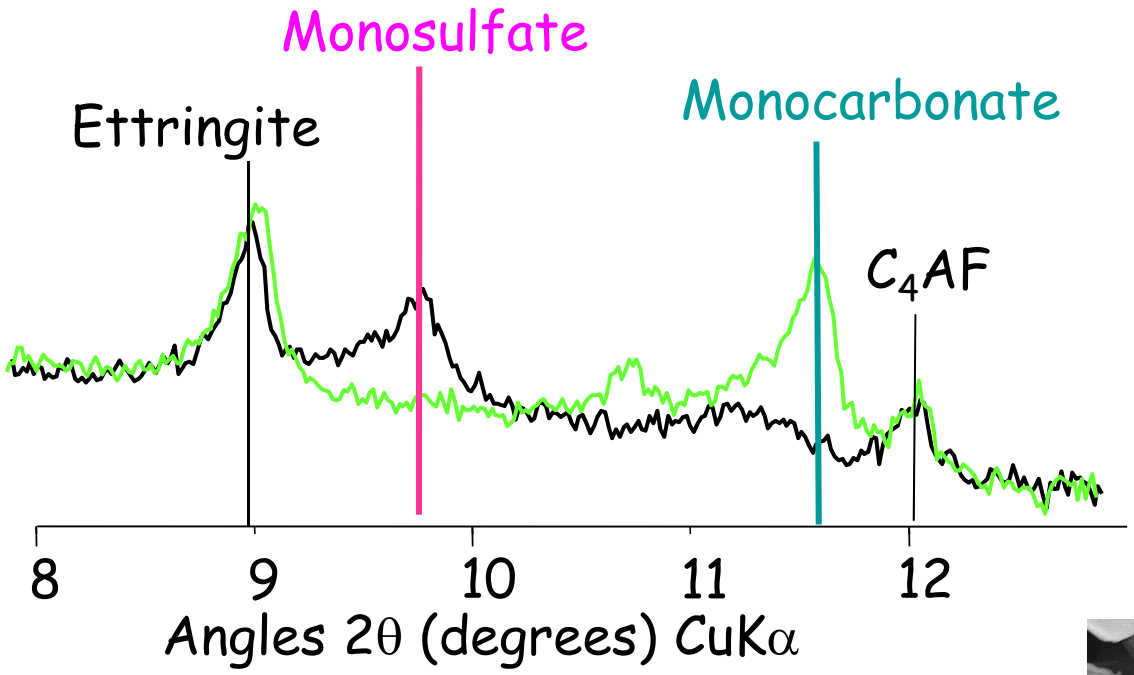


Monosulfate: $4CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$

SO_4^{2-}

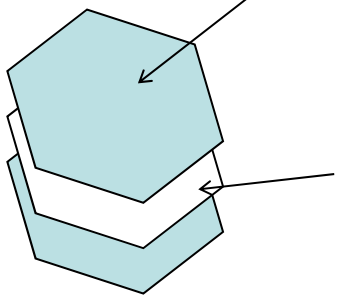


Solid solution CO_3-AFm – SO_4-AFm?



Main difference:
AFm phases

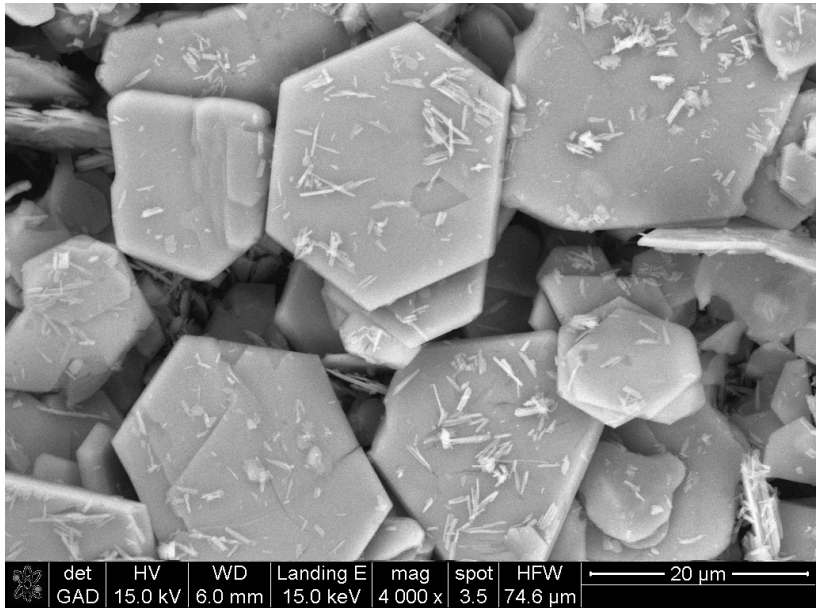
$[Ca_2(Al, Fe)(OH)_6]_2^{2+}$



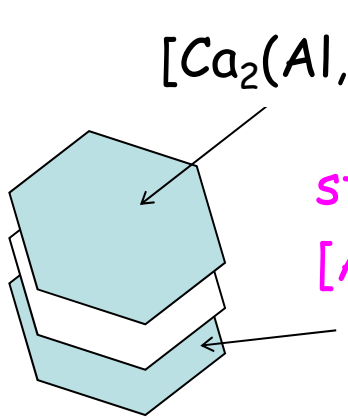
Monosulfate
$[SO_4, 6H_2O]^{2-}$
Monocarbonate
$[CO_3, 5H_2O]^{2-}$

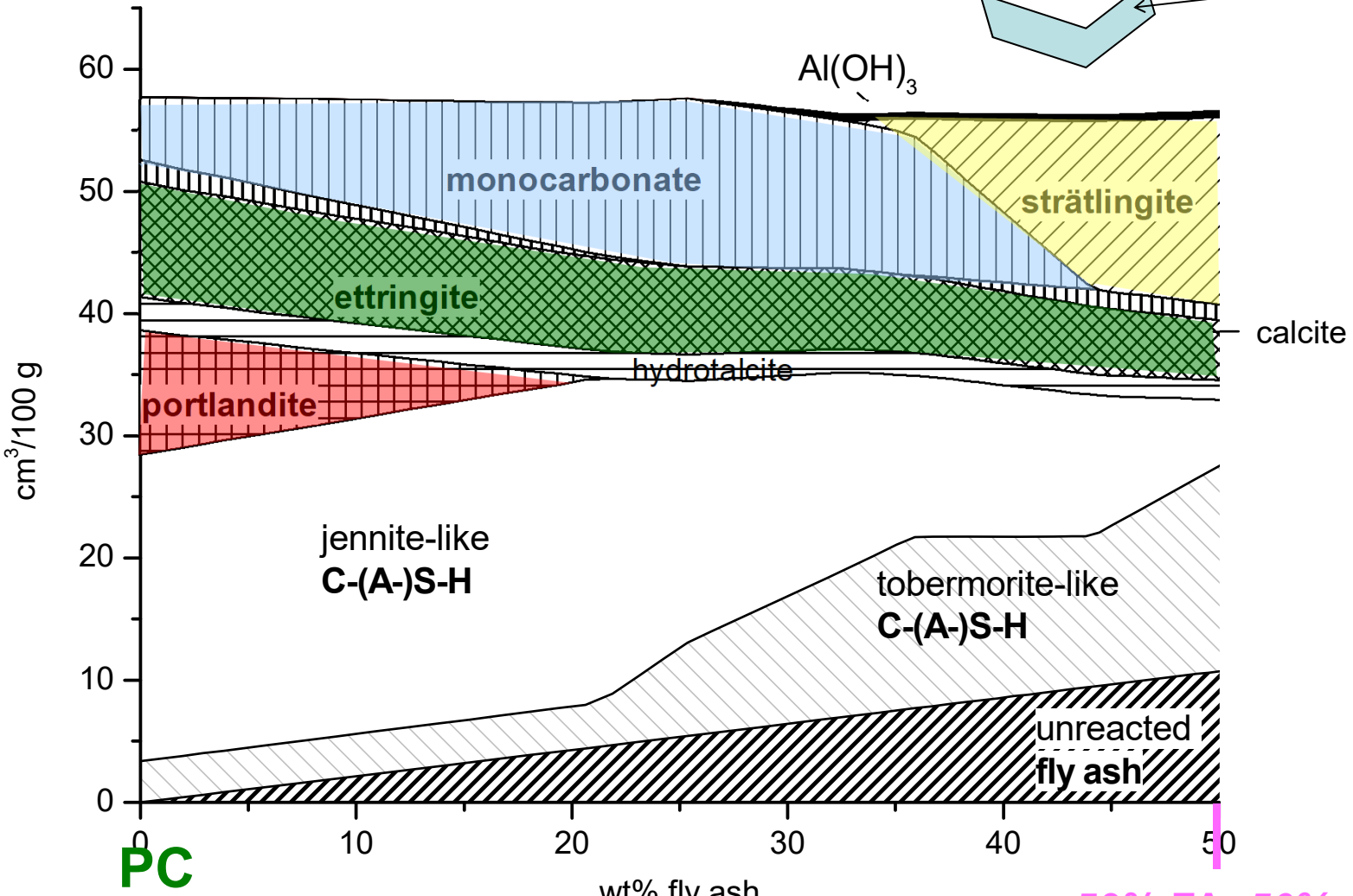
Solid solution not probable:

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



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





Lothenbach ea (2011) CCR 41 1244-1256

50% FA, *50% reacted*

Ettringite:

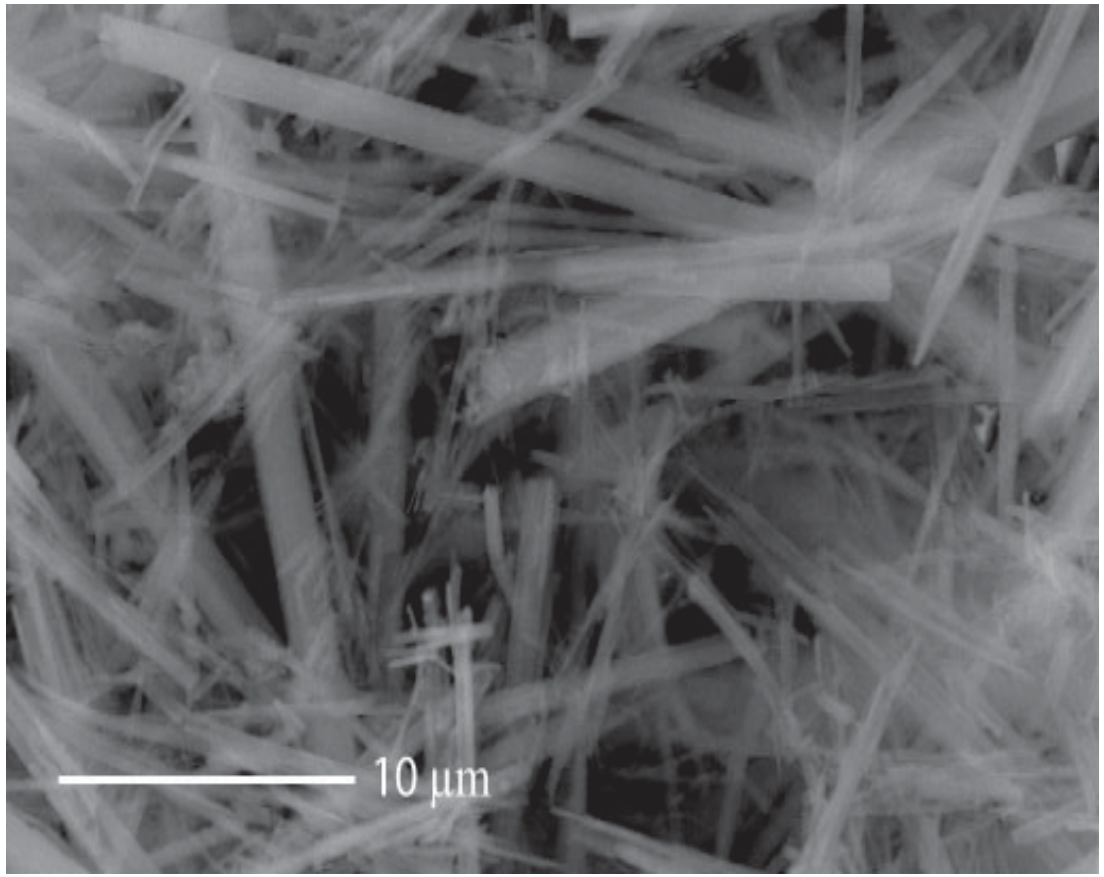
$C_6As_3H_{32}$

high water content

-> voluminous

-> low density 1.8 kg/dm^3

-> good space filling



Takes up other ions
(solid solutions)

-> Al ↔ Fe

-> SO_4^{2-} ↔ CO_3^{2-}, CrO_4^{2-}, …

solid solution with thaumasite

$C_6As_3H_{32} \leftrightarrow C_6S_2s_2c_2H_{30}$

Ettringite:

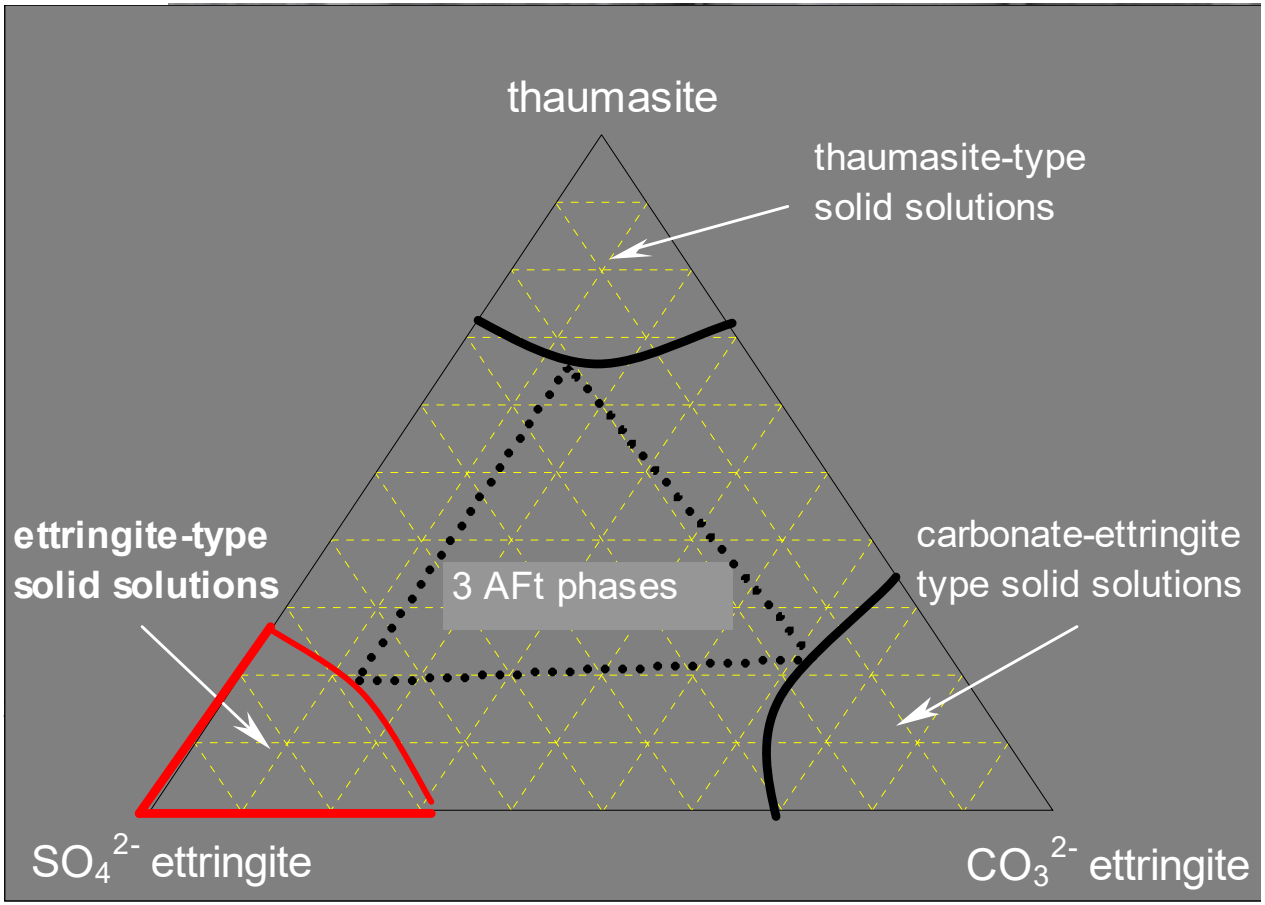
$C_6As_3H_{32}$

high water content

-> voluminous

-> low density 1.8 kg/dm

-> good space filling



Takes up other ions
(solid solutions)

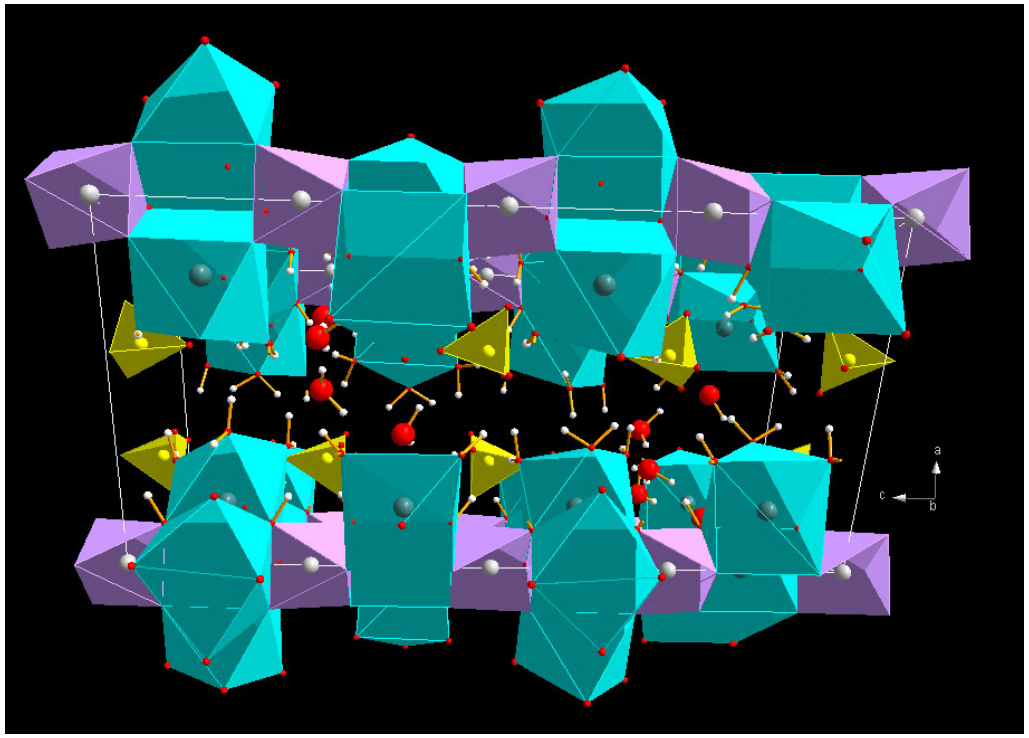
-> Al ↔ Fe

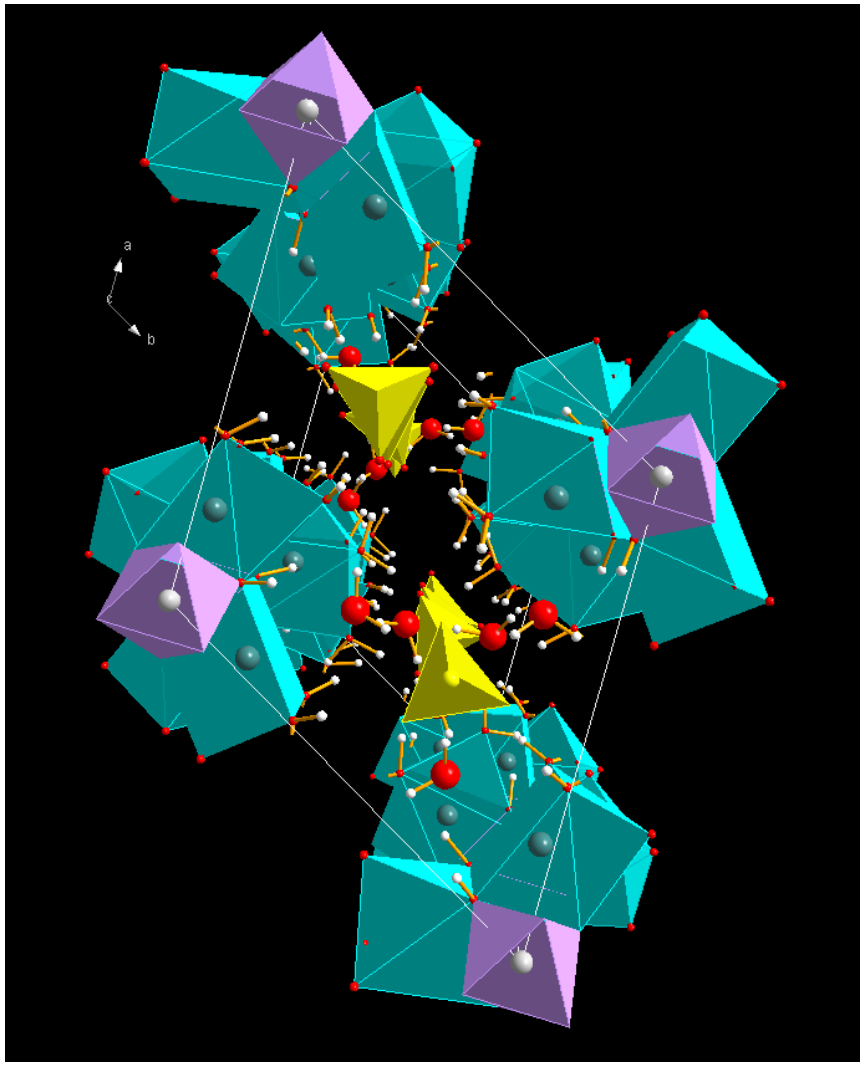
-> SO_4^{2-} ↔ CO_3^{2-}, CrO_4^{2-}, …

solid solution with thaumasite

$C_6As_3H_{32} \leftrightarrow C_6S_2s_2c_2H_{30}$

71





ettringite

crystal system: hexagonal

a=1.12 nm

c=2.14 nm

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

Hydrogarnets:

