清華大學

Empa
Materials Science and Technology

# Lecture 02a
# What is GEMS

***first tutorials***

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Software development/fitting tools/kinetic:

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Dan Miron

PAUL SCHERRER INSTITUT
PSI

# Thermodynamic modelling

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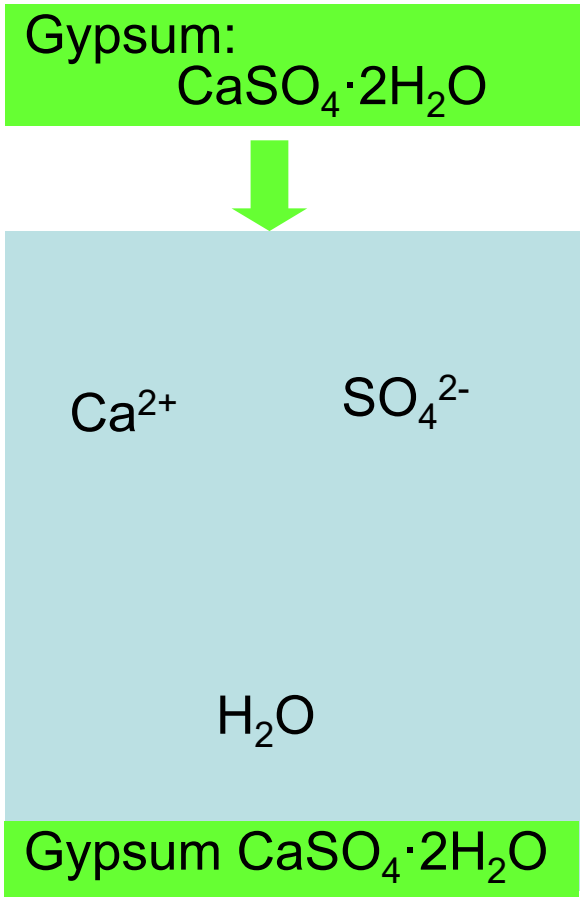
1. Short overview thermodynamic modelling
   a. chemical equilibrium
   b. modelling software
   c. databases

2. What is GEMS?
3. Installation of GEMS
4. First tutorials
   - Calculation of single systems:
     - Equilibrium $C_3A$, gypsum, portlandite
   - Parameter variations *(process)*
     - calcite, temperature, …

# 2 Thermodynamic modelling

## Example chemical equilibria: Gypsum in a glass of water




Reaction:

$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

Solubility product

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} \cdot \{H_2O\}^2 / \{CaSO_4 \cdot 2H_2O\}$

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$

{} : activity; []: concentration

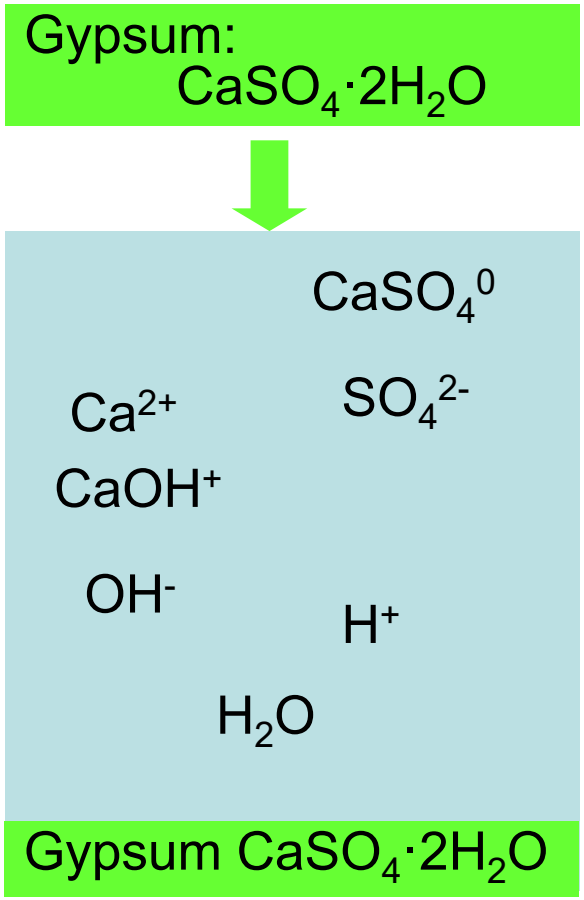
$\{Ca^{2+}\} = [Ca^{2+}]\ \gamma_{Ca2+}$ $\gamma$ **Activity coefficient**