$C_3AS_xH_{6-2x}$

Solid solutions

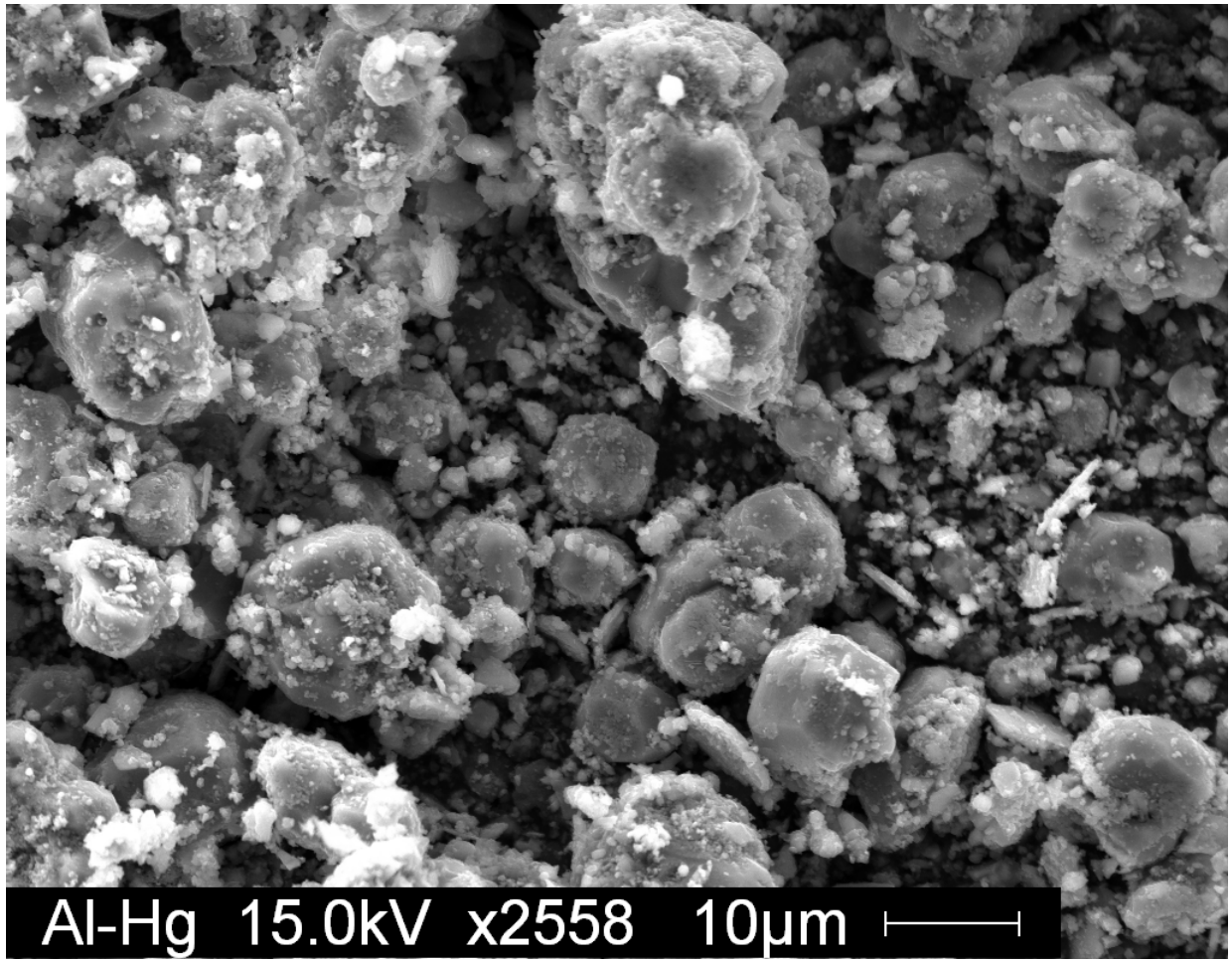
-> Al ↔ Fe

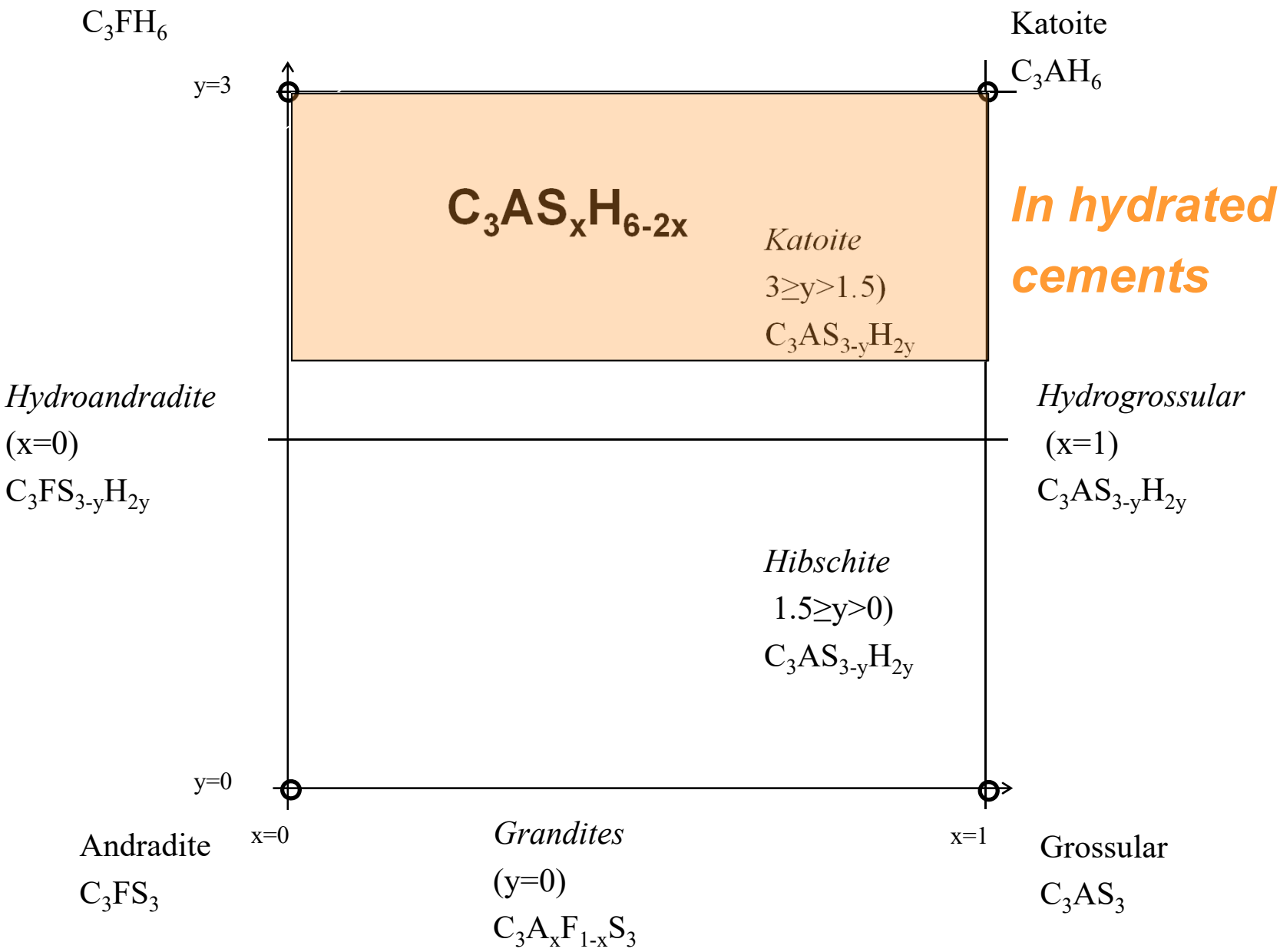
-> SiO_2^0↔ $2H_2O$

low water content

-> higher density

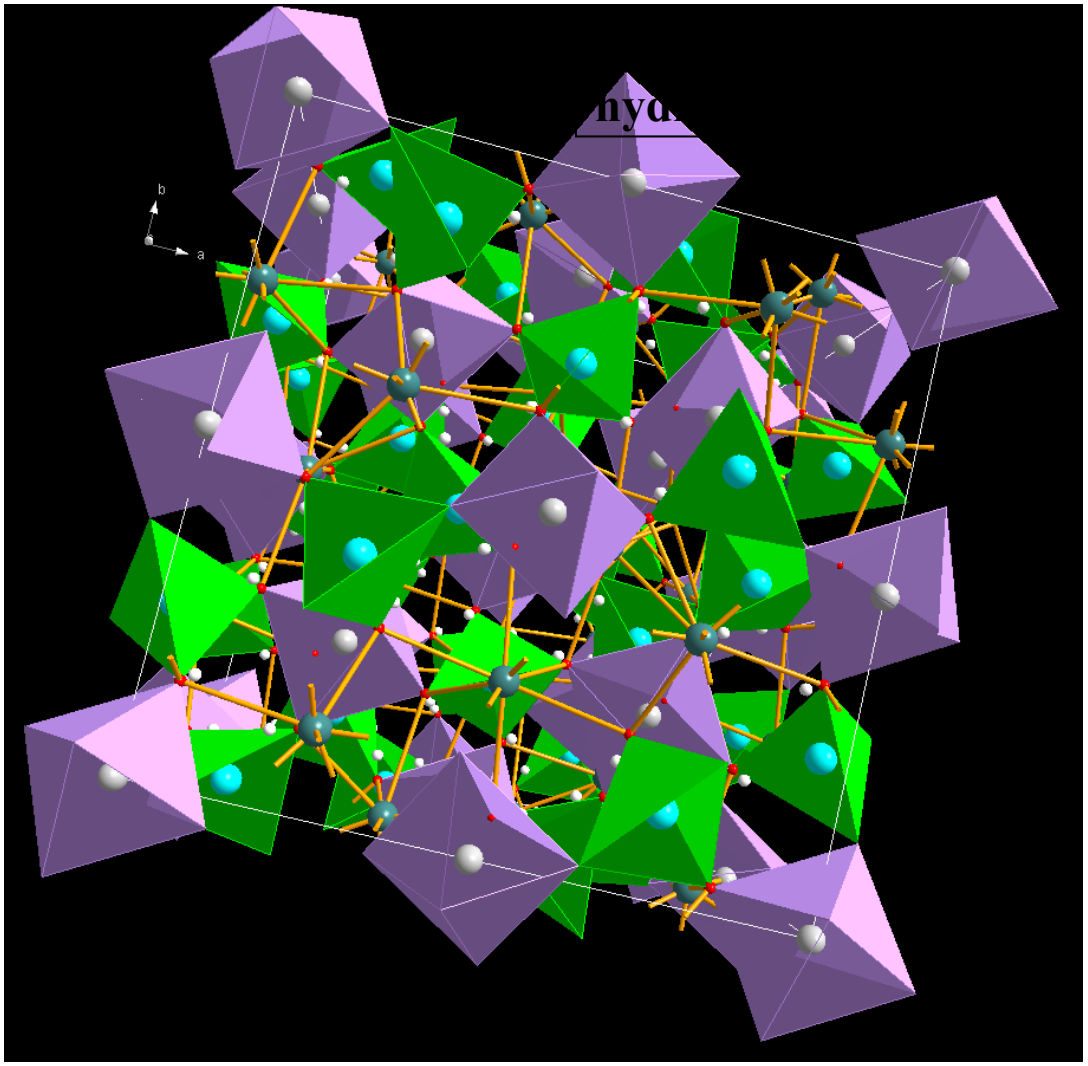
> 2.5 kg/dm^3




C_3FH_6
Katoite
C_3AH_6
y=3
$C_3AS_xH_{6-2x}$
Katoite
3≥y>1.5)
$C_3AS_{3-y}H_{2y}$
In hydrated cements
Hydroandradite
(x=0)
$C_3FS_{3-y}H_{2y}$
Hydrogrossular
(x=1)
$C_3AS_{3-y}H_{2y}$
Hibschite
1.5≥y>0)
$C_3AS_{3-y}H_{2y}$
y=0
x=0
x=1
Andradite
C_3FS_3
Grandites
(y=0)
$C_3A_xF_{1-x}S_3$
Grossular
C_3AS_3

Hydrogarnets:

$C_3AS_xH_{6-2x}$



$Ca_3 Al_2 Si_{1.092} O_{12} H_{7.632}$

Katoite (y=1.9):

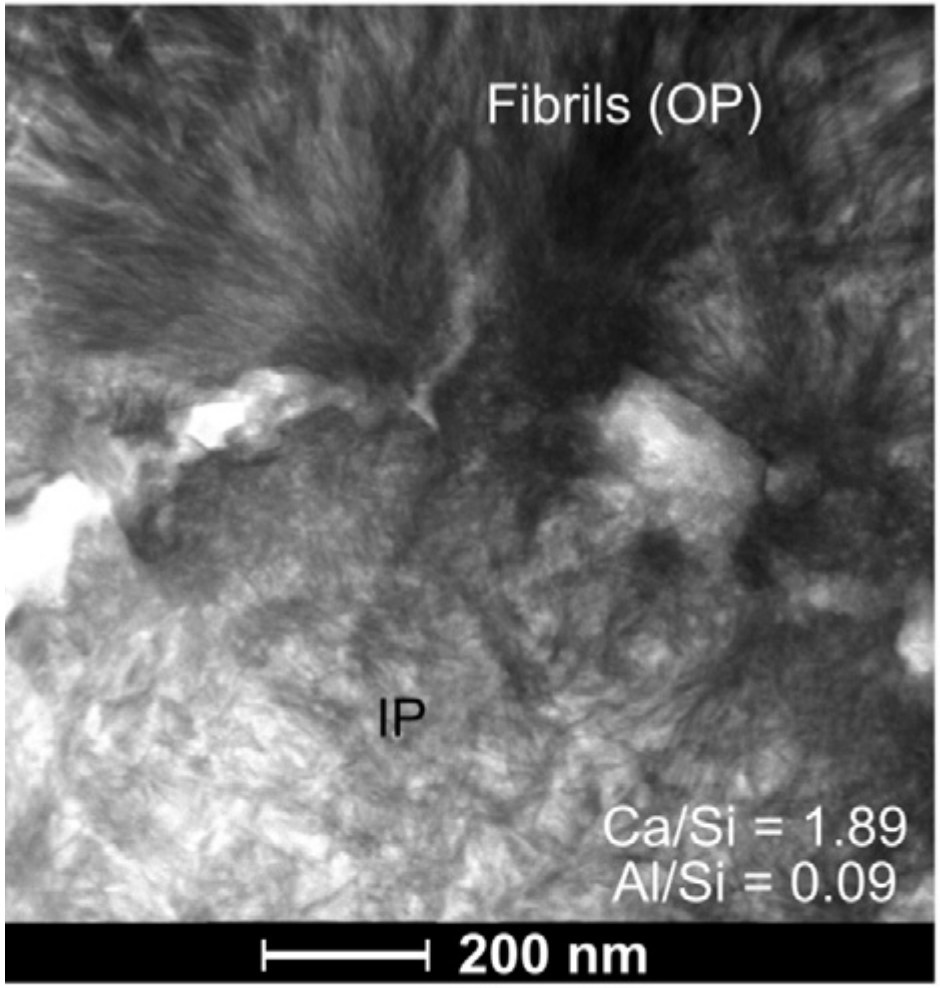
crystal system: cubic

a=1.22 nm

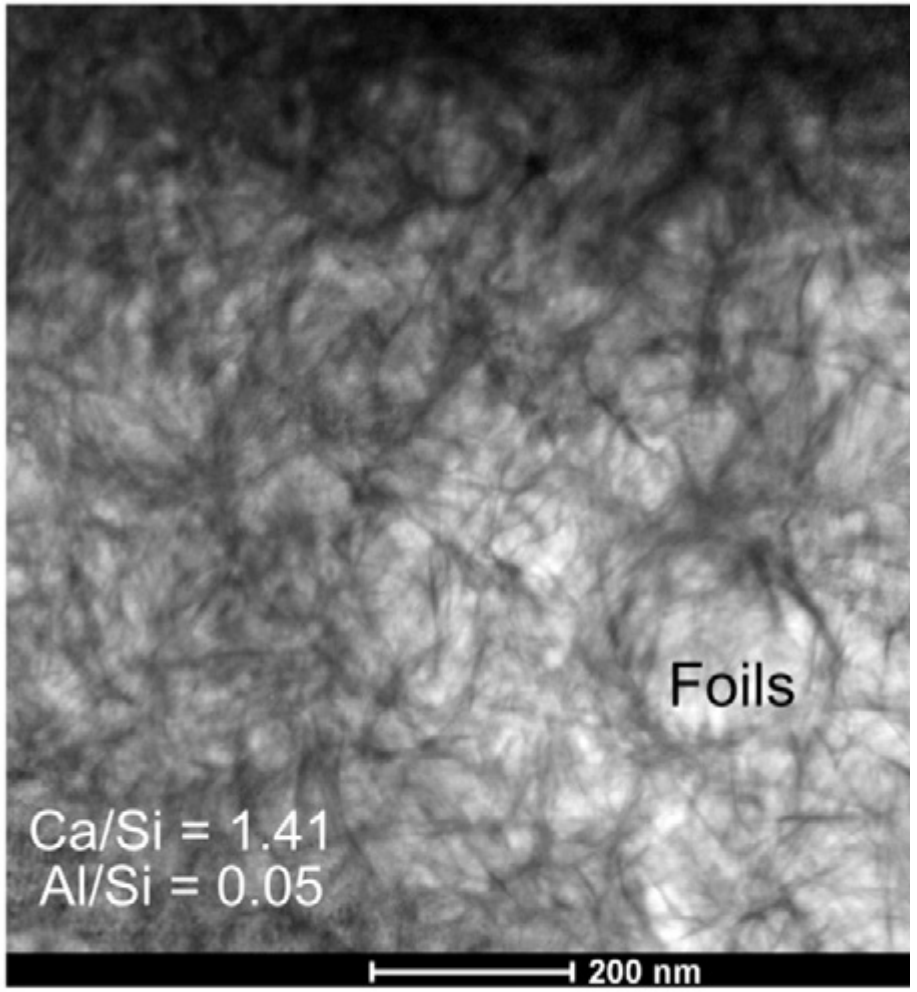
* Ferro et al. European J. Min. 15 (2003) 419- 426

C-S-H in cements

Foil like morphology at low Ca/Si



a) Plain cement (PC), 90 days, 20°C

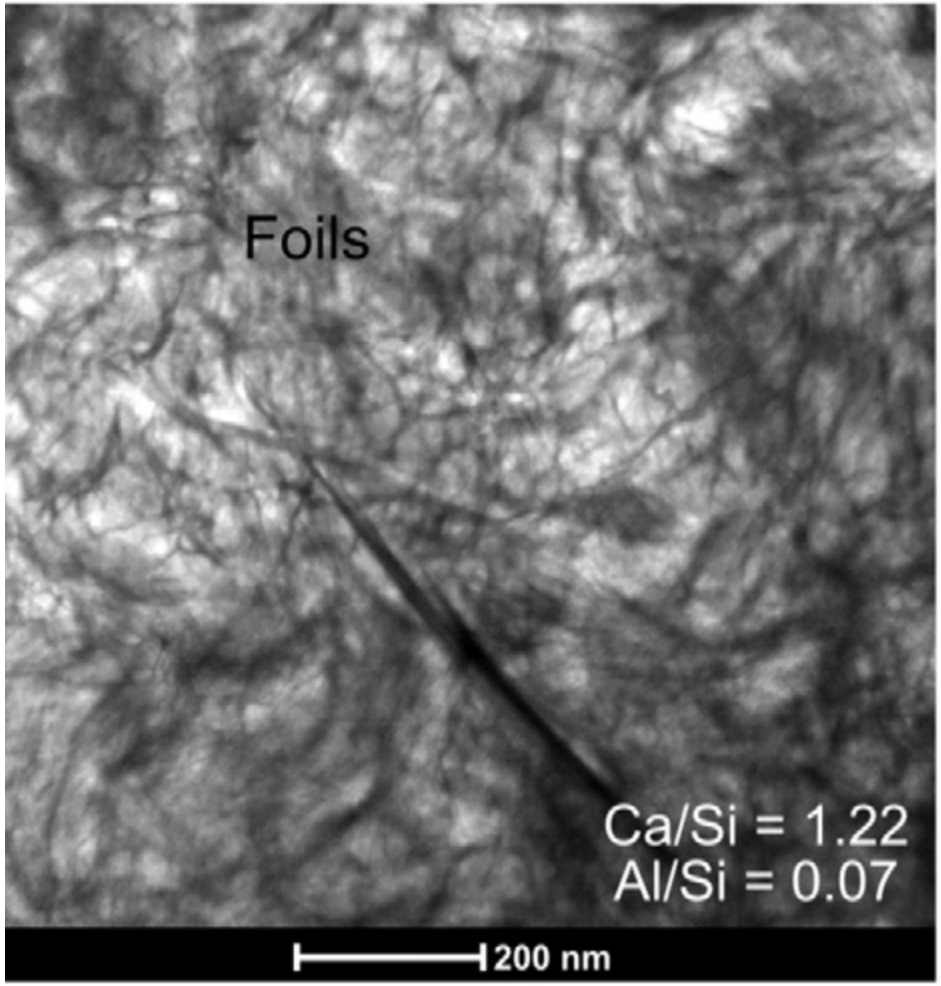


(b) PC 10SF, 90 days, 20°C

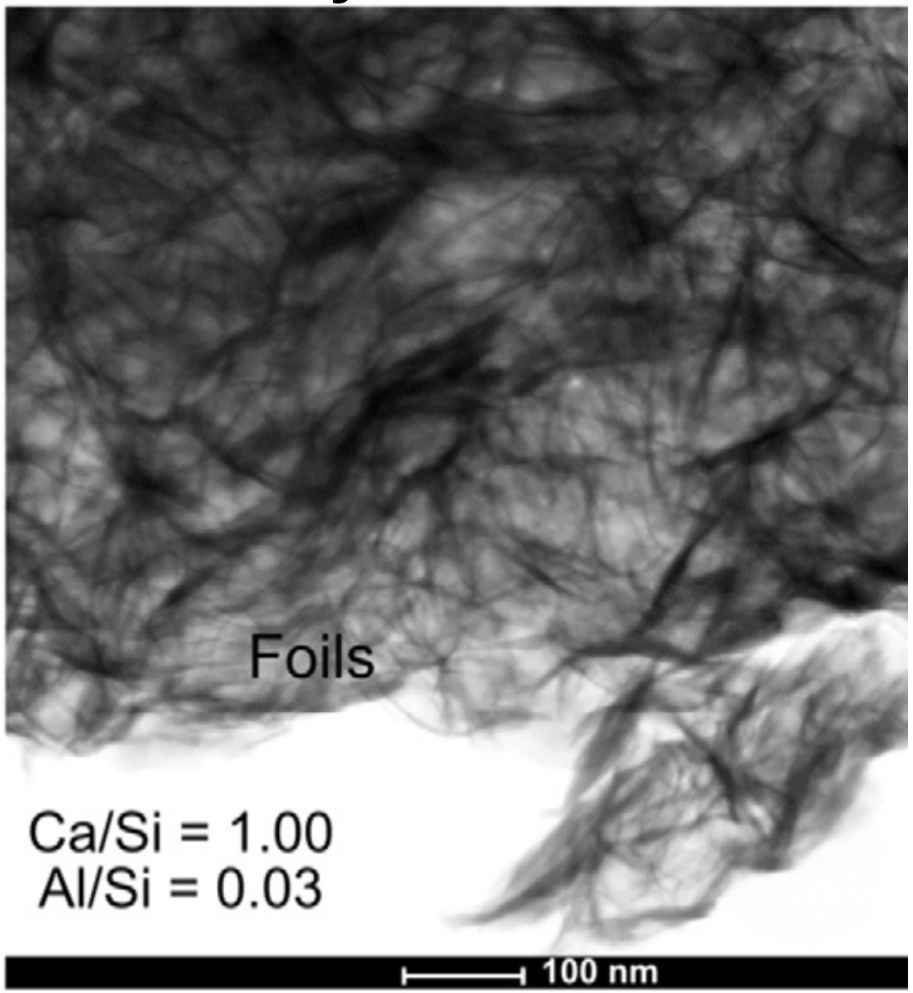
Rossen ea (2015) CCR 75

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

Comparable morphology in PC and synthetic C-S-H



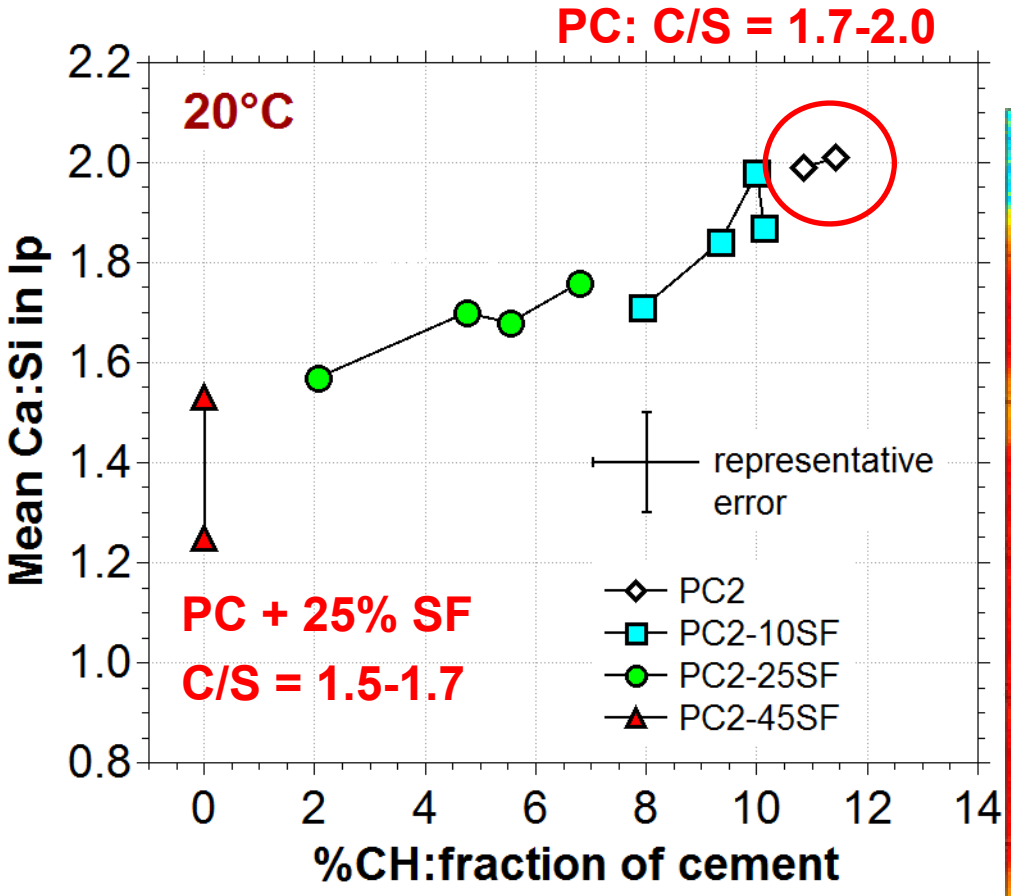
(c) PC(Q) 20SF, 90 days, 20°C

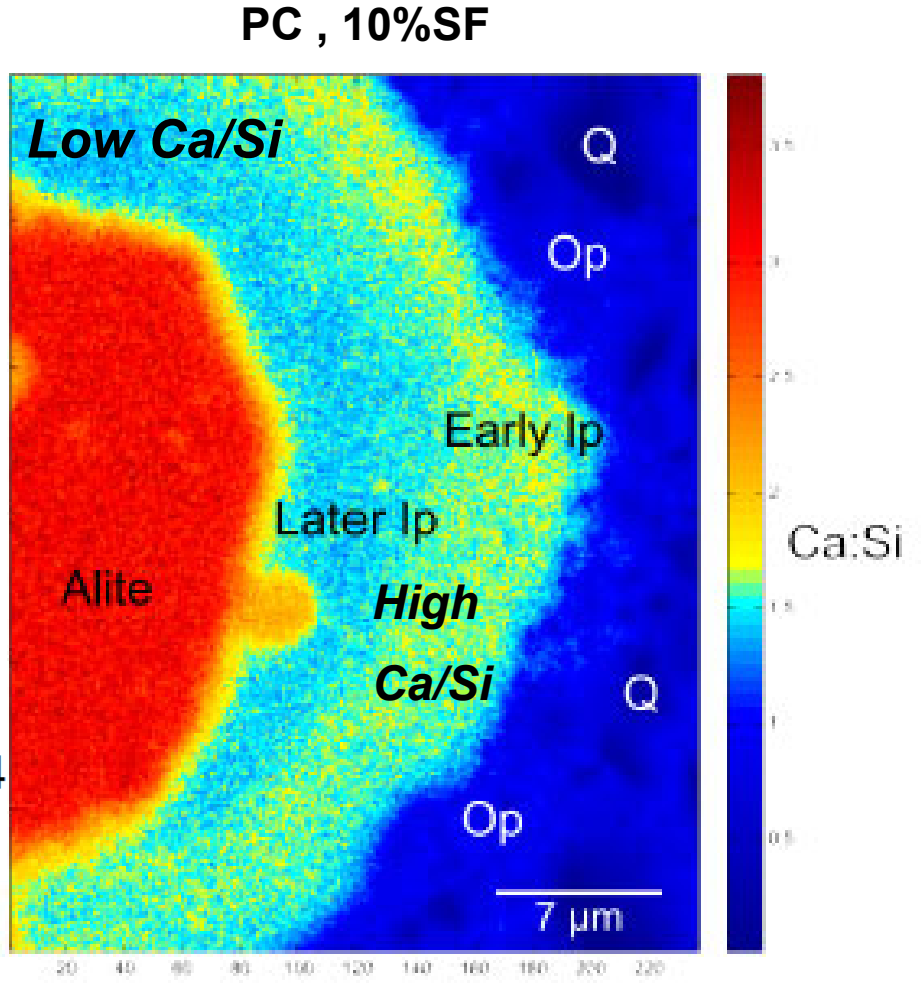


(d) Synthetic C-S-H, 20°C

Rossen ea (2015) CCR 75

C-S-H in Pastes





PC + SCM's:

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

Rossen ea (2015) CCR

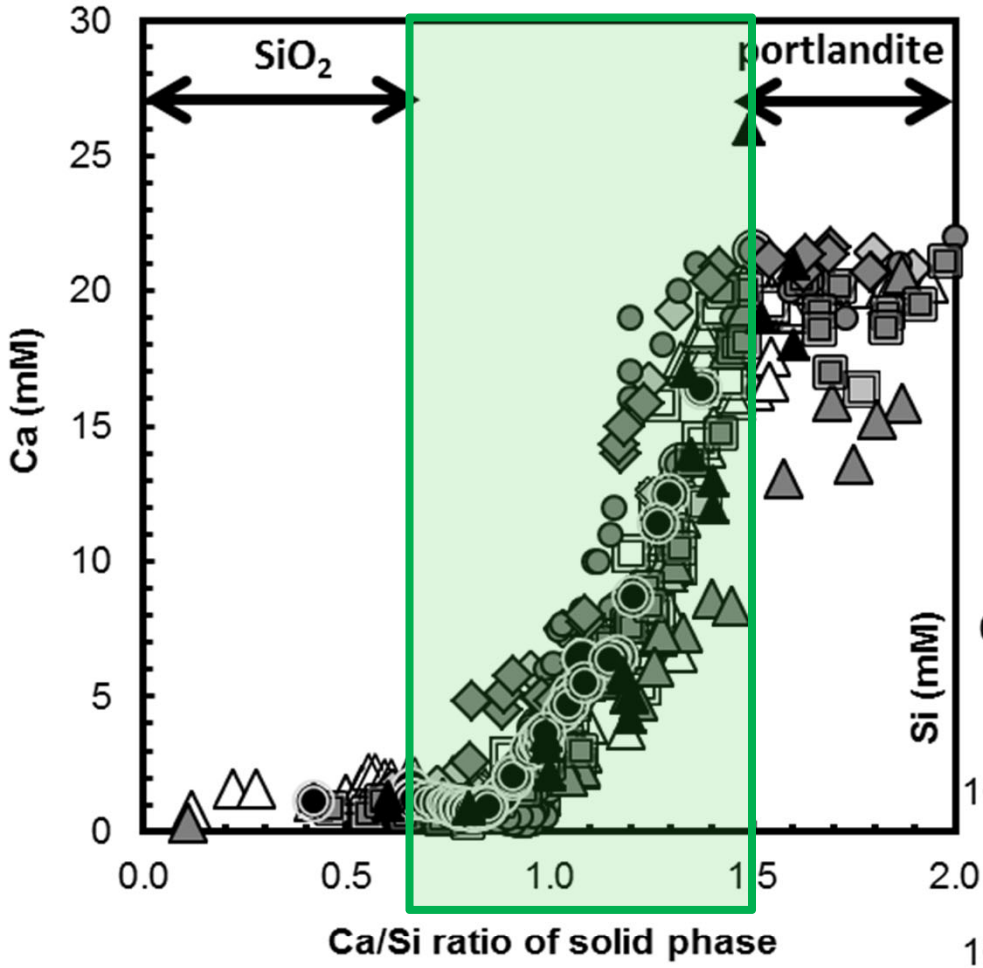
78

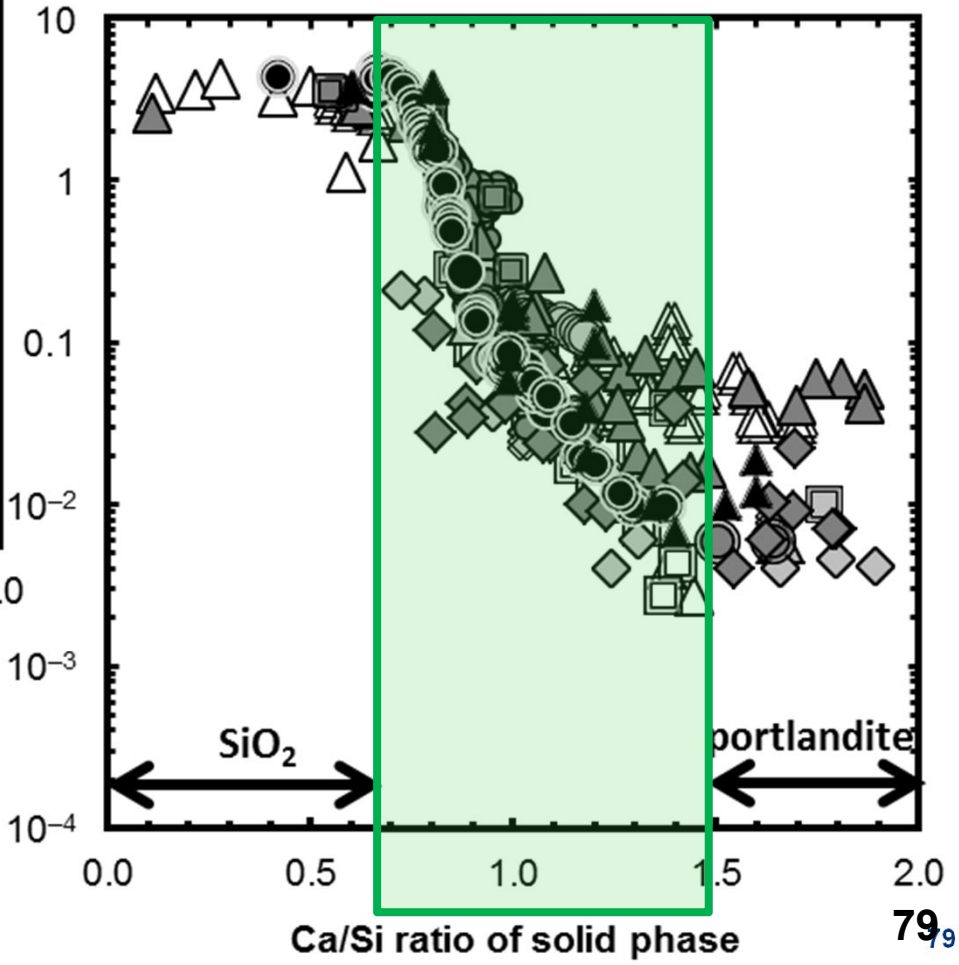
C-S-H: range of compositions

Empa
Materials Science and Technology

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

1.7-2 PC pastes





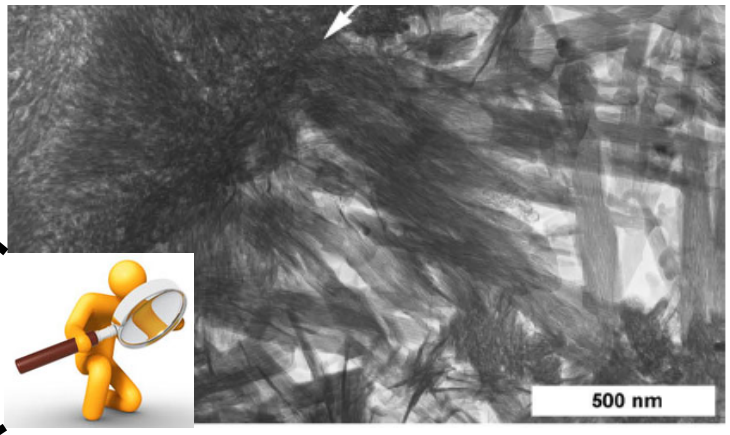
Lothenbach, Nonat (2015) CCR

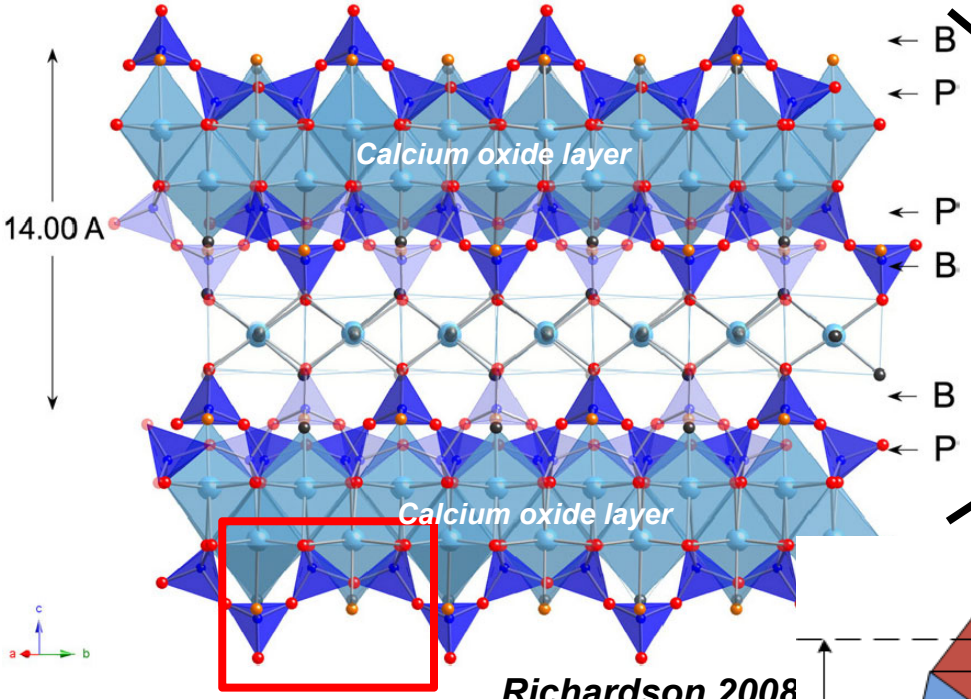
79

C-S-H

=> structurally imperfect tobermorite

Richardson, 2004

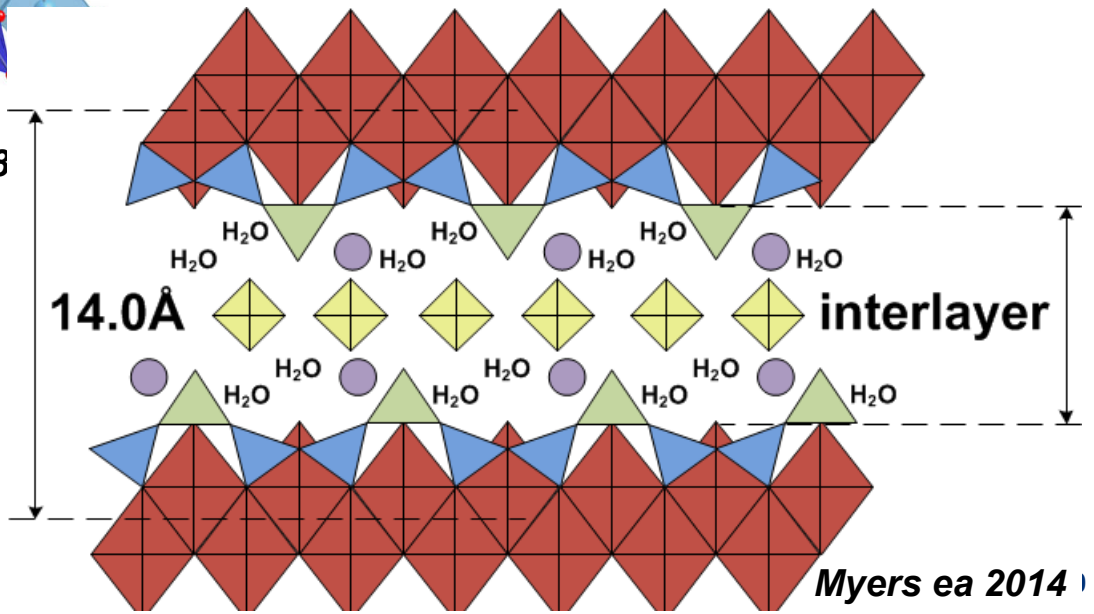




Richardson 2008

Dreierketten chain

Ca Si O



Myers ea 2014

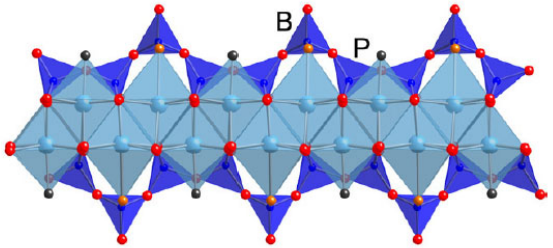
Richardson (2014):

Structure: clino tobermorite

Not ortho tobermorite

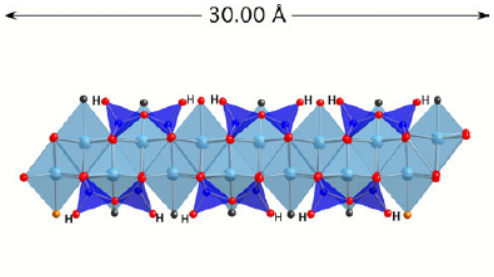
C-S-H structure: Variation of Ca/Si ratio

Richardson 2008



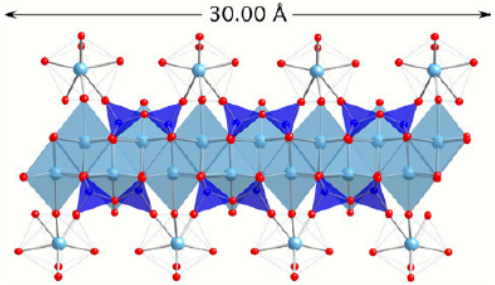
Ca/Si=0.67

- **Infinite chain**



Ca/Si=1.0

- **Dimer, pentamer, …**



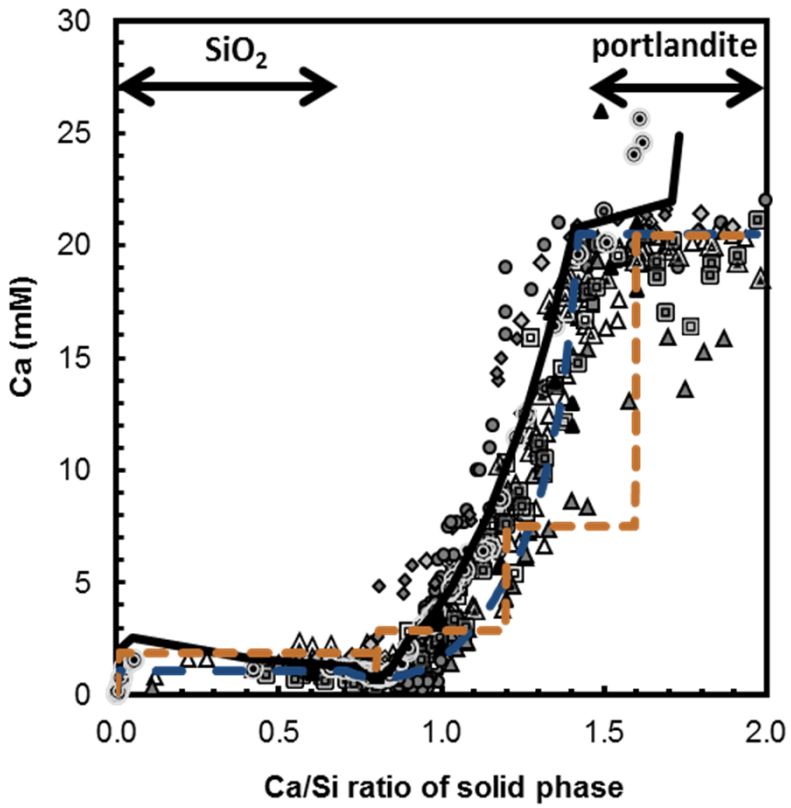
Ca/Si=1.50

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

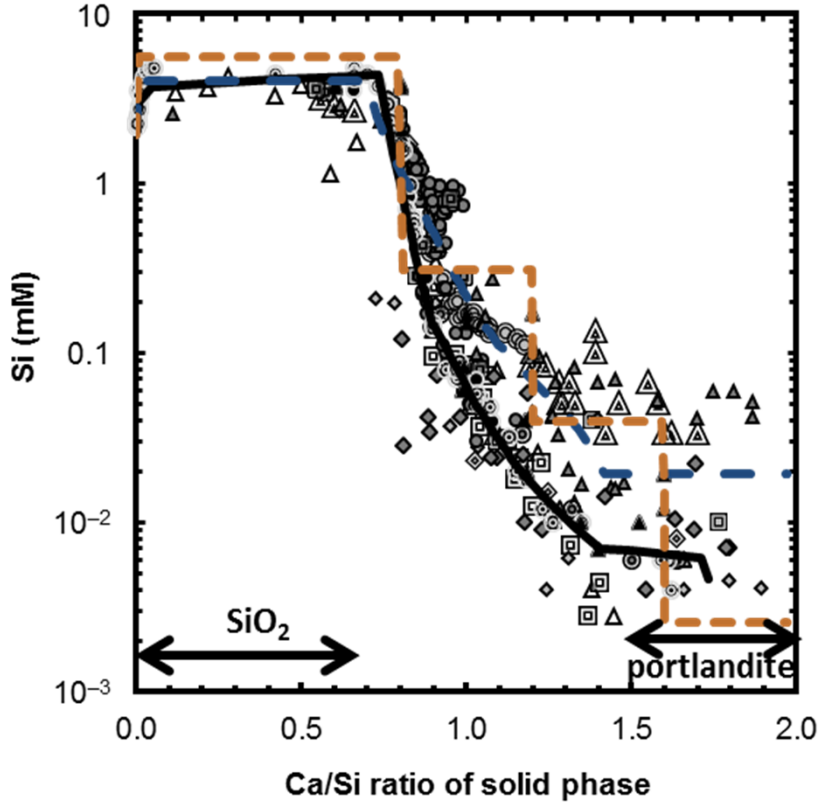
81

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

[Ca]



[Si]



3 different CSH

$C_{0.8}SH_{1.5}$
$C_{1.2}SH_{2.1}$
$C_{1.6}SH_{2.6}$

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

Solid solution

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

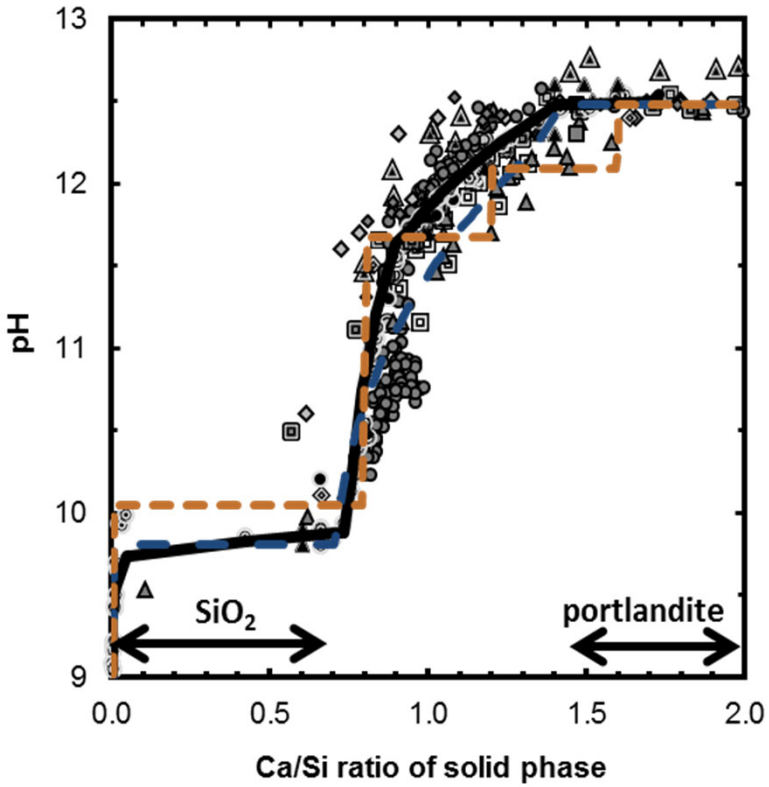
Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

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

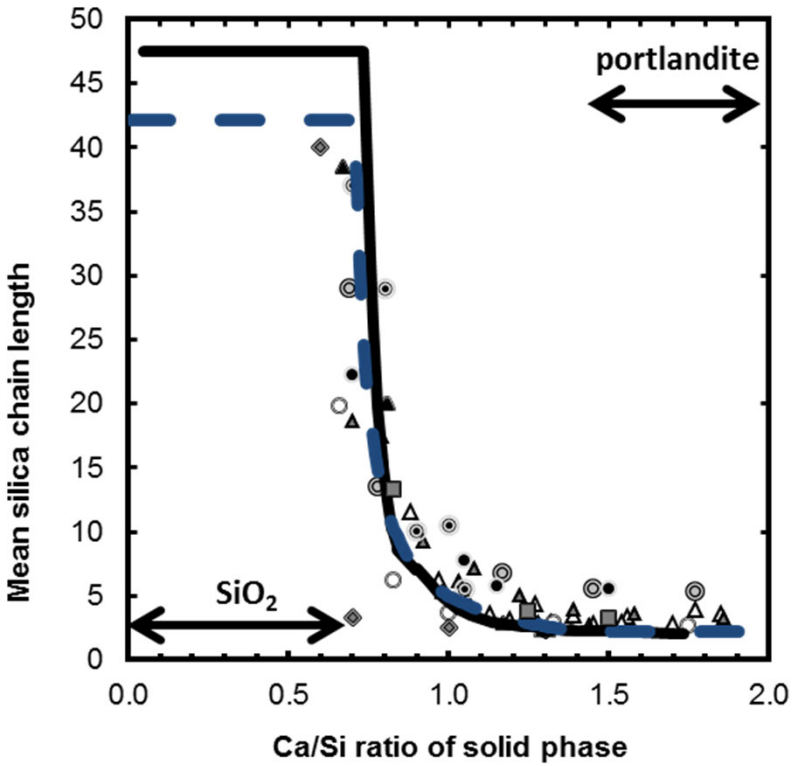
Different types of thermodynamic (geochemcial) models for C-S-H

Empa
Materials Science and Technology

pH



Mean Chain Length



3 different CSH

~~$C_{0.8}SH_{1.5}$~~
~~$C_{1.2}SH_{2.1}$~~
~~$C_{1.6}SH_{2.6}$~~

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

Solid solution

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

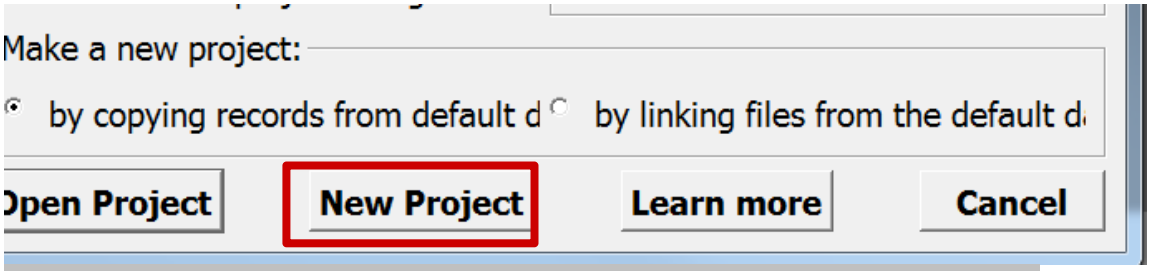
Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