$$\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI$$

extended Debye-Hückel

# 2 Thermodynamic modelling

## Example chemical equilibria: Gypsum in a glass of water

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Solubility product

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$

Complex formation: Equilibrium constants

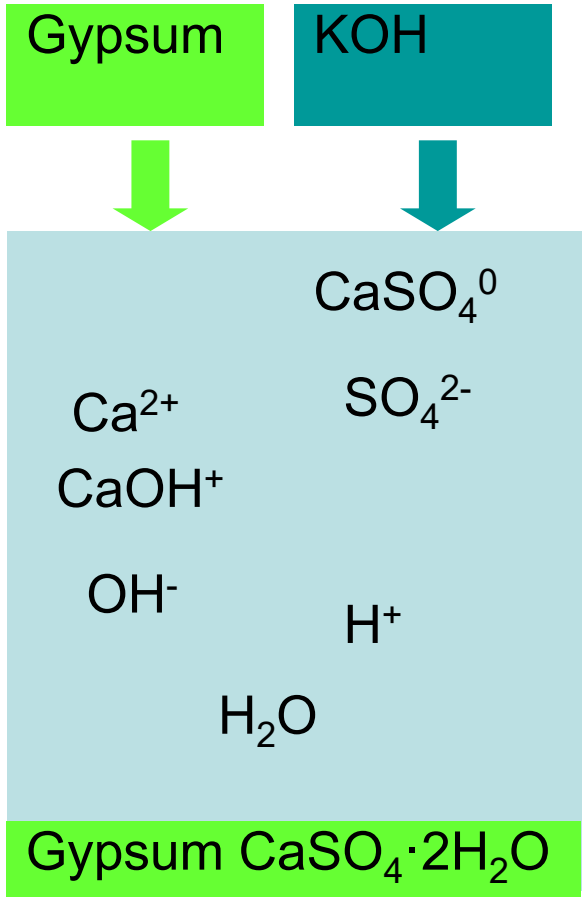
$K = \{CaOH^+\}/\{Ca^{2+}\} \cdot \{OH^-\} = 10^{1.22}$

$K = \{CaSO_4^0\}/\{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{2.3}$

$K = \{H^+\} \cdot \{OH^-\} = 10^{-14.00}$

# 2 Thermodynamic modelling

Chemical equilibria:




**1 Concentration of Ca, $SO_4$?**

**2 What happens if we add KOH?**

?

Solubility products

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$

$K_{S0} = \{Ca^{2+}\} \cdot \{OH^-\}^2 = 10^{-5.20}$

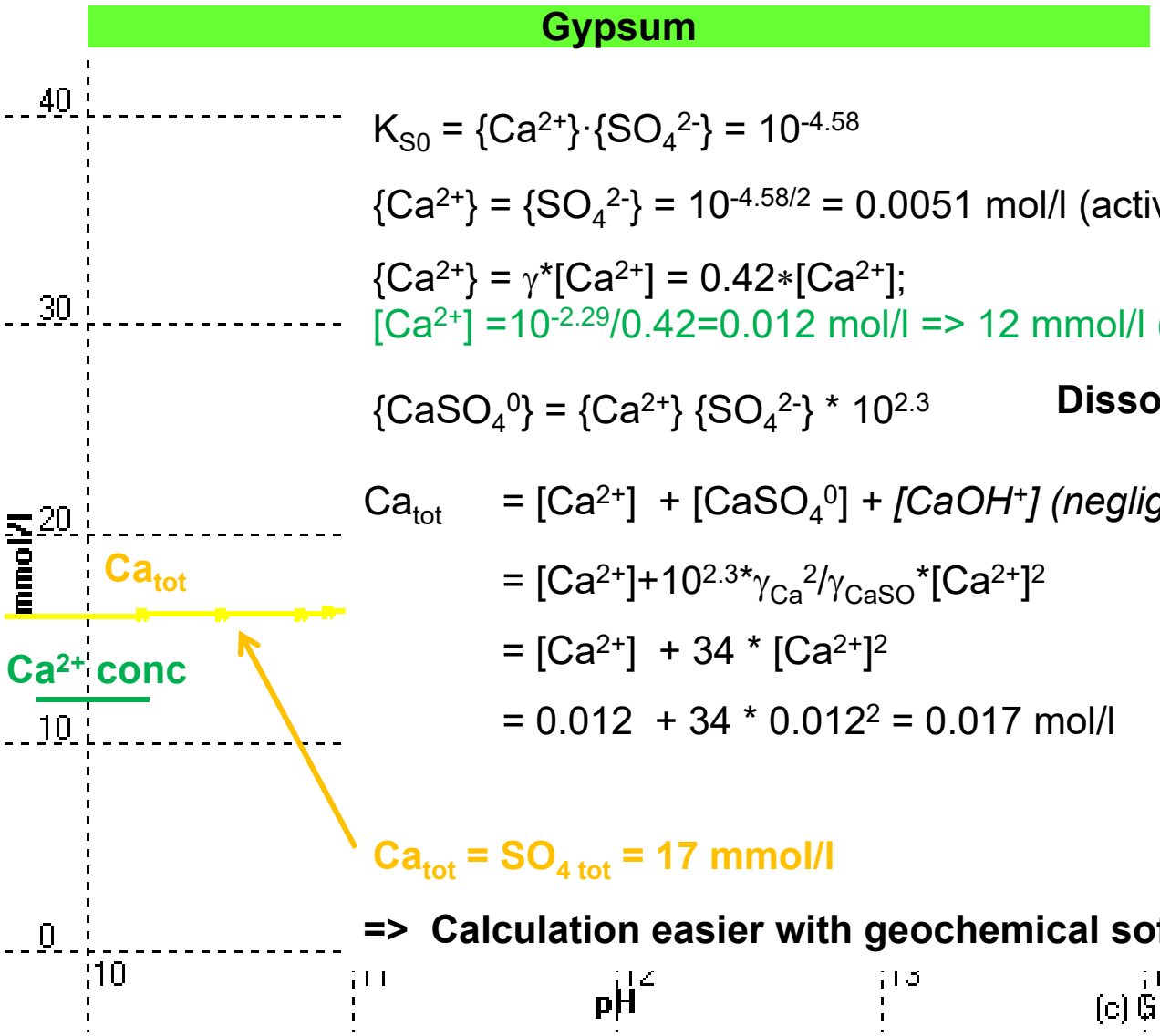
Equilibrium constants

$K = \{CaOH^+\} / \{Ca^{2+}\} \cdot \{OH^-\} = 10^{1.22}$

$K = \{CaSO_4^0\} / \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{2.3}$

$K = \{H^+\} \cdot \{OH^-\} = 10^{-14.00}$

# Solubility of gypsum




$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\} = 10^{-4.58}$

$\{Ca^{2+}\} = \{SO_4^{2-}\} = 10^{-4.58/2} = 0.0051$ mol/l (activity scale)

$\{Ca^{2+}\} = \gamma^*[Ca^{2+}] = 0.42*[Ca^{2+}];$
$[Ca^{2+}] = 10^{-2.29}/0.42 = 0.012$ mol/l => 12 mmol/l (concentration)