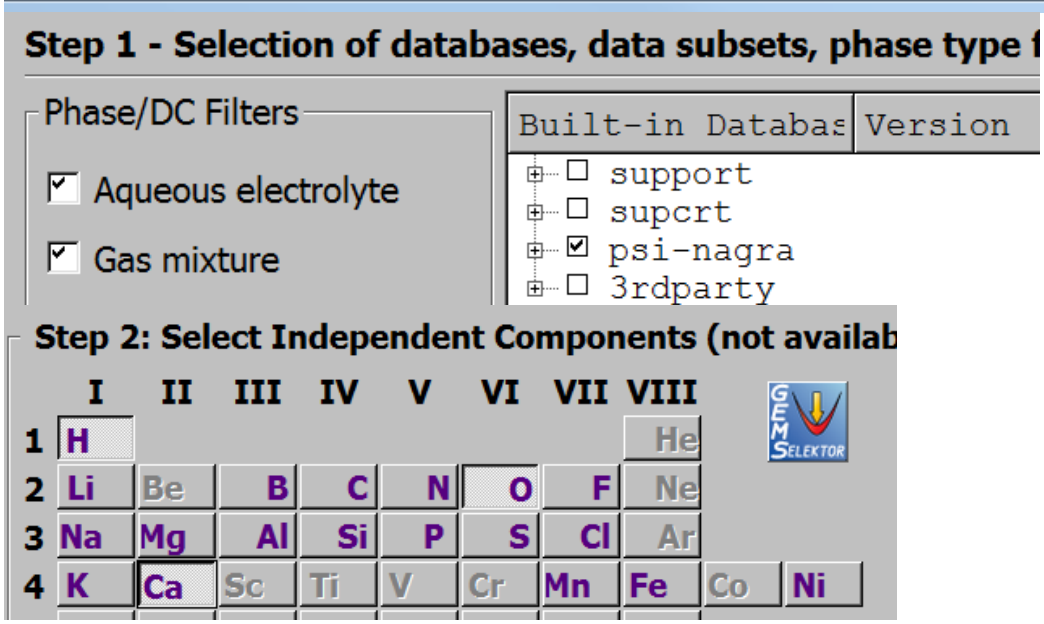
Haas, Nonat (2015) CCR 68, 124-138

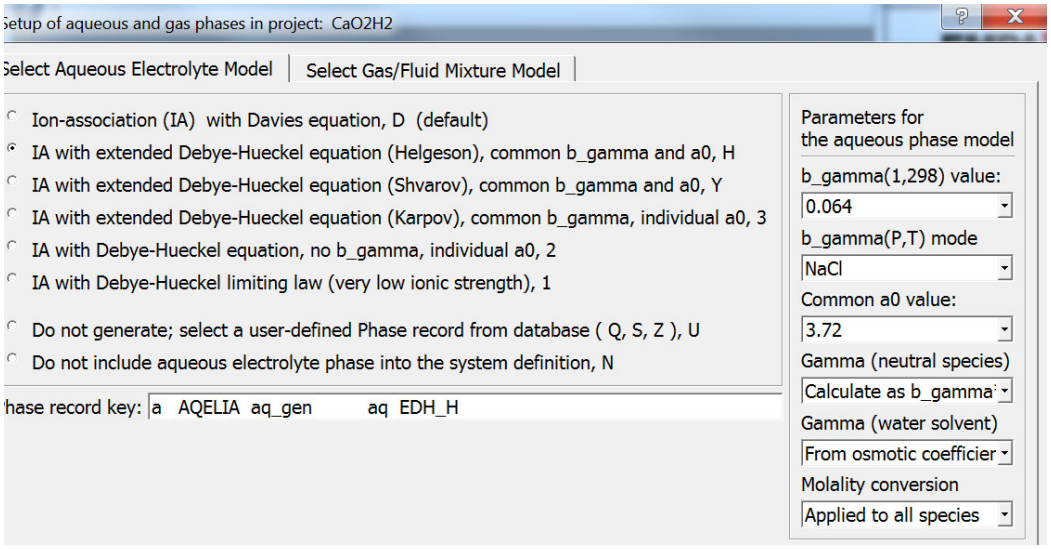
Thermodynamic data

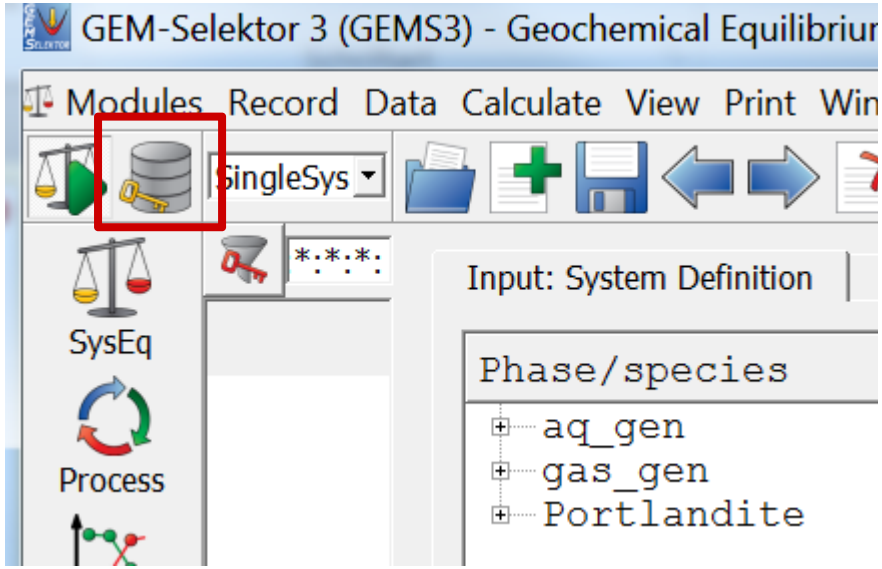
1. Databases
2. Portlandite solubility and speciation
3. Saturation indices
4. Hydrates
5. **How to create new entries for thermodynamic data in GEMS:**
   a) **Dcomp**
   b) **ReacDC**
   c) **Temperature and pressure plots**
   d) **Thermodynamic phases**

=> Self study







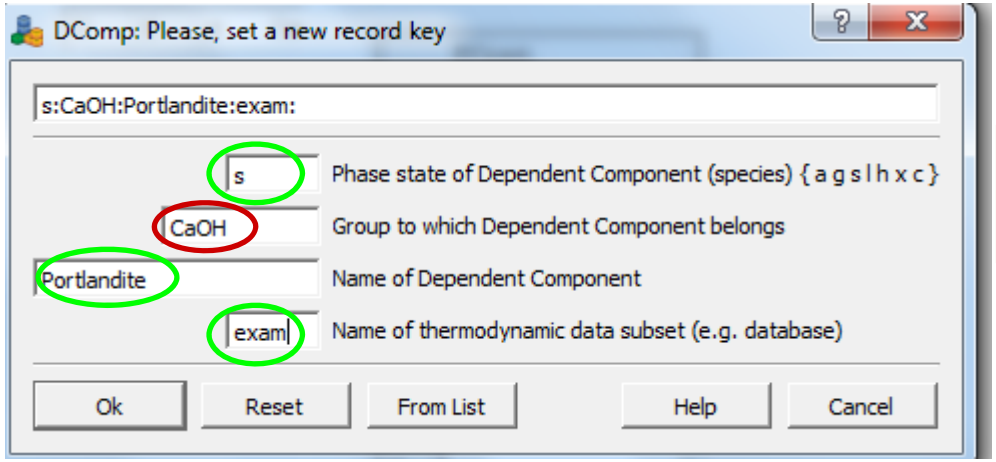


Create new project,
Name it CaO2H2,
Psi nagra database
Select Ca, O, H
Select Helgeson, NaCl
Open
Go back to database

DComp– creation of new entries

Empa
Materials Science and Technology

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

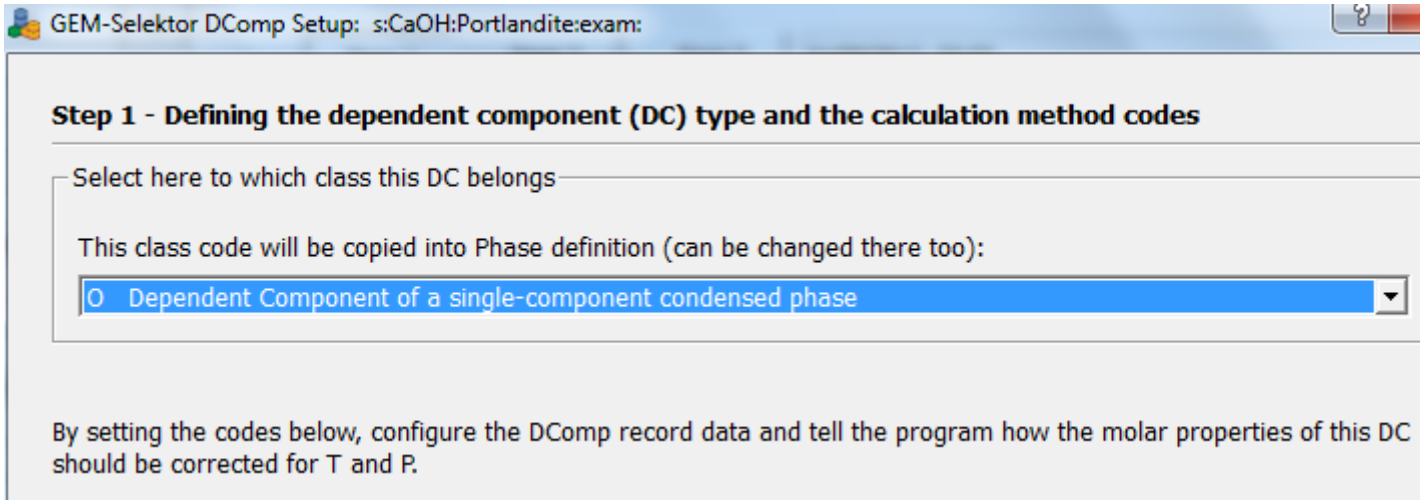
Comment (e.g. cem … cement; Exam: Example)

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

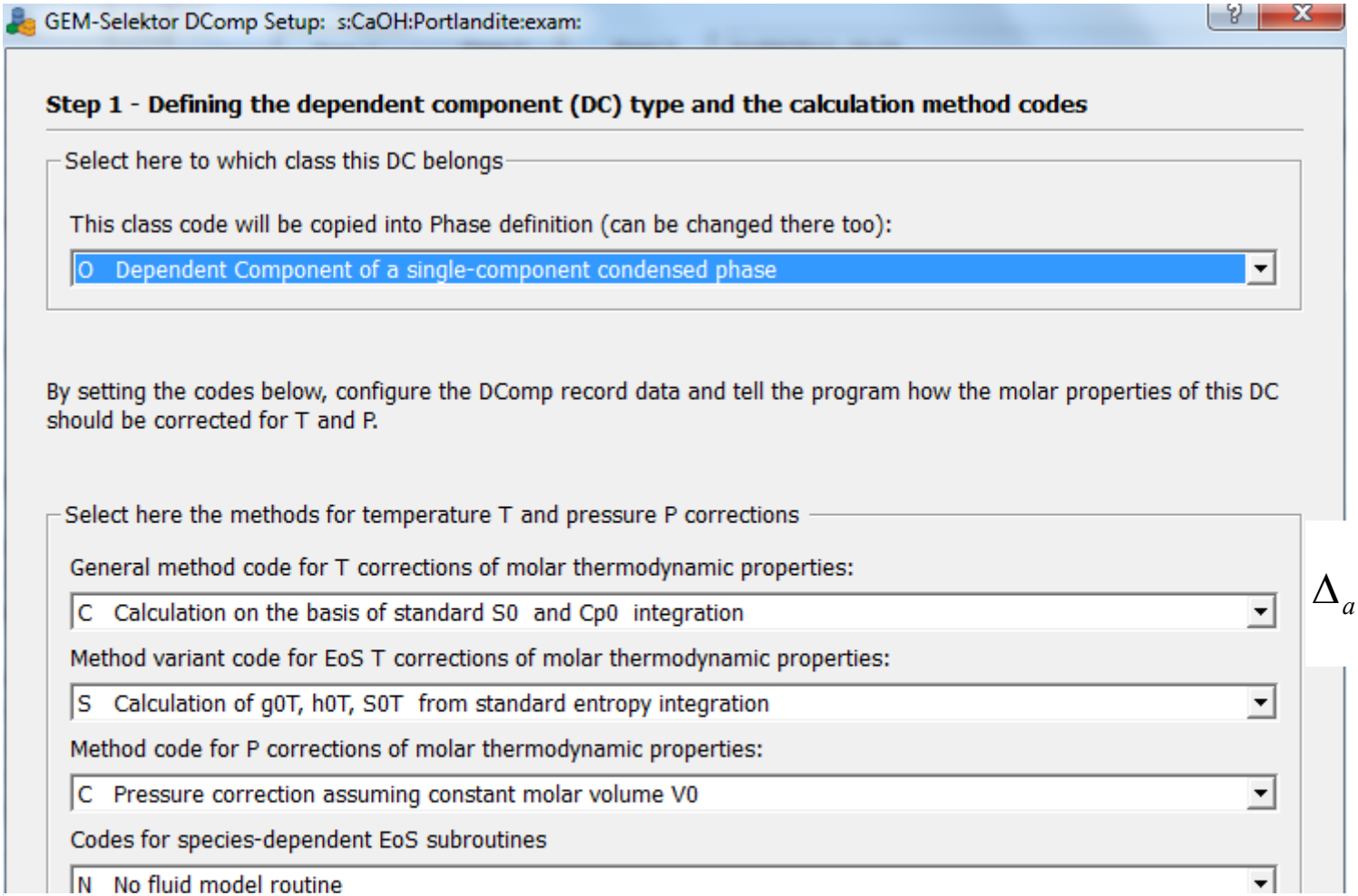
O: solid phase

S: Aqueous species

M: Major end-member *(solvent)*
J: Junior end-member *(solute)*



DComp– creation of new entries



Optional parameters for experienced users, else leave default values

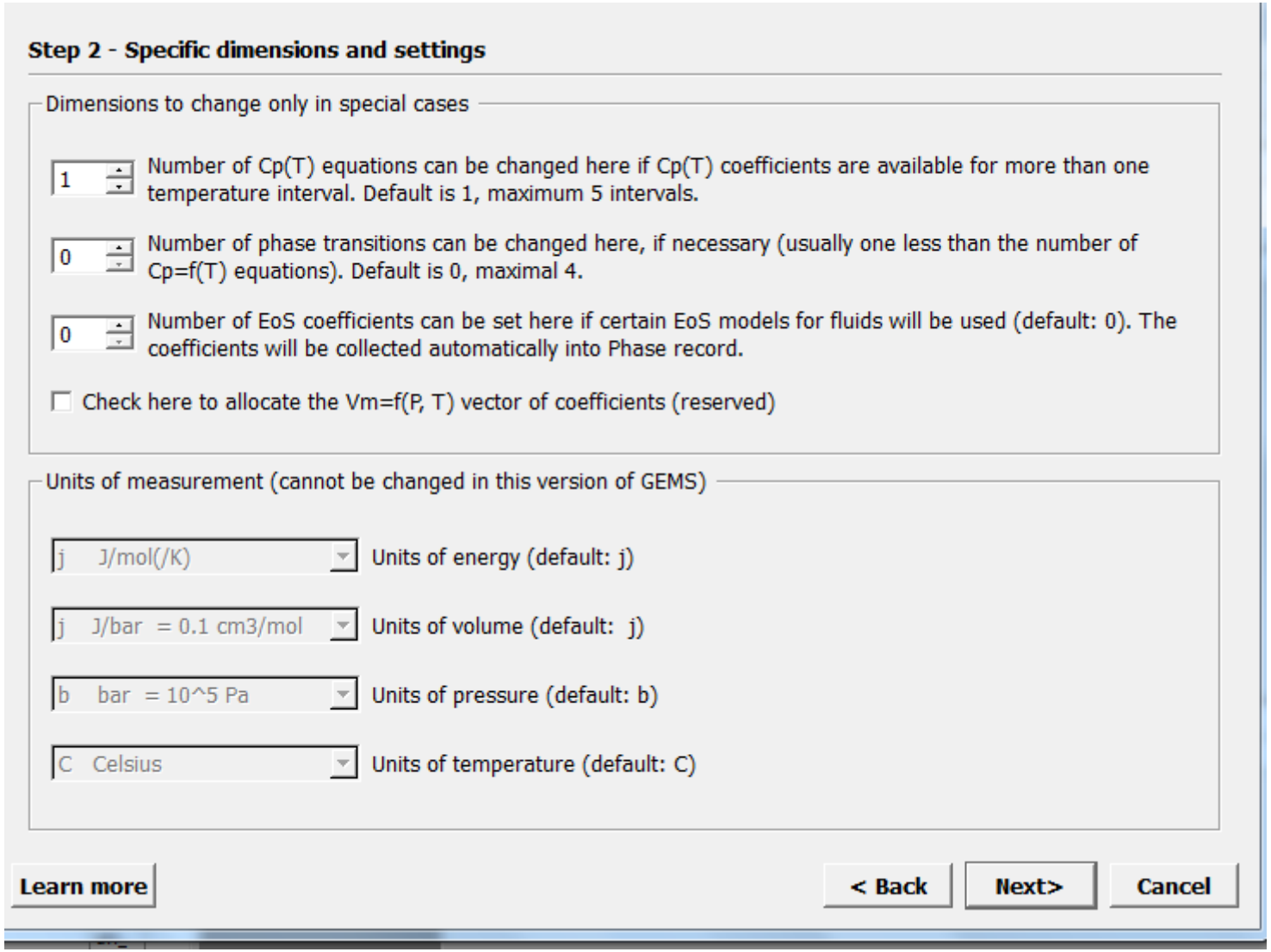
Default: "CS"

$$\Delta_a G^o_T = \Delta_f G^o_{T_0} - \int_{T_0}^{T} S^o_T dT$$

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

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	---	---

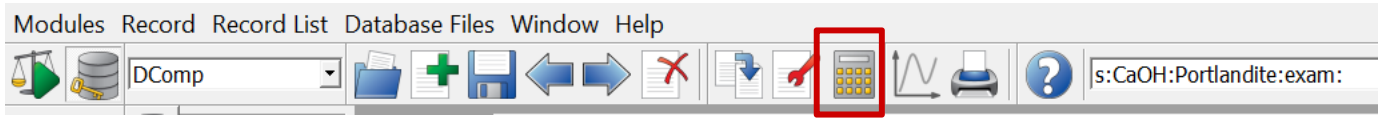
Robie_Hem:1995:pap: | All

Enter G (in J/mol) and S

H will be calculated

Cp on page 2

Press calculate



DComp :: Thermochemical/EoS data format f

Page 1 | Page 2 | 03/05/2017, 10

C S C N | O j j b C + -

Temperature range

	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

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

$$= 186.7 - 0.022*298.15 - 1600/\sqrt{(298.15)} = 87.5$$

Empa
Materials Science and Technology

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

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

name

Portlandite

Chemical composition (defined format)

Ca(OH)2

Mass (g/mol) from composition

charge

Activity coefficents

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 cm^3/mol)

Free energy (J/mol)

Enthalpy (J/mol) calcualted from S and G

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

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

Pressure Temperature

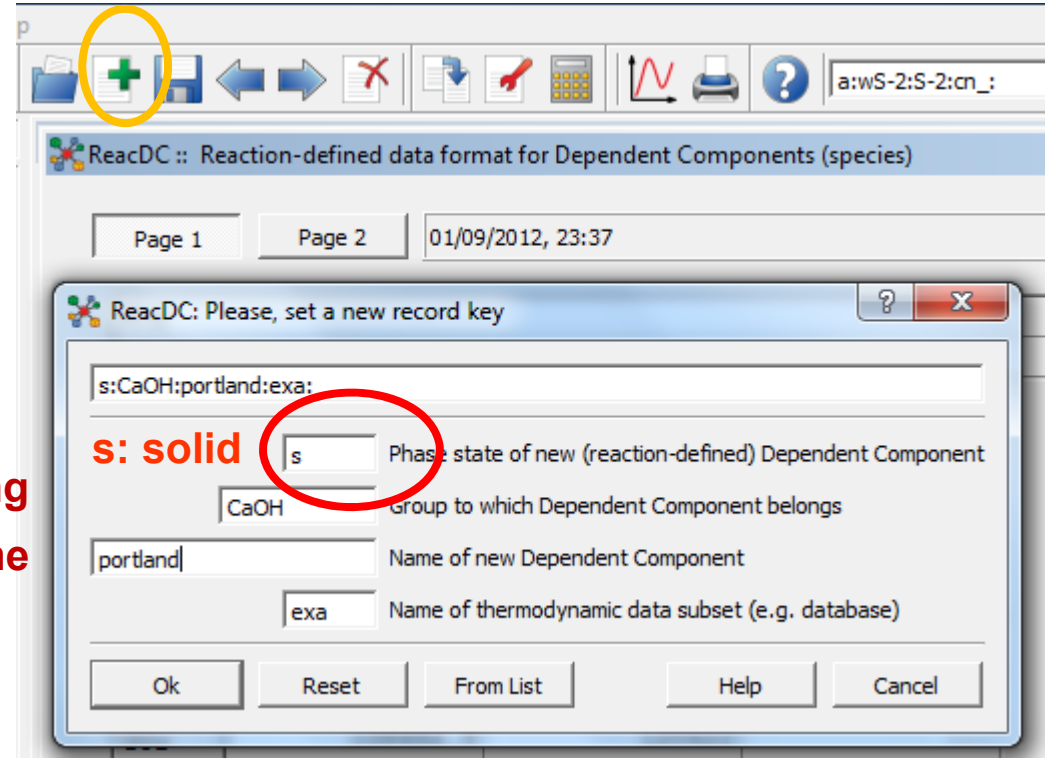
	log K_{S0}^*	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/r
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
$SiO_{2,am}$	1.476	-848.90	-903	41	47	0.034	$-1.13 \cdot 10^6$		29

3) GEMS: reactions (ReacDC): new

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

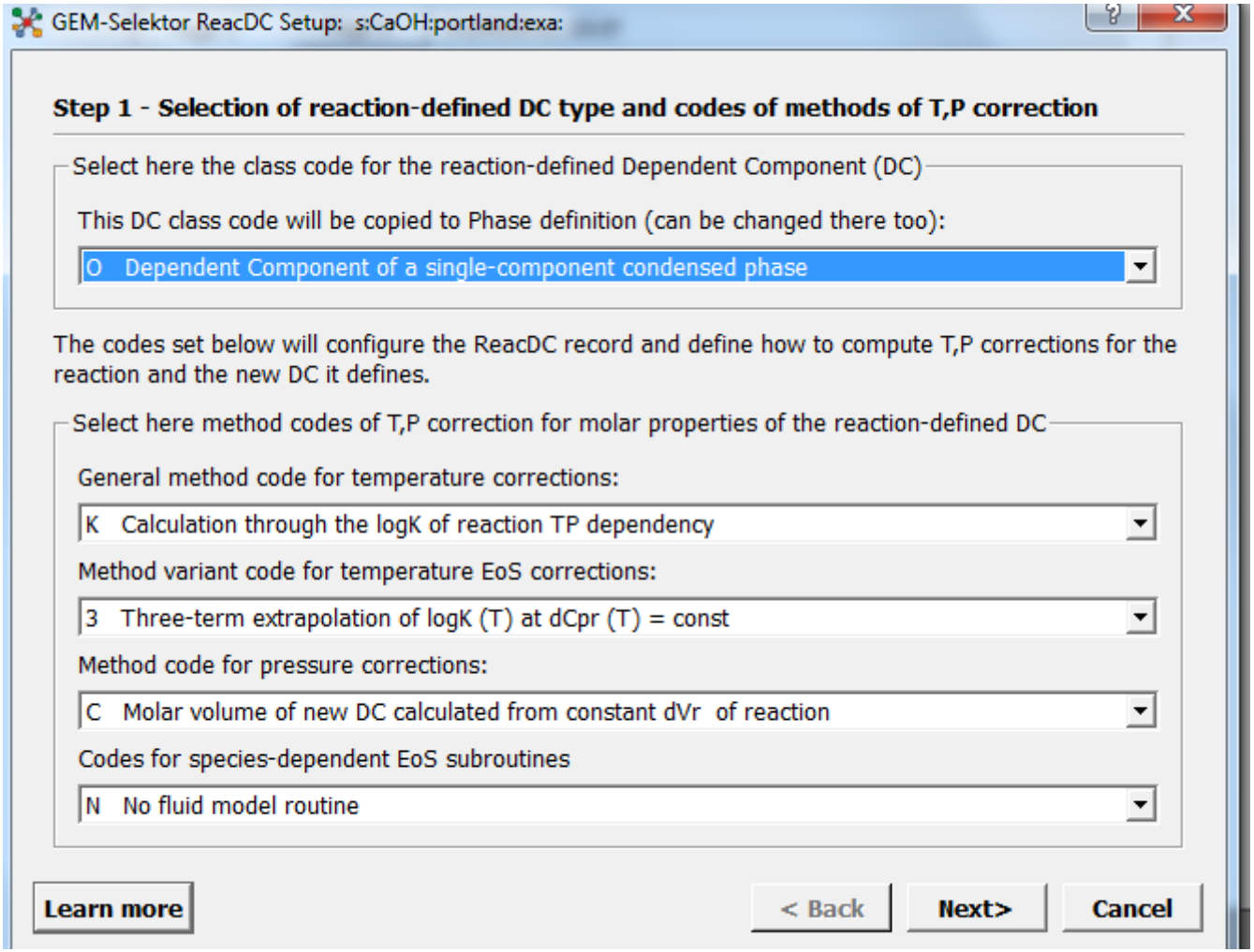
$\{Ca^{2+}\}\{OH^-\}/\{Ca(OH)_2\} = 10^{-5.2}$



Elements:ordering

Component name

Data base: «example»



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

(K) 3

Three-term extrapolation of log*K (T)* at *dCpr(T)* = const (preferable). Enter non-[empty] values into the `CpOr[0,0]` cell, and into either `HOr[0,0]` or `SOr[0,0]` cells (another must contain [empty]); enter a non-empty value in either `logKr[0,0]`, `logKr[0,1]` or `GOr[0,0]` cells (the other two cells and `GOr[0,1]` must contain [empty]). Then re-calculate and save the record. Use this code combination also for the PRONSPREP calculation.

C

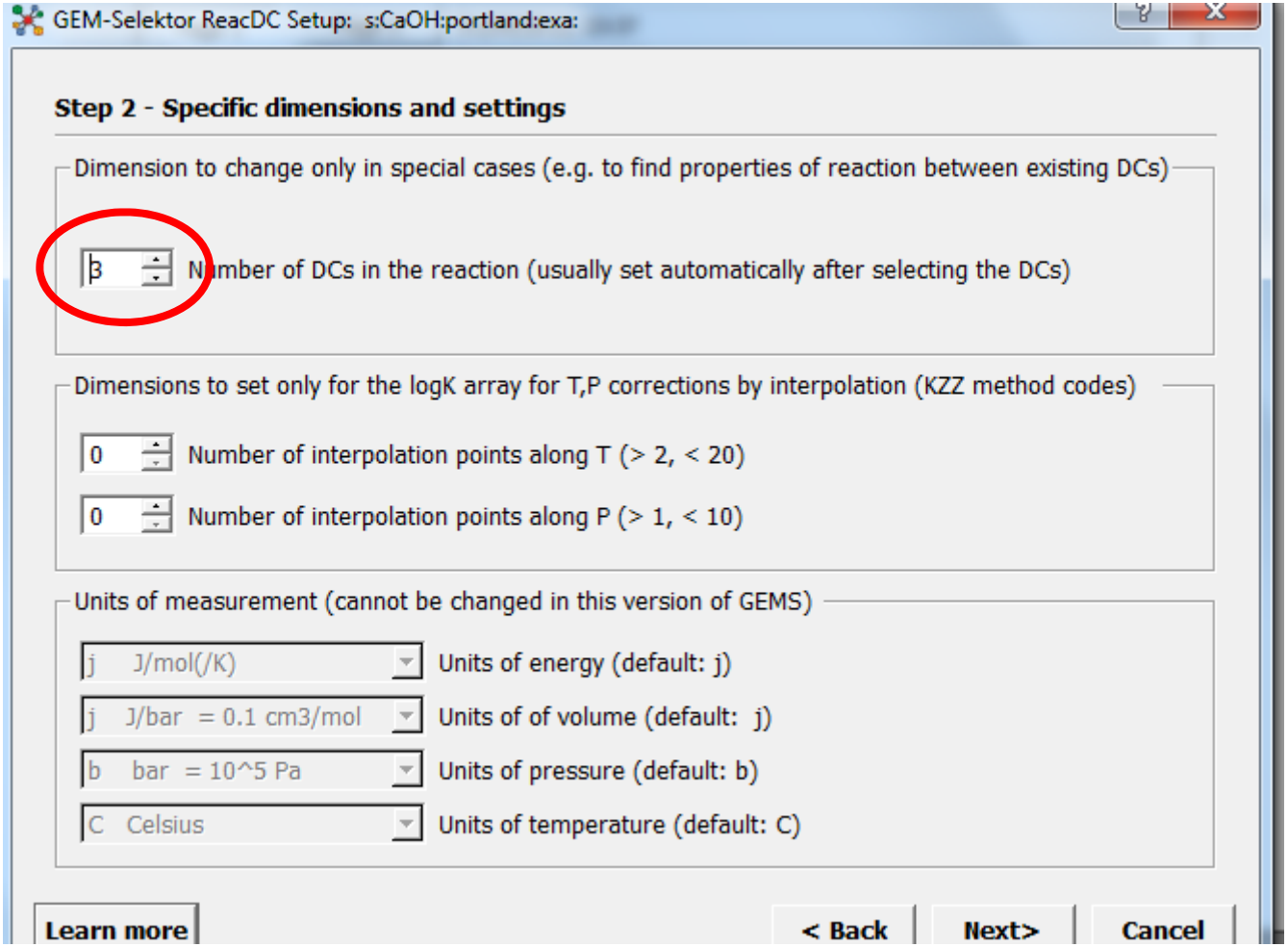
Molar volume of species V^o (in DComp) or dVr of reaction (in ReacDC) is assumed to be constant, independent of P and T (may be used for minerals up to a 1-2 kbar pressures at low-to-moderate temperatures).

3) GEMS: reactions (ReacDC): new

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

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



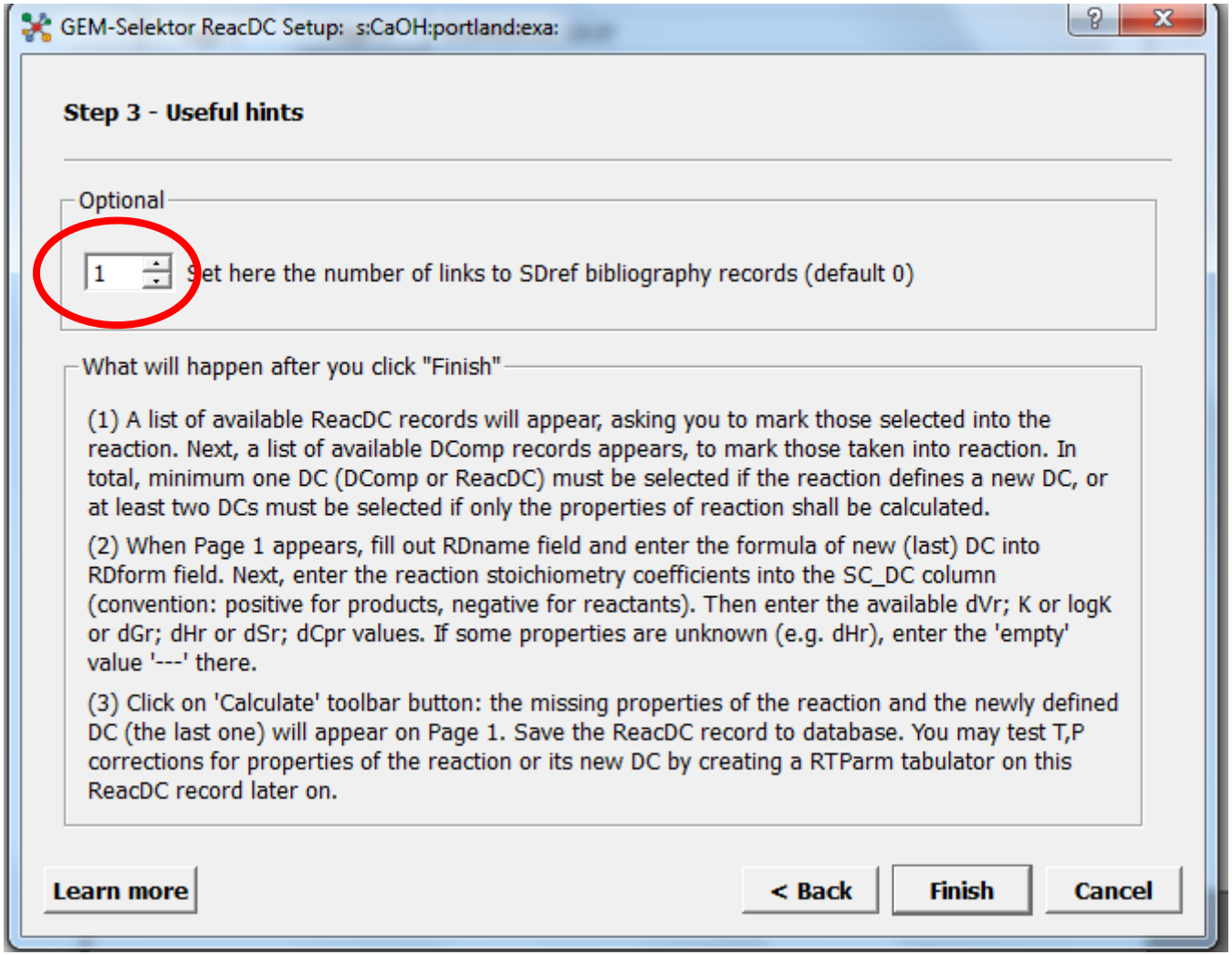
Ca^{2+}, OH^-, $Ca(OH)_2$

3) GEMS: reactions (ReacDC)

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

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



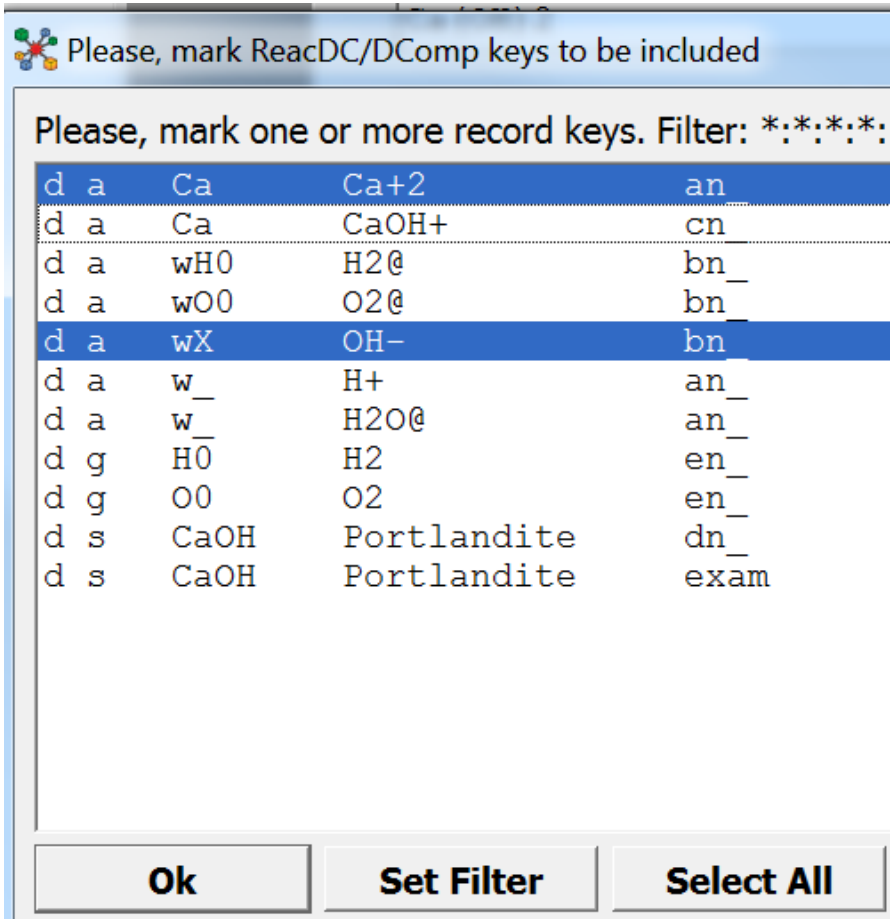
Literature reference

3) GEMS: reactions (ReacDC)

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

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



Chose existing compounds;

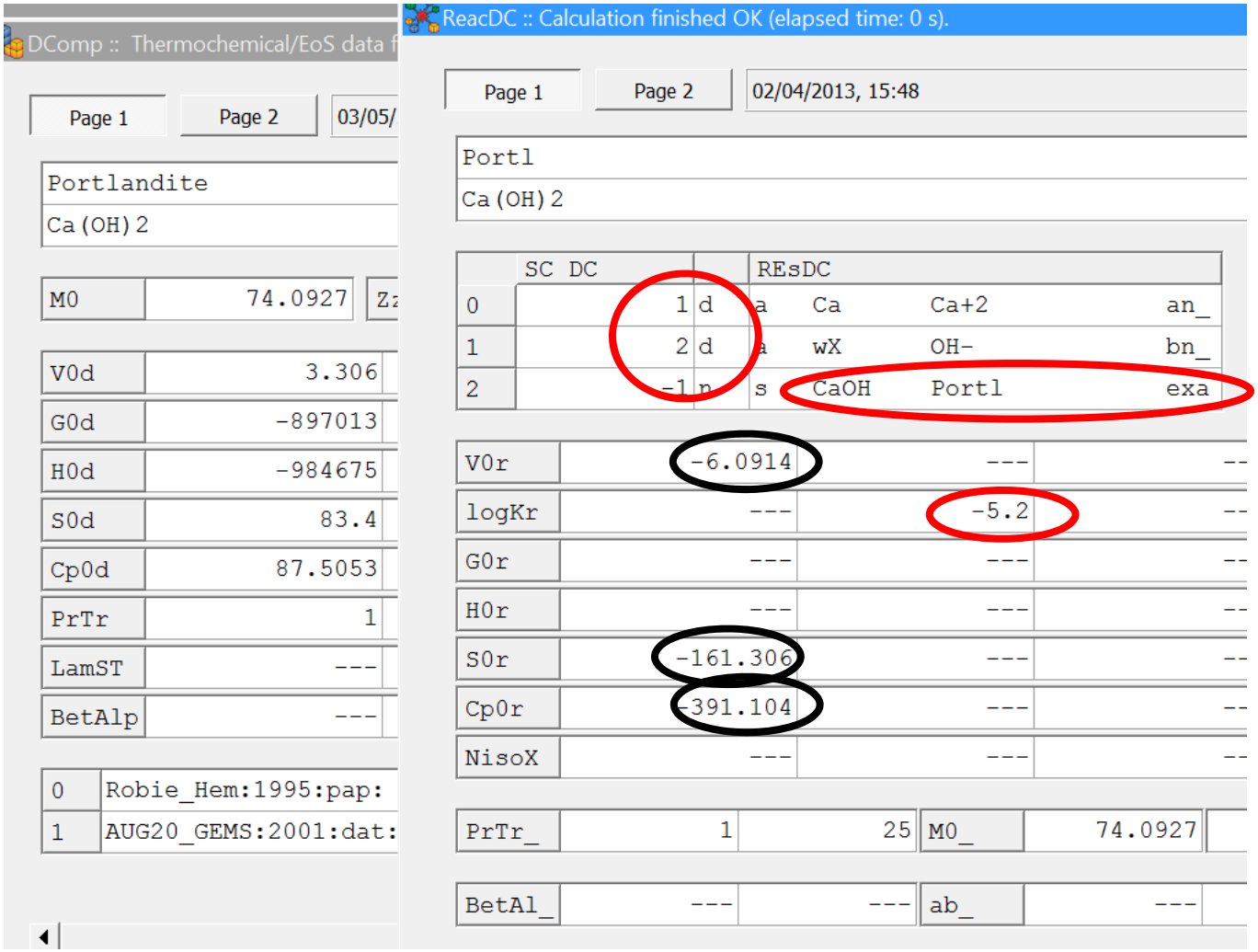
New compound «$Ca(OH)_2$» will be made by the programme

3) GEMS: reactions (ReacDC)

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

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



Reaction coefficients

New component

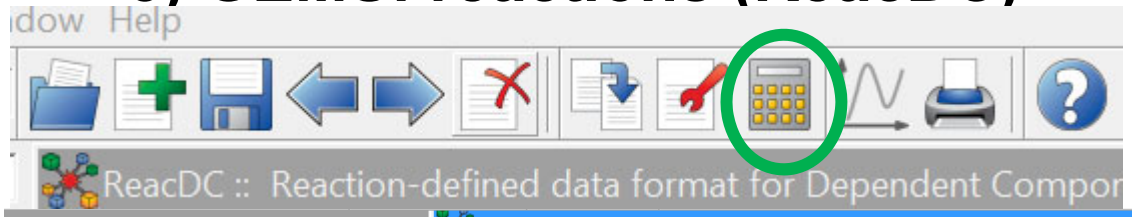
Volume changes

Log K

S reaction

Cp reaction

3) GEMS: reactions (ReacDC)



Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

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

DComp :: Thermochemical/EoS data f

Page 1 | Page 2 | 03/05/

Portlandite
Ca(OH)2

M0	74.0927
V0d	3.306
G0d	-897013
H0d	-984675
S0d	83.4
Cp0d	87.5053
PrTr	1
LamST	---
BetAlp	---

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

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

Portl
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	Portl	exa

V0r	-6.0914	3.30596
logKr	6.3095734e-006	-5.2
G0r	29681.819	-897011.82
H0r	-18411.565	-984675.43
S0r	-161.306	83.3999
Cp0r	-391.104	87.505

Volume

Gf

S

Cp

	log K_{SO}*	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [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	$-1.13\cdot10^6$		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			O	j	j	b	C		+	-	-	-	-	-	-	-

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

	TCint
0	0
1	426.85

	P int
0	0
1	1

	aiLgKr
0	128.397
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 $\Delta Cp_T = \Delta Cp_{T_0} = const$

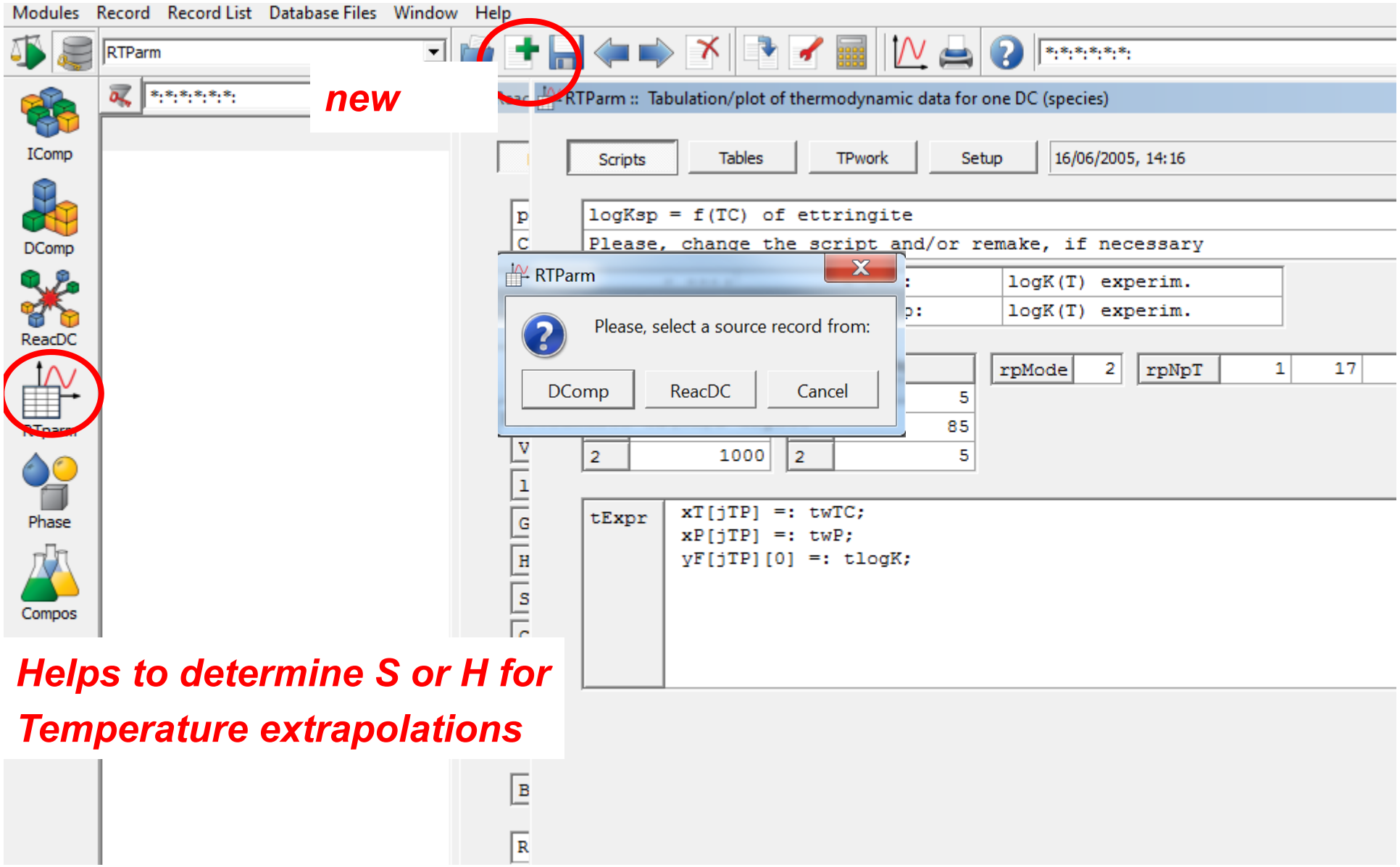
$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

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

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H^0_{T_0} - \Delta_r Cp_{T_0} T_0)$$

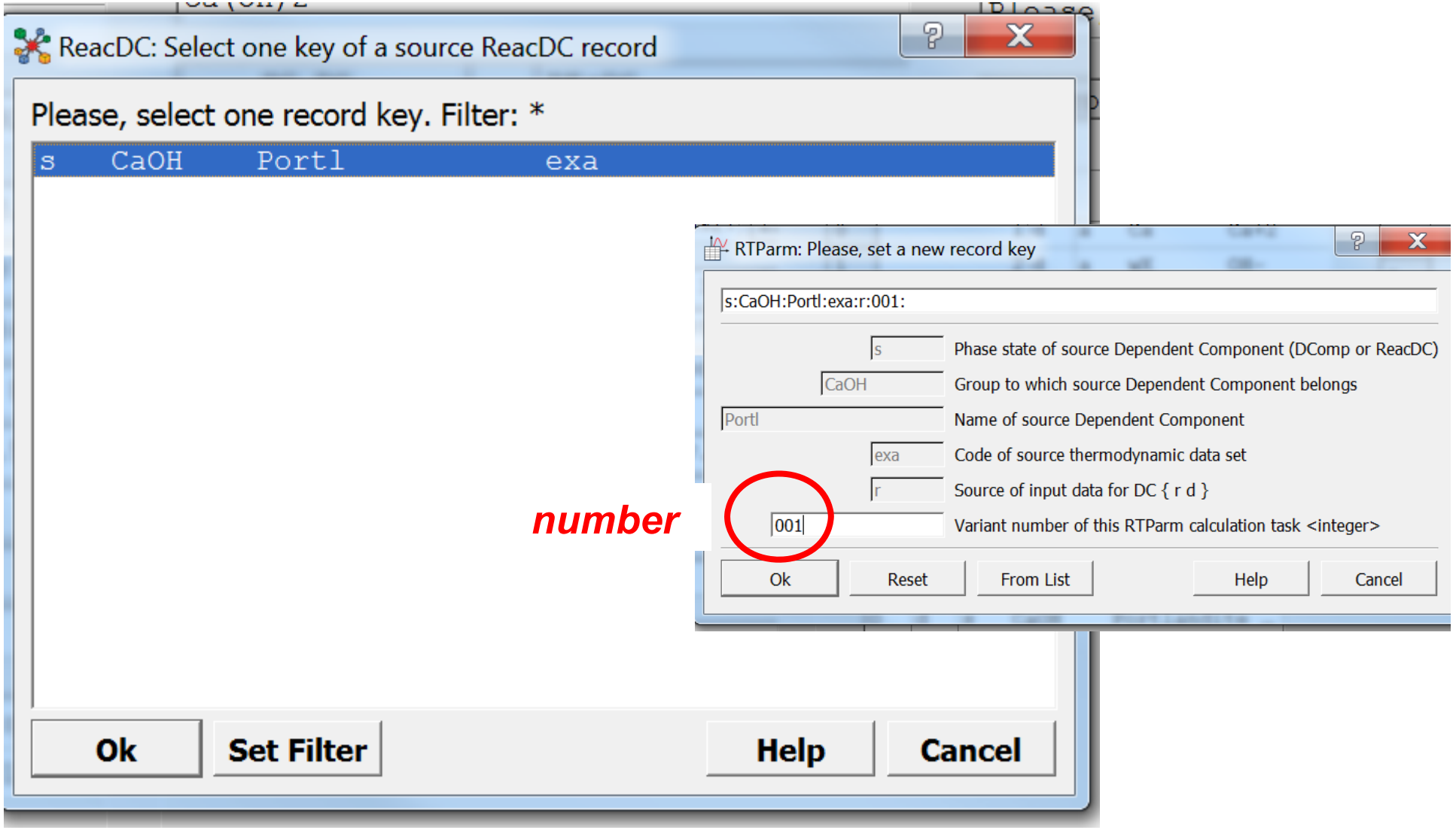
$$A_3 = \frac{0.4343}{R} \cdot \Delta_r Cp_{T_0} = \frac{0.4343}{8.3145} \cdot -391.1 = -20.43$$

4.) Plot of temperature/pressure dependent thermodynamic data

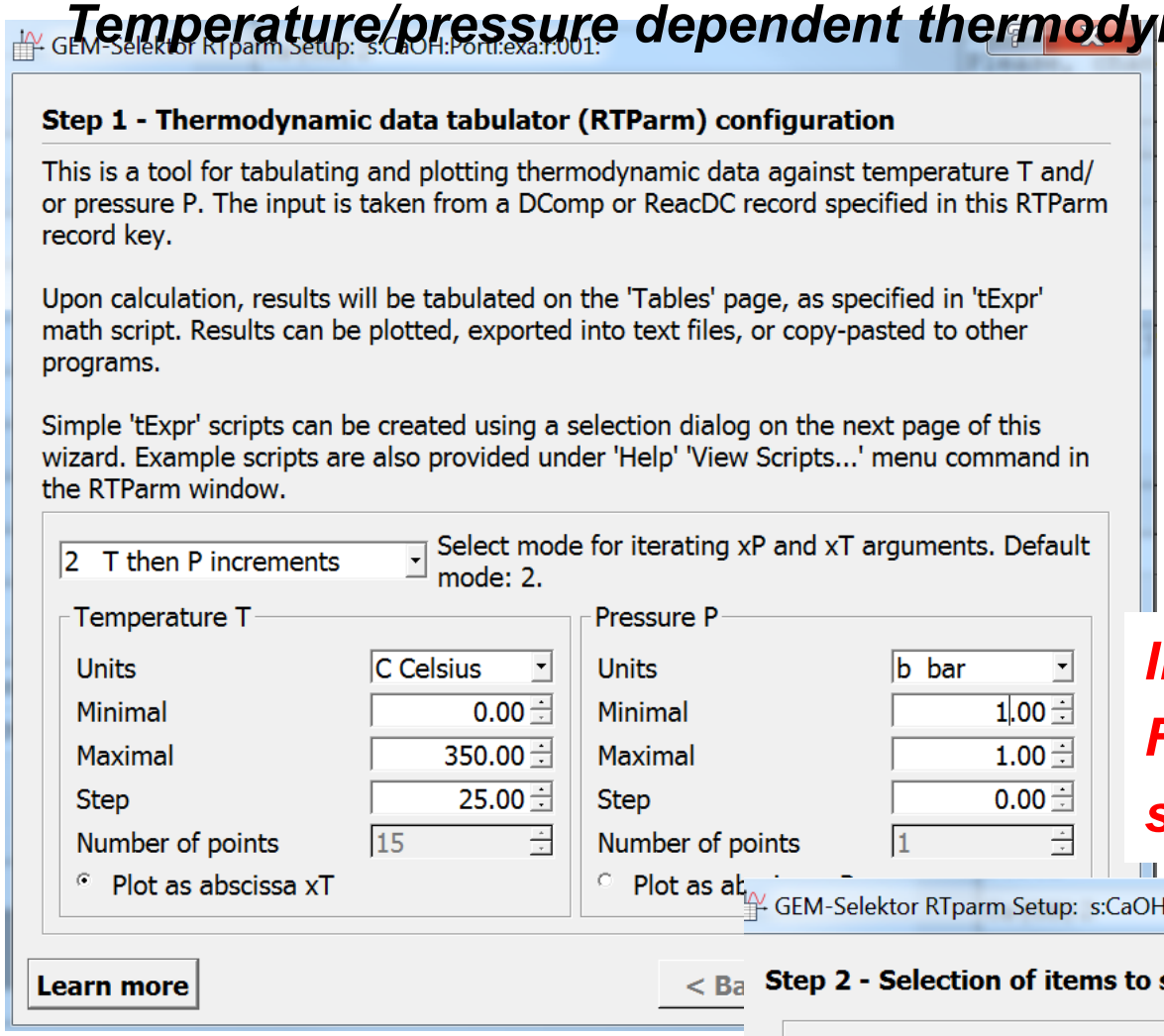


Helps to determine S or H for Temperature extrapolations

Temperature/pressure dependent thermodynamic data



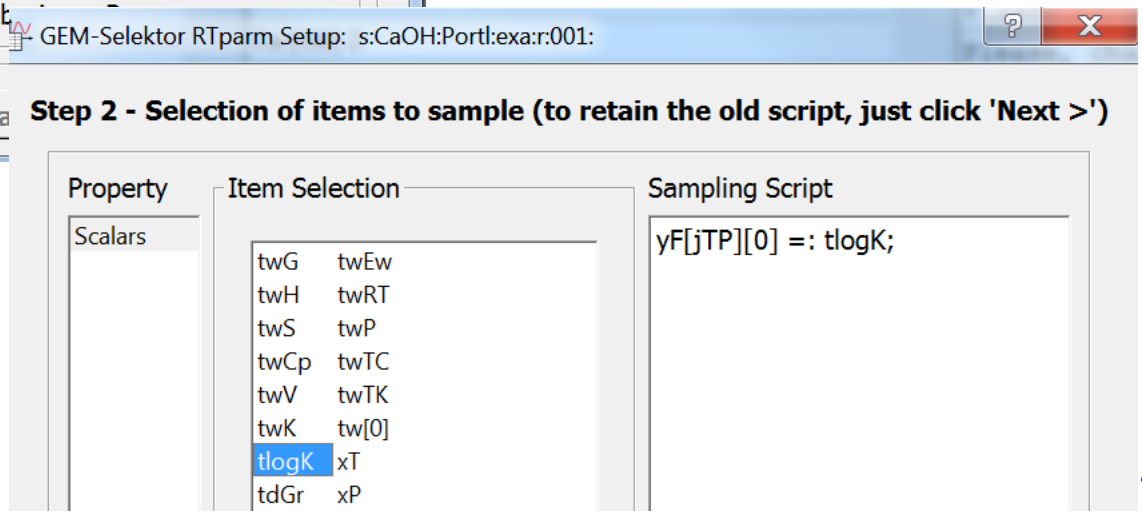
Temperature/pressure dependent thermodynamic data



Initial

Final

step



Temperature/pressure dependent thermodynamic data

Empa
Materials Science and Technology

GEM-Selektor RTparm Setup: s:CAOH:Ca(OH)2:cem: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.

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
Plot as abscissa xT		Plot as abscissa xP	

Start value
Stop value
Step

Learn more | < Back | Next> | Ca

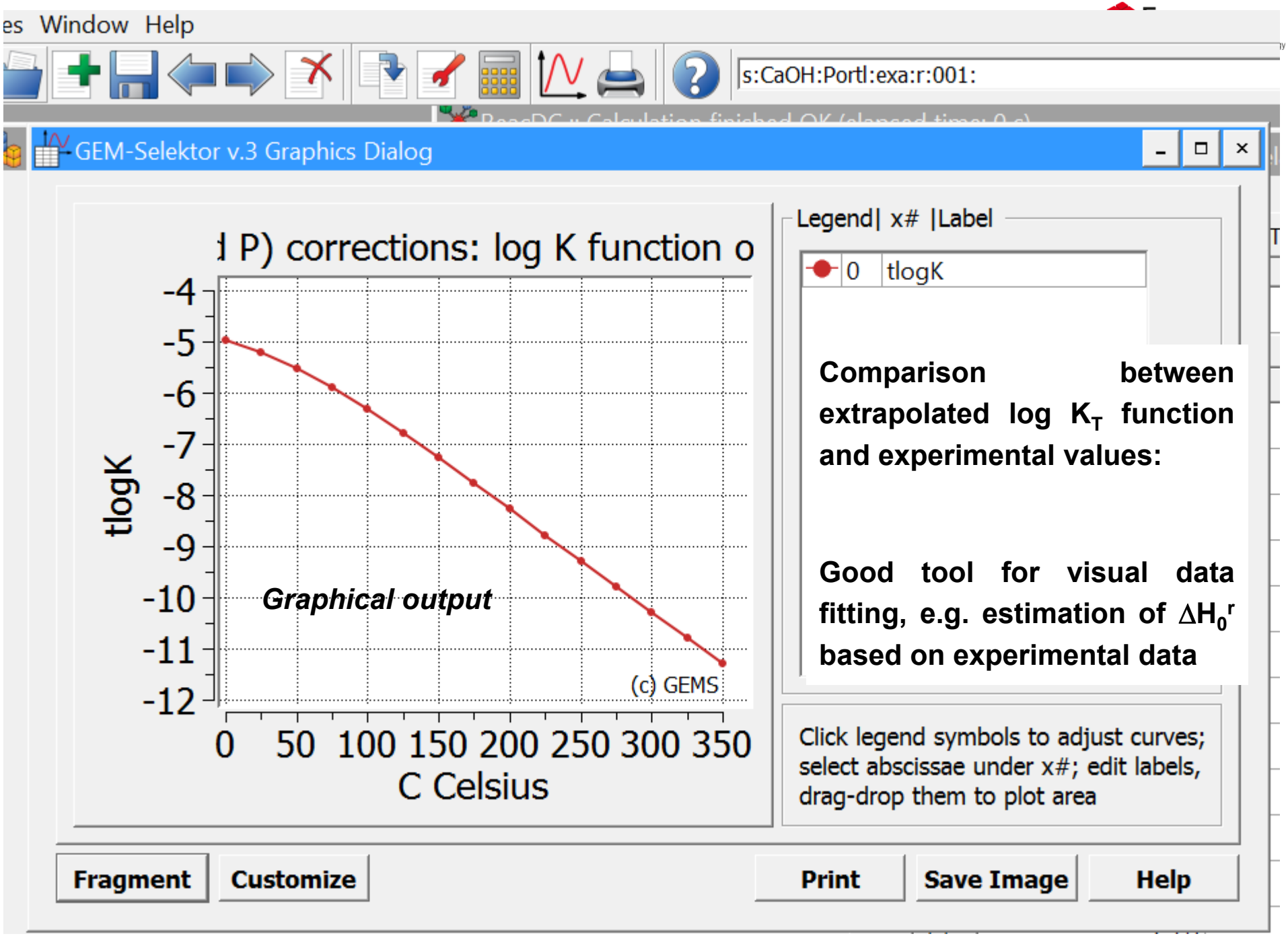
calc. values

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

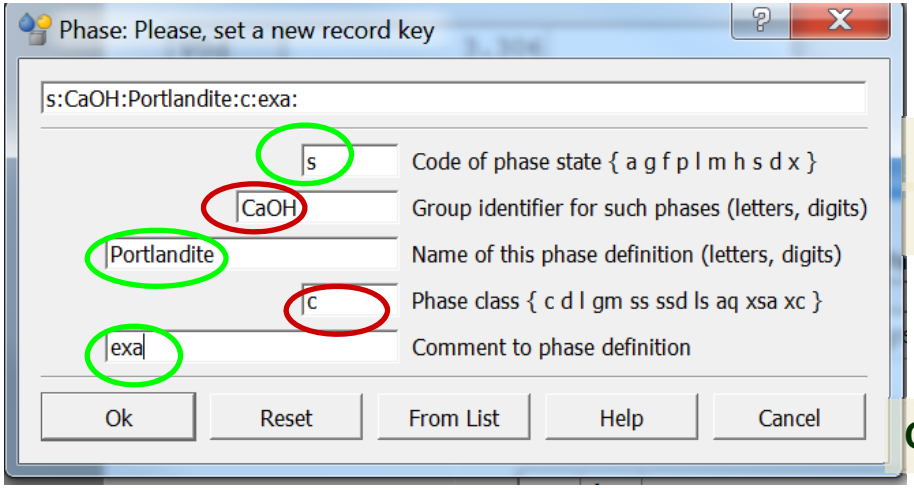
Scripts | Tables | TPwork | Setup | 03/05/2017, 14:50

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


es Window Help
s:CaOH:Portl:exa:r:001:
GEM-Selektor v.3 Graphics Dialog
l P) corrections: log K function o
tlogK
-4
-5
-6
-7
-8
-9
-10
-11
-12
0 50 100 150 200 250 300 350
C Celsius
Graphical output
(c) GEMS
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 state (s … solid; a … aqueous; g … gaseous)

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

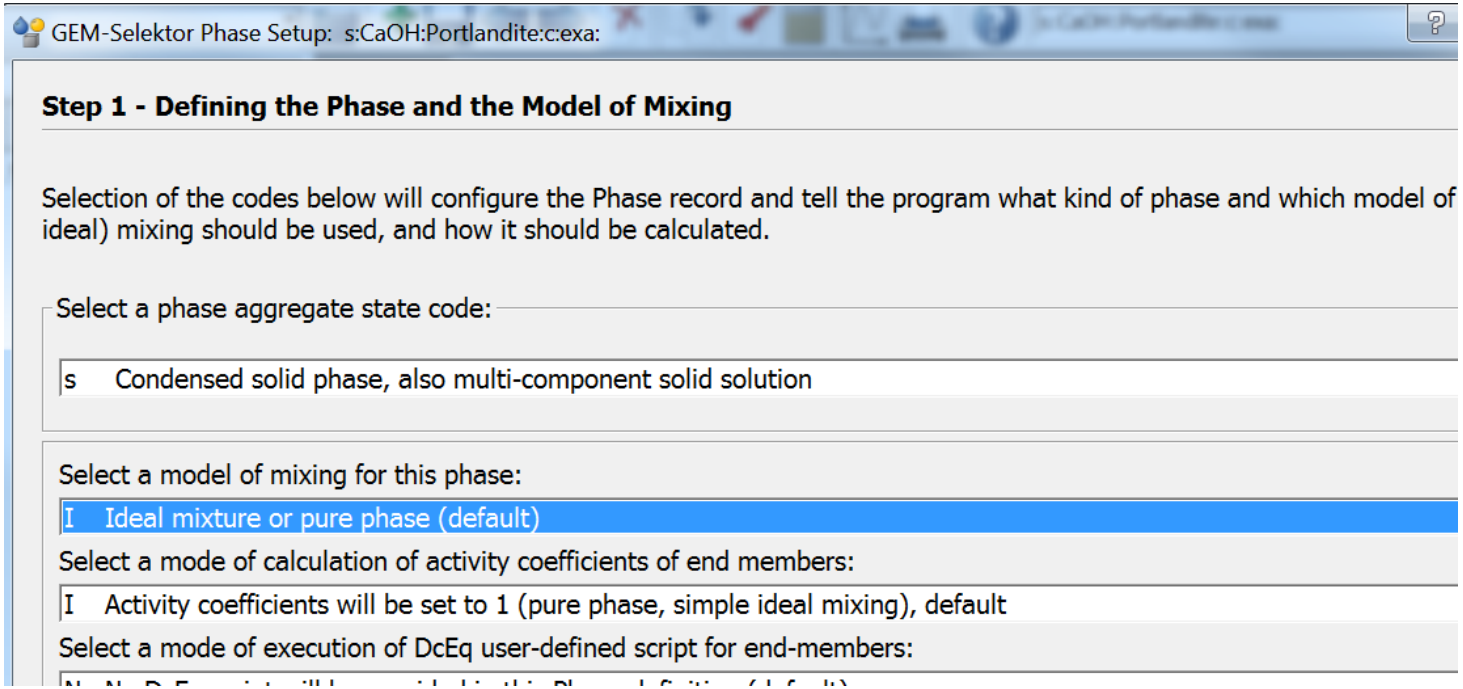
c: condensed solid (single compound); ss: solid solution; aq: Aqueous

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

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

<u>Optional:</u> Choice of mixing model if a non ideal solid solution is included

I for Single phase or ideal solid solution:

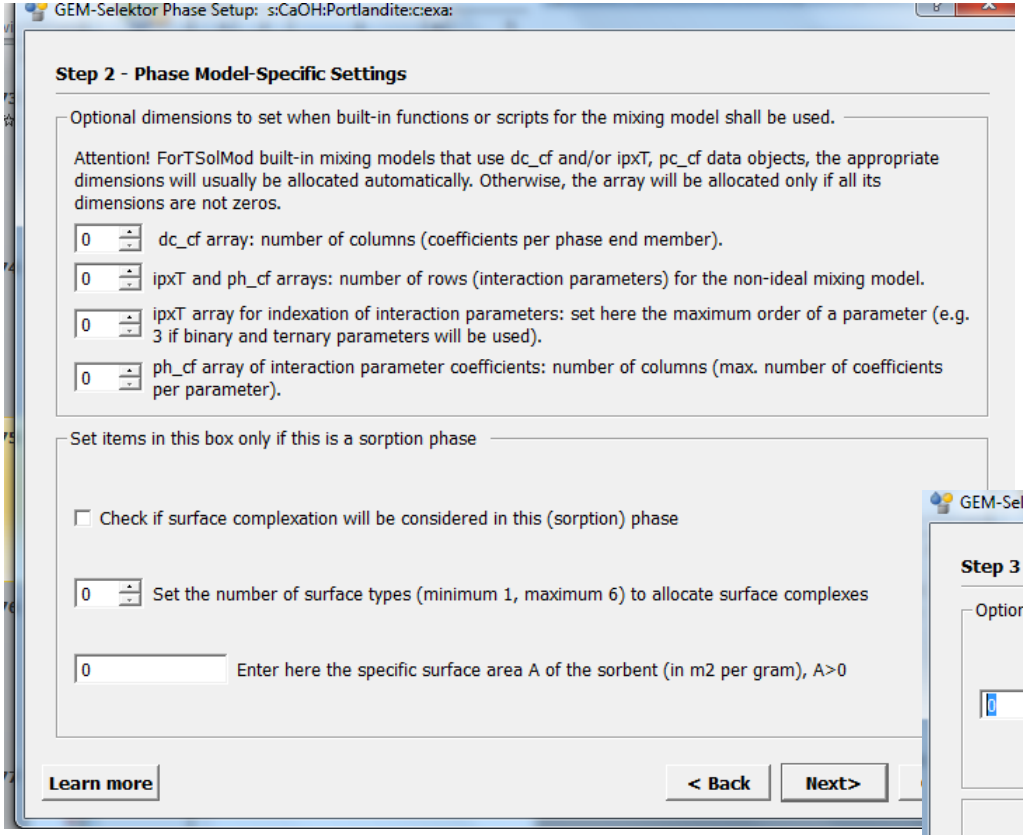


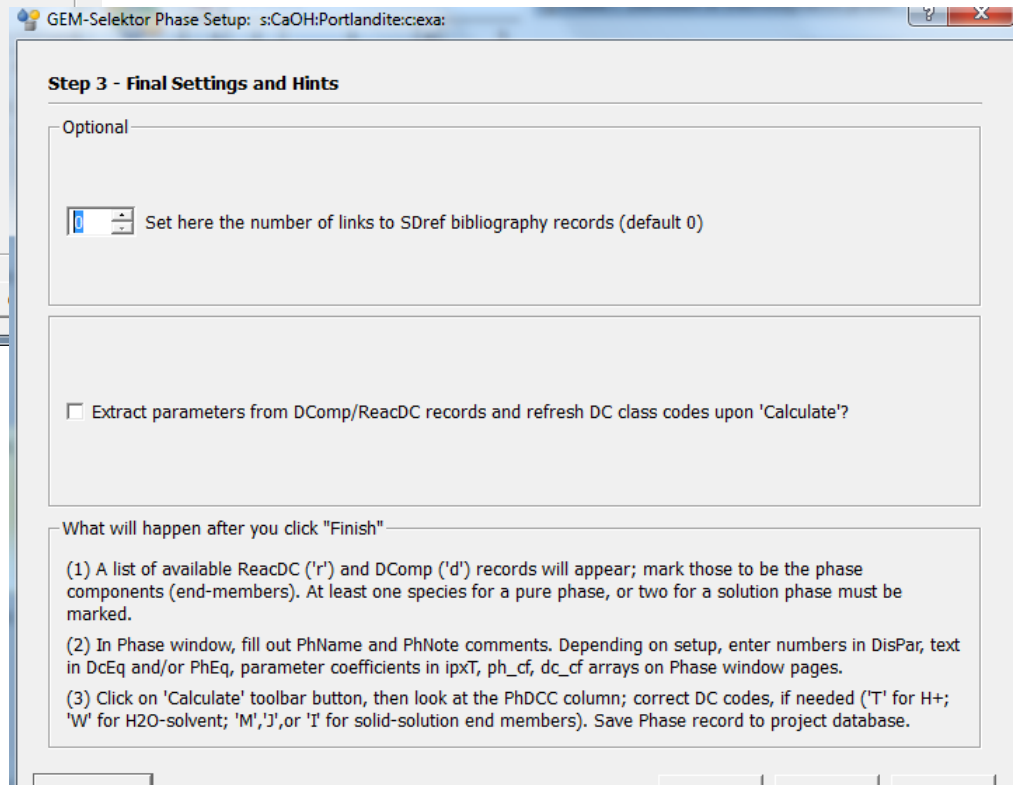
5.) Thermodynamic Phases – creation of entries

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 a(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



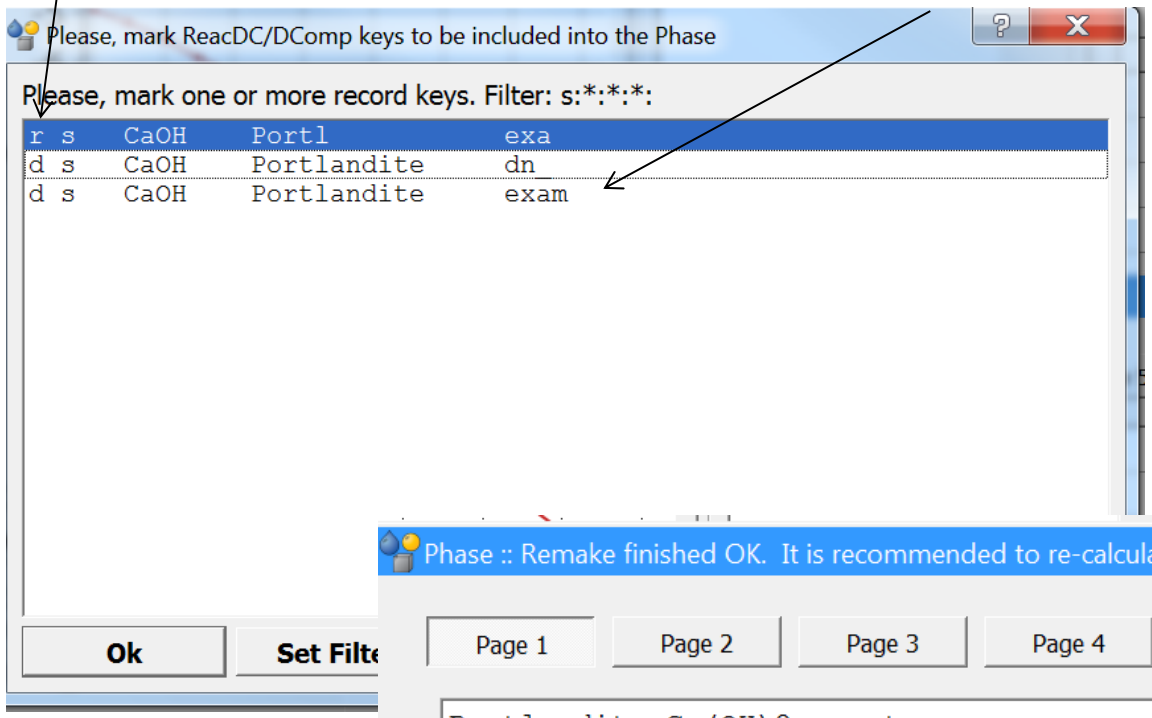


Optional parameters only for experienced users, otherwise leave default values

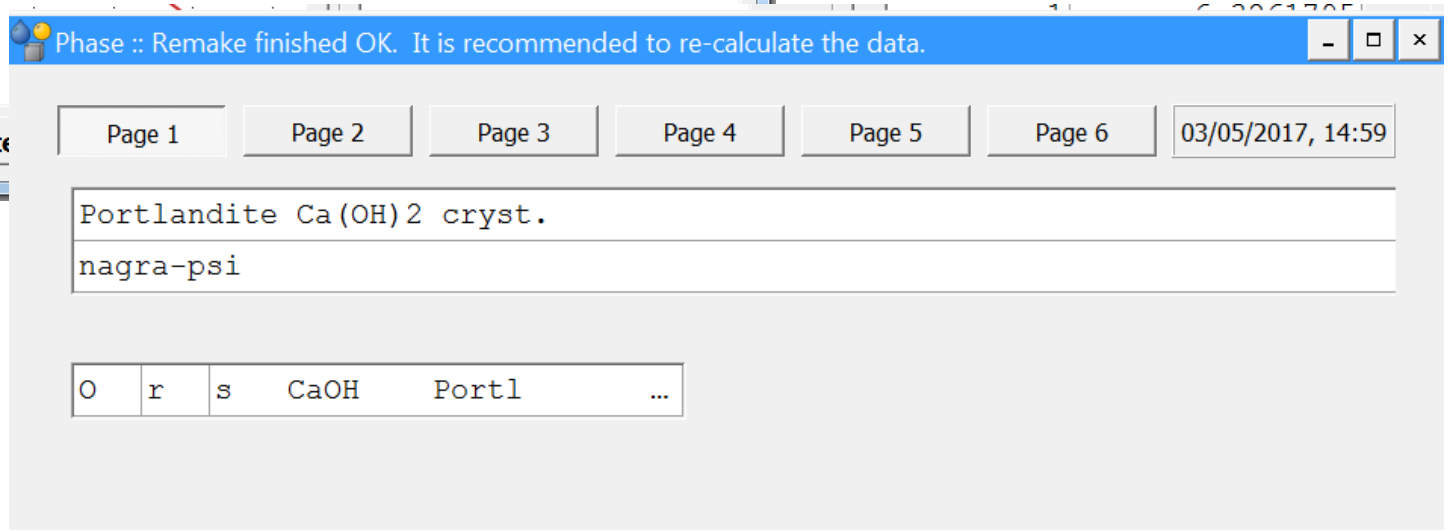
5.) Thermodynamic Phases – creation of entries

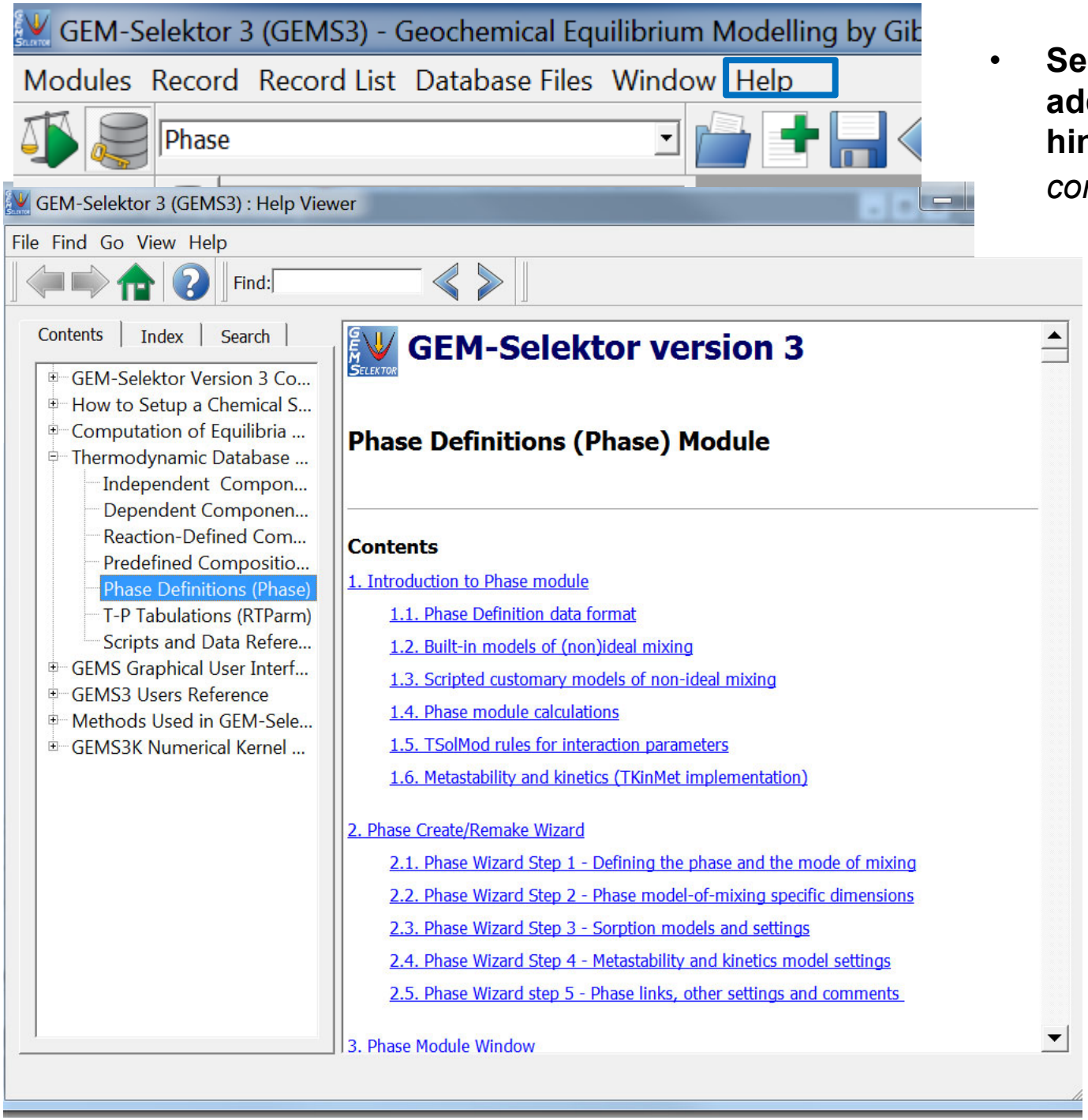
Mark dependent component to be included in the project database

a) either from ReacDC **b) or from DComp**



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

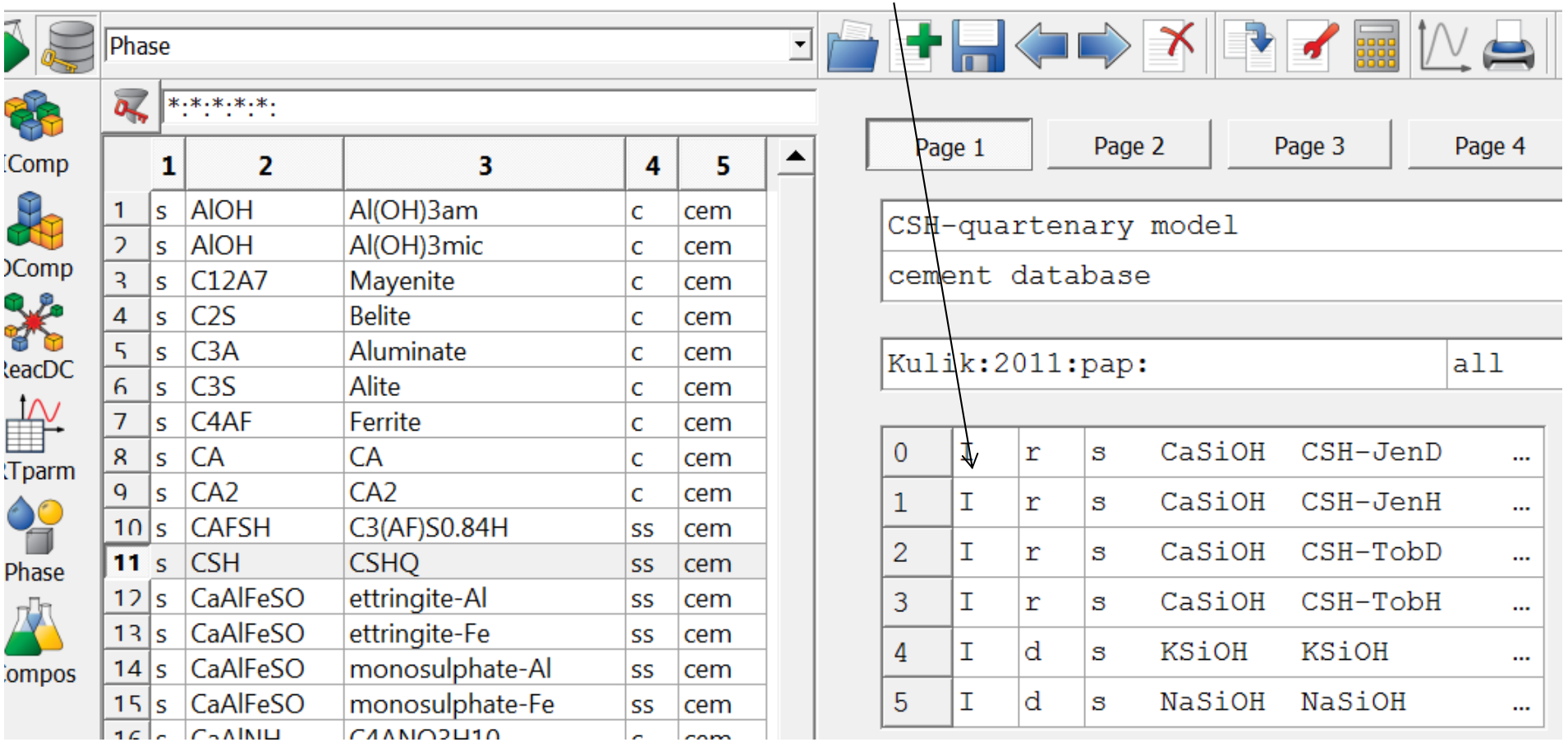




- **See** “Help:Help” **for additional information or hints** *(Partially still under construction)*

5.) Thermodynamic Phases – creation of entries

b) Solid solution



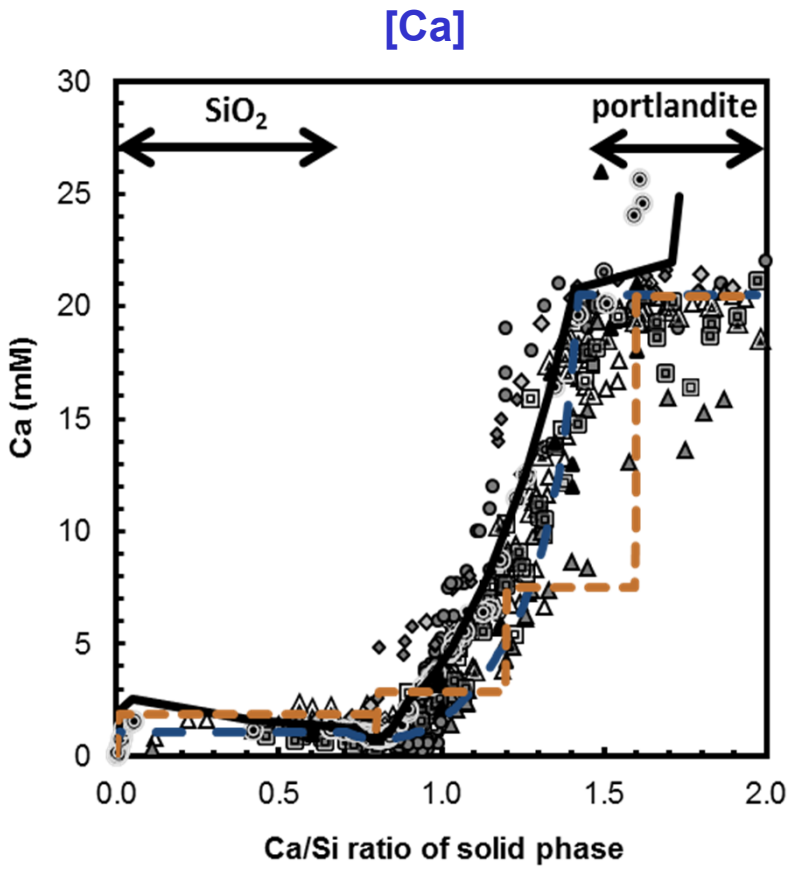
	1	2	3	4	5
1	s	AlOH	Al(OH)3am	c	cem
2	s	AlOH	Al(OH)3mic	c	cem
3	s	C12A7	Mayenite	c	cem
4	s	C2S	Belite	c	cem
5	s	C3A	Aluminate	c	cem
6	s	C3S	Alite	c	cem
7	s	C4AF	Ferrite	c	cem
8	s	CA	CA	c	cem
9	s	CA2	CA2	c	cem
10	s	CAFSH	C3(AF)S0.84H	ss	cem
11	s	CSH	CSHQ	ss	cem
12	s	CaAlFeSO	ettringite-Al	ss	cem
13	s	CaAlFeSO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

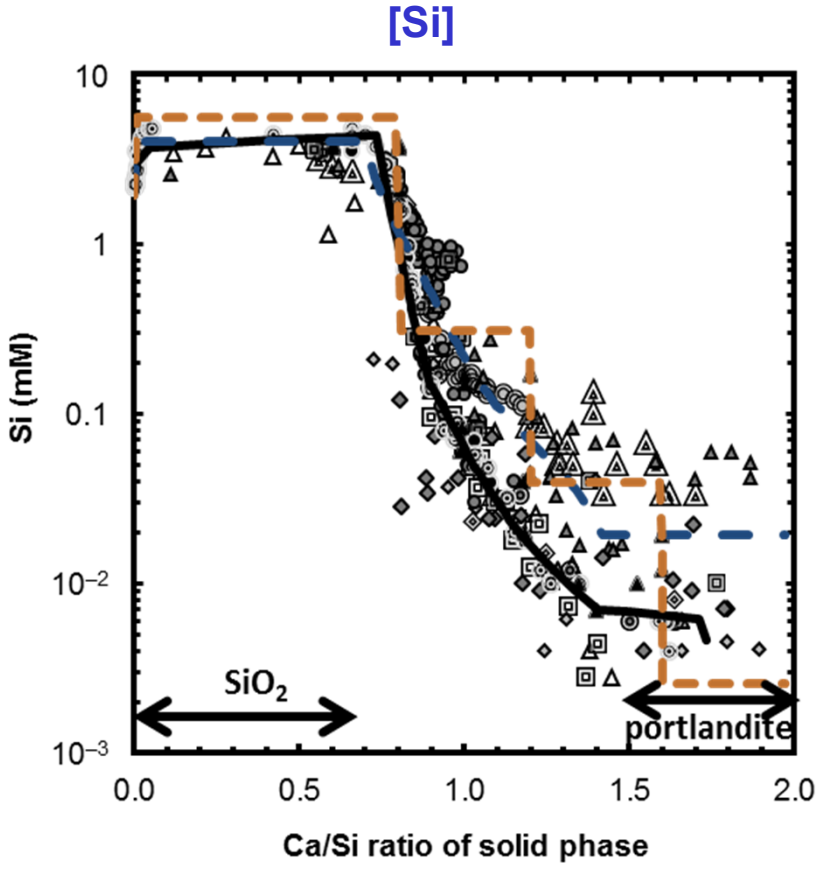
0	I	r	s	CaSiOH	CSH-JenD ...
1	I	r	s	CaSiOH	CSH-JenH ...
2	I	r	s	CaSiOH	CSH-TobD ...
3	I	r	s	CaSiOH	CSH-TobH ...
4	I	d	s	KSiOH	KSiOH ...
5	I	d	s	NaSiOH	NaSiOH ...

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

Plus $(KOH)_{2.5}SiO_2H_2O$) and $(NaOH)_{2.5}SiO_2H_2O$) to **estimate** alkali uptake

Other thermodynamic models for C-S-H





3 different CSH

$C_{0.8}SH_{1.5}$
$C_{1.2}SH_{2.1}$
$C_{1.6}SH_{2.6}$

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

Solid solution: CSHT

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

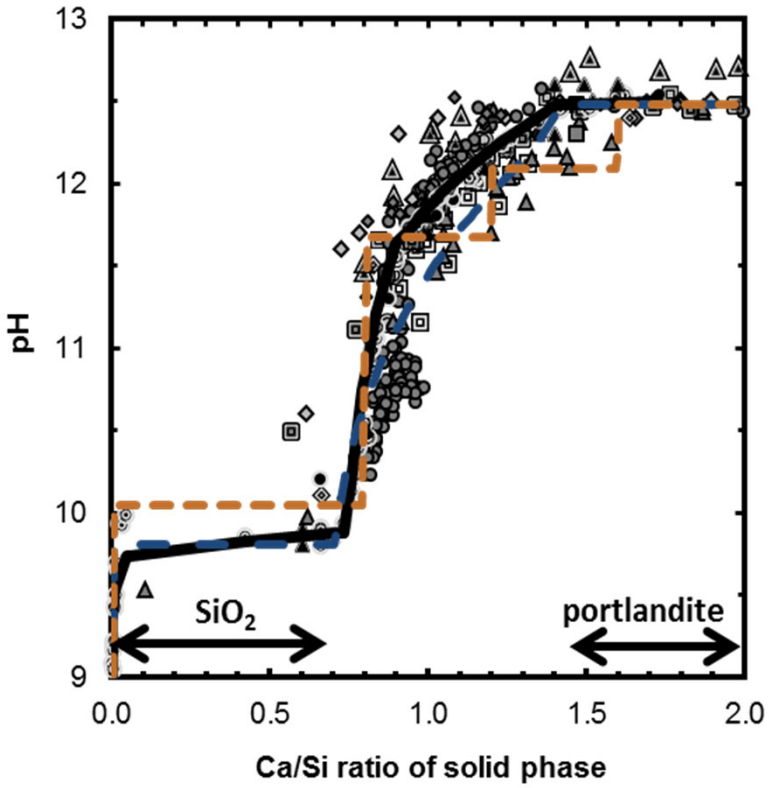
Surface reaction model

Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

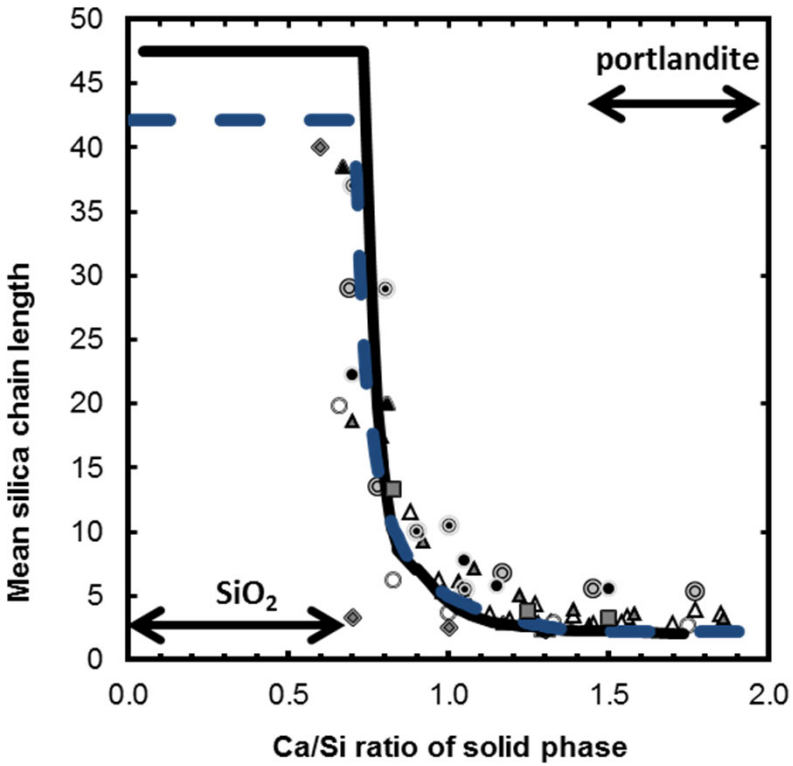
Haas Nonat (2015) CCR 68, 124-138

Thermodynamic models for C-S-H

pH



Mean Chain Length



~~3 different CSH~~

~~$C_{0.8}SH_{1.5}$~~

~~$C_{1.2}SH_{2.1}$~~

~~$C_{1.6}SH_{2.6}$~~

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

Solid solution

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

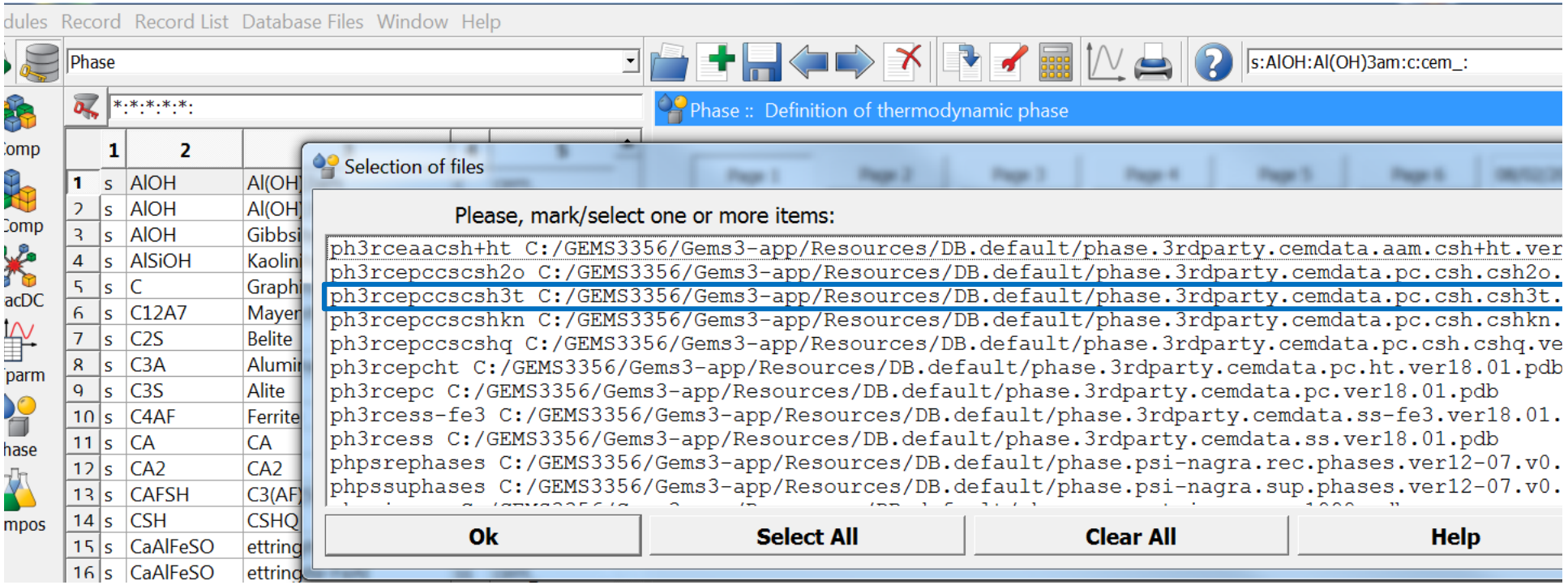
Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

Haas Nonat (2015) CCR 68, 124-138

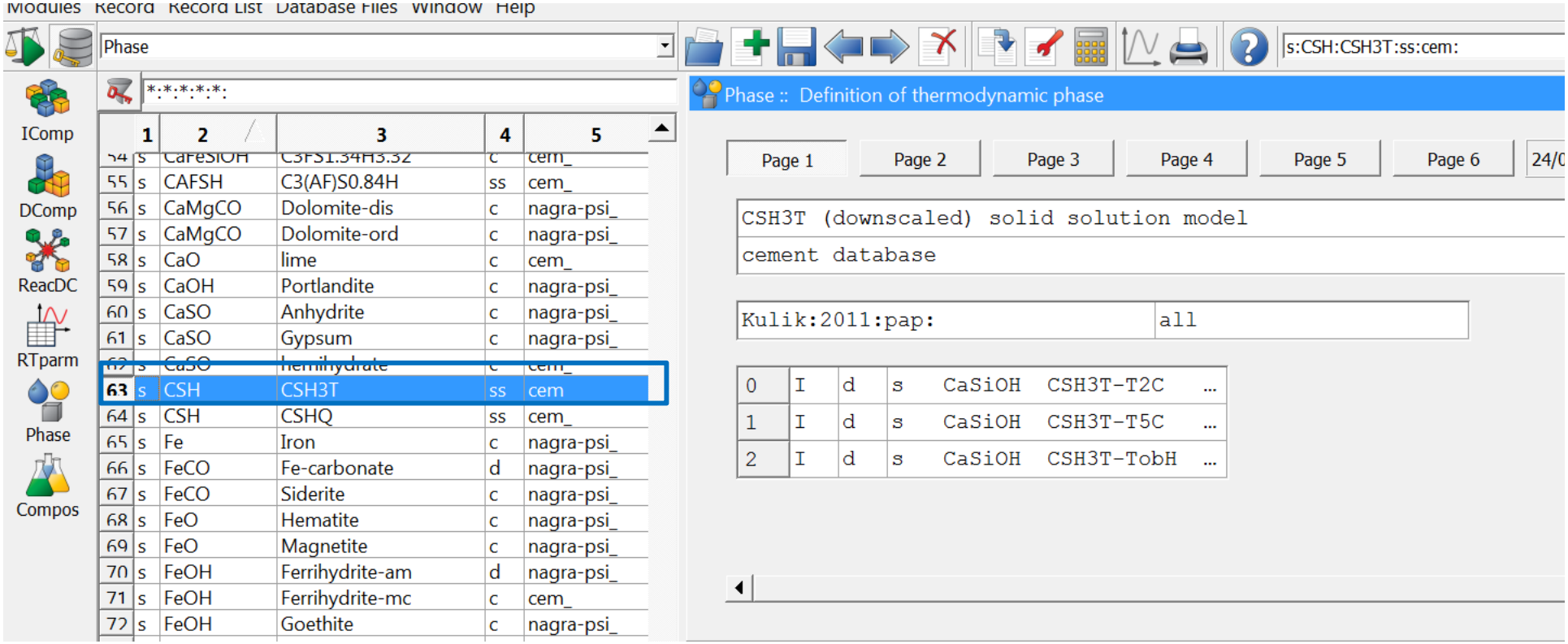
Selection of CSH model

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"



Selection of CSH models

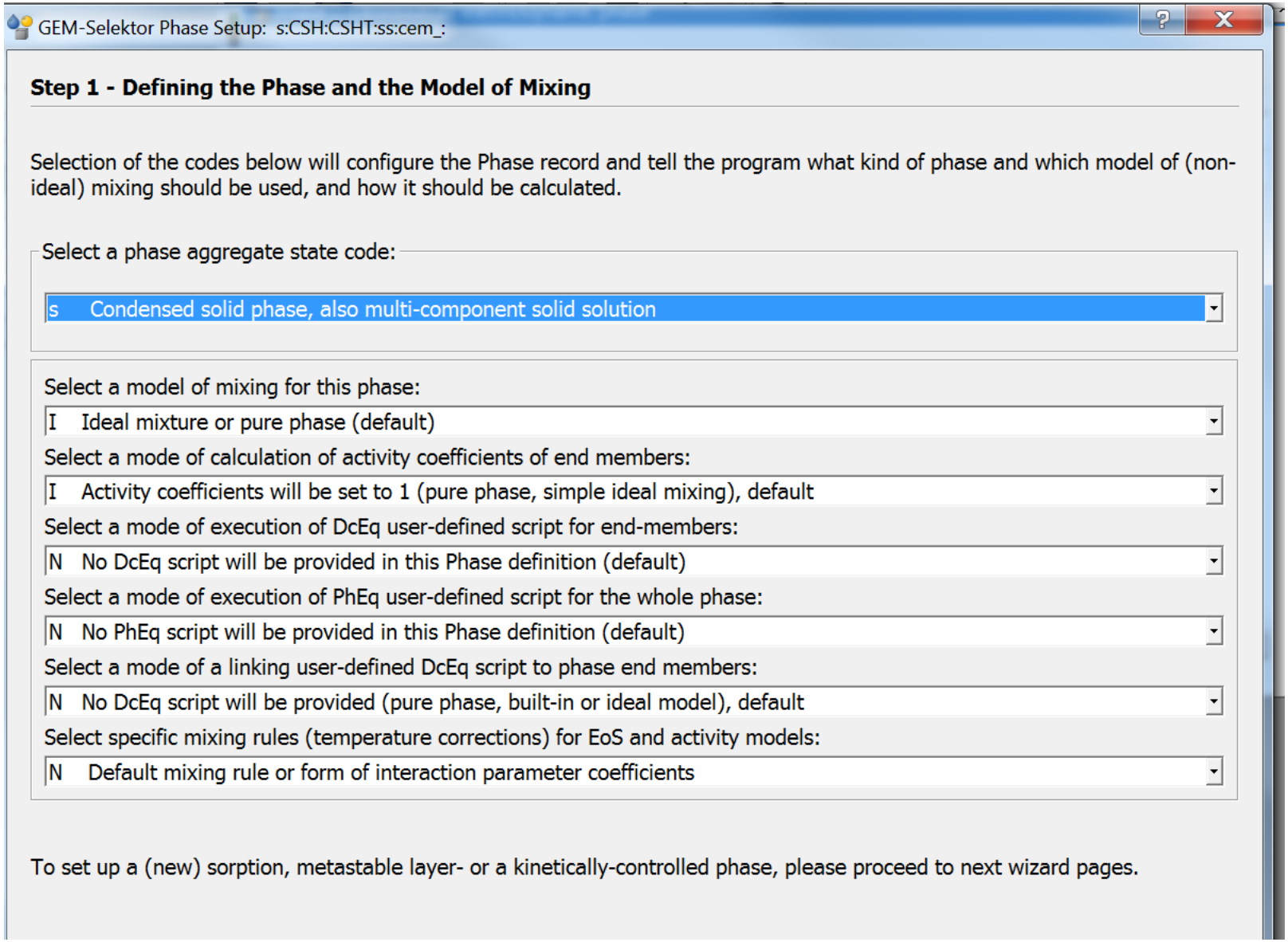


CSH T (Kulik 2011): Ca/Si = 0.67 to 1.5

further information

5.) Thermodynamic Phases – Treatment of solid solutions

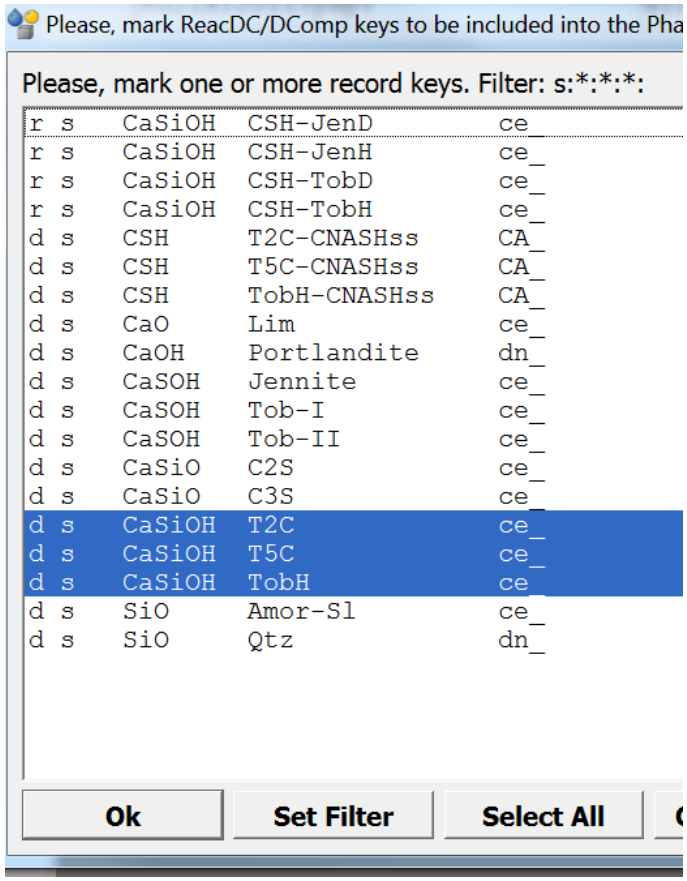
a) Ideal solid solutions, e.g. C-S-H

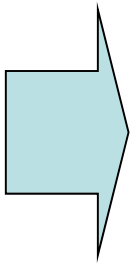


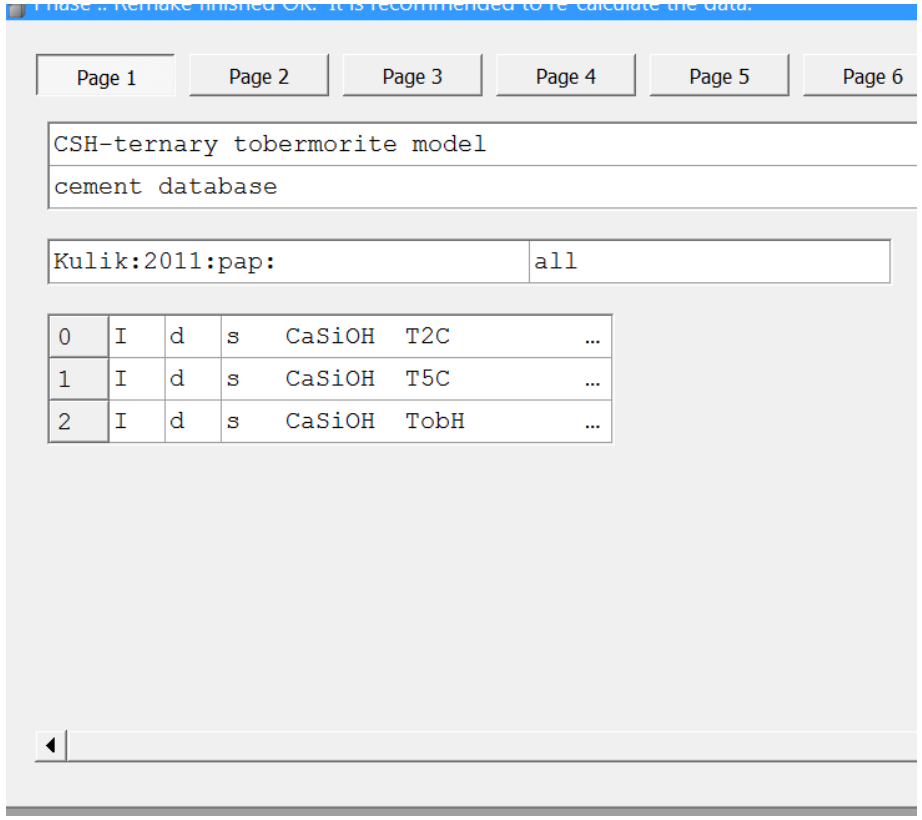
GEMS – Database management

5.) Thermodynamic Phases – Treatment of solid solutions

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







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

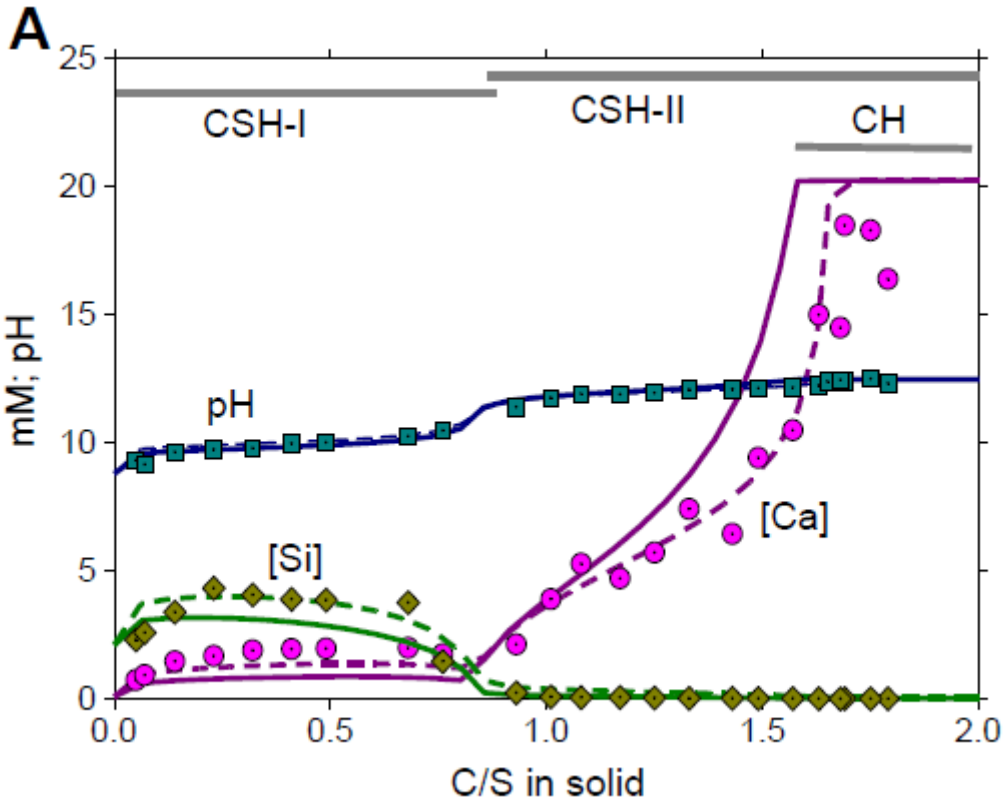
Ideal solid solution phase

CSH «Tob-Jennite»: used in Cemdata07

CSHII: Ca/Si 0.83 to 1.67

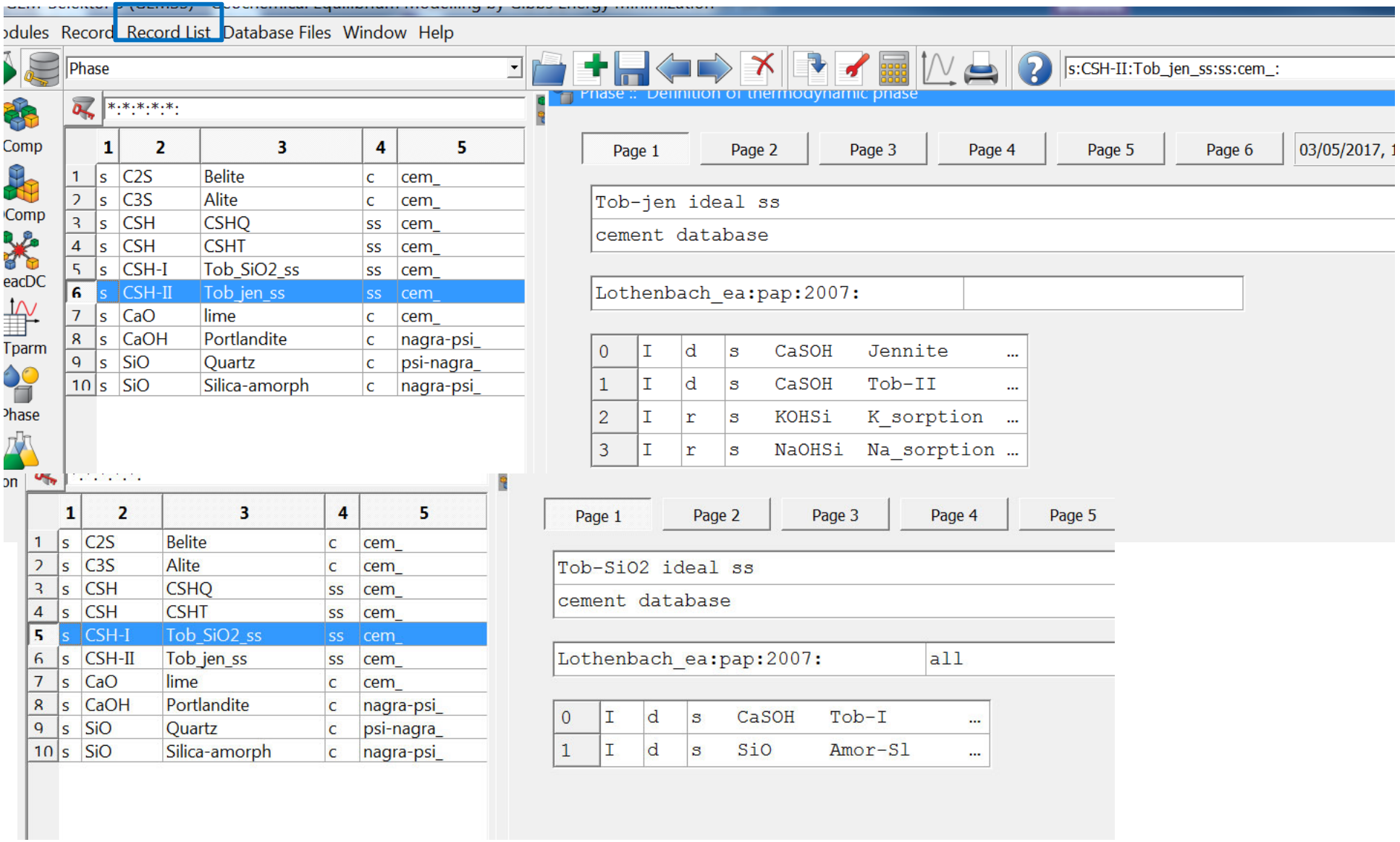
i) CSH-I solid solution system with the end-members SiO_2 (am) and tobermorite (Tob-I: $(CaO)_2(SiO_2)_{2.4}\cdot(H_2O)_{3.2}$) and

ii) CSH-II solid solution system with the end-members jennite $(CaO)_{1.67}(SiO_2)_1\cdot(H_2O)_{2.1}$ and tobermorite (Tob-II: $(CaO)_{0.83}(SiO_2)_1\cdot(H_2O)_{1.3}$).



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

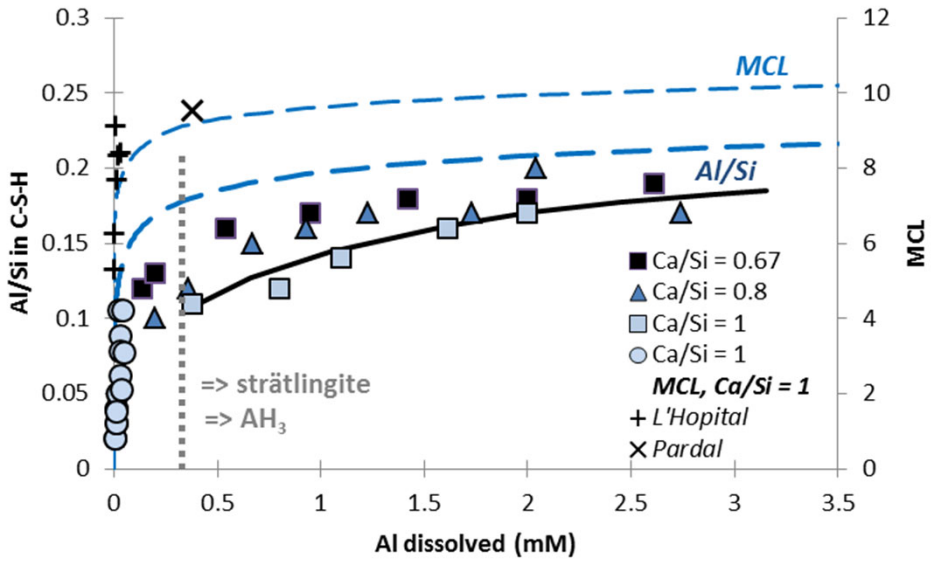
CSH «Tob-Jennite»: used in Cemdata07

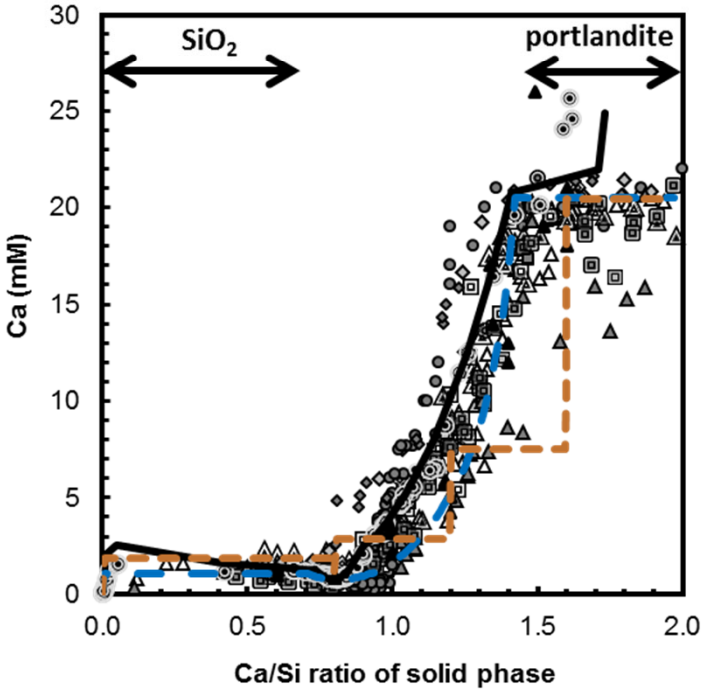


	1	2	3	4	5
1	s	C2S	Belite	c	cem_
2	s	C3S	Alite	c	cem_
3	s	CSH	CSHQ	ss	cem_
4	s	CSH	CSHT	ss	cem_
5	s	CSH-I	Tob_SiO2_ss	ss	cem_
6	s	CSH-II	Tob_jen_ss	ss	cem_
7	s	CaO	lime	c	cem_
8	s	CaOH	Portlandite	c	nagra-psi_
9	s	SiO	Quartz	c	psi-nagra_
10	s	SiO	Silica-amorph	c	nagra-psi_

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

Al-uptake in CSH



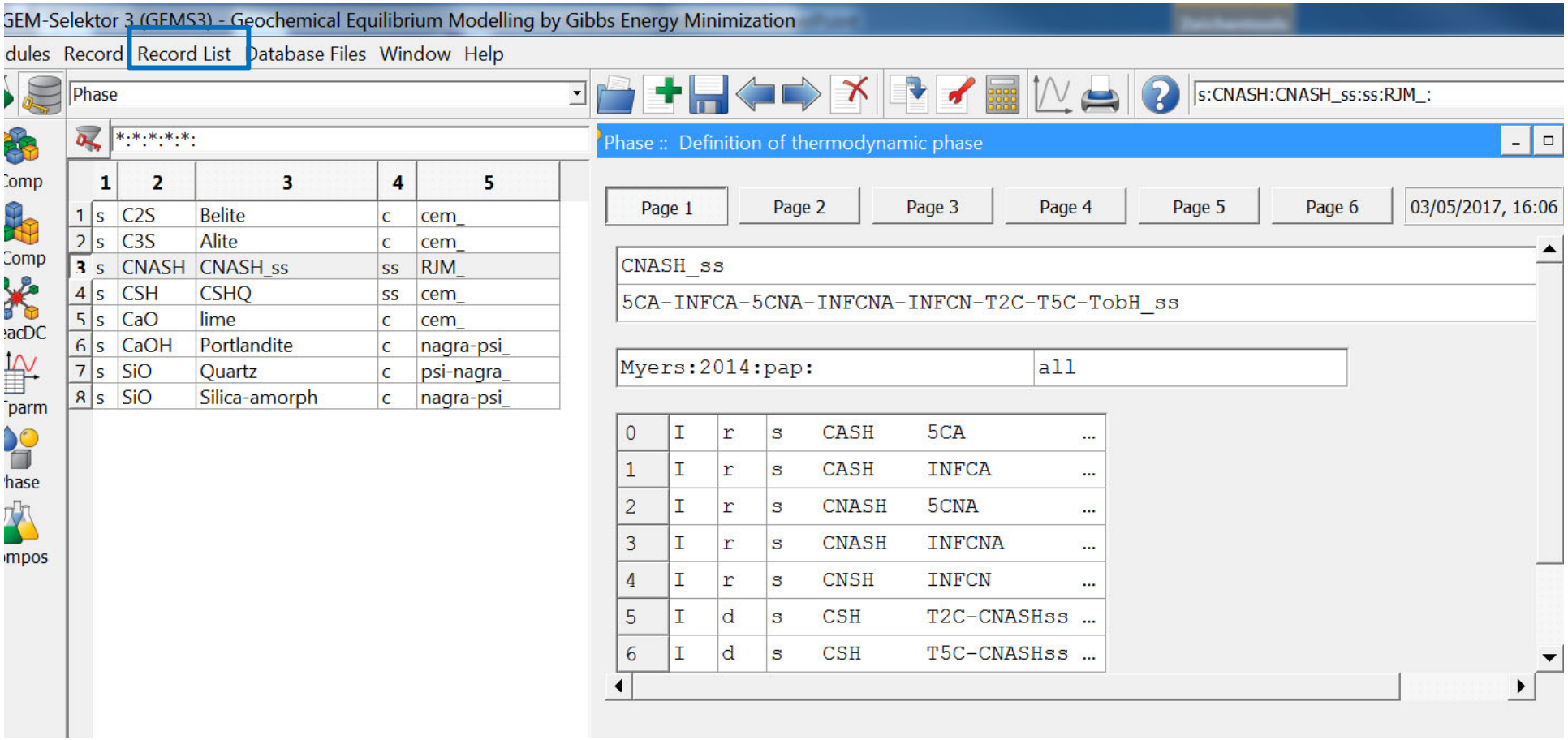


Sorption (Haas & Nonat) and solid solution (Kulik ea, Myers ea) Models:

- 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)



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

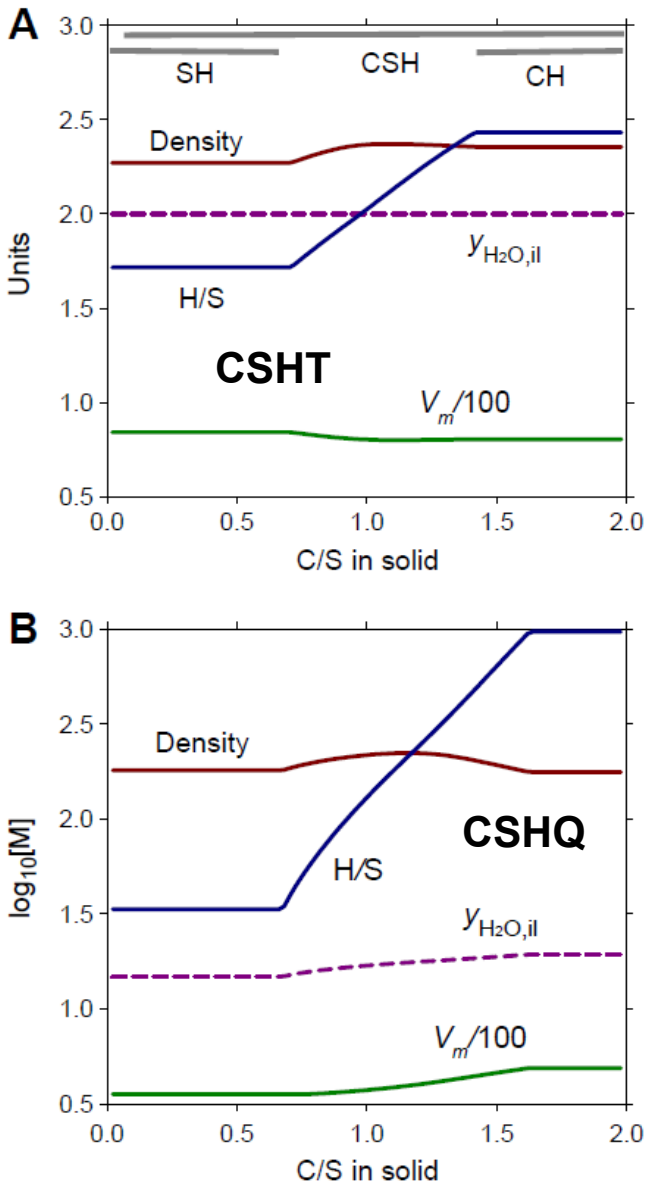


Fig. 8. Variations of density (in g cm^{-3}), volume V_m (in cm^3 mol^{-1}), interlayer H_2O mole fraction $y_{H2O,il}$, and H_2O/SiO_2 mole ratio H/S of the C-S-H phase, as predicted by the downscaled CSH3T simple ideal model Table 5 (A) and by the downscaled CSHQ simple ideal model Table 6 (B).