$\{CaSO_4^0\} = \{Ca^{2+}\}\{SO_4^{2-}\} * 10^{2.3}$ **Dissolved complexes**

$Ca_{tot} = [Ca^{2+}] + [CaSO_4^0] +$ *$[CaOH^+]$ (negligable at pH < 11.5)*

$= [Ca^{2+}] + 10^{2.3}*\gamma_{Ca}{}^2/\gamma_{CaSO}*[Ca^{2+}]^2$

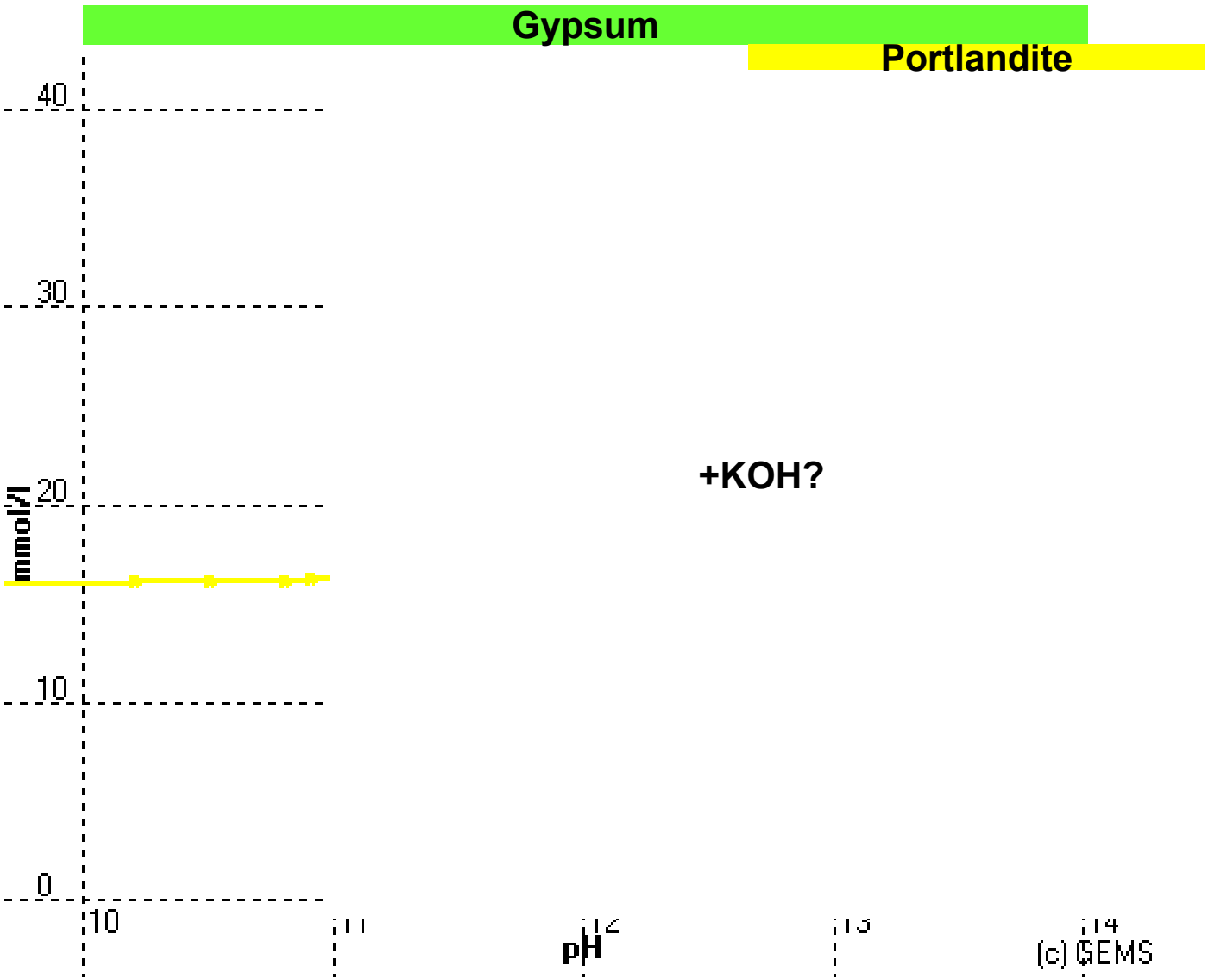
$= [Ca^{2+}] + 34 * [Ca^{2+}]^2$

$= 0.012 + 34 * 0.012^2 = 0.017$ mol/l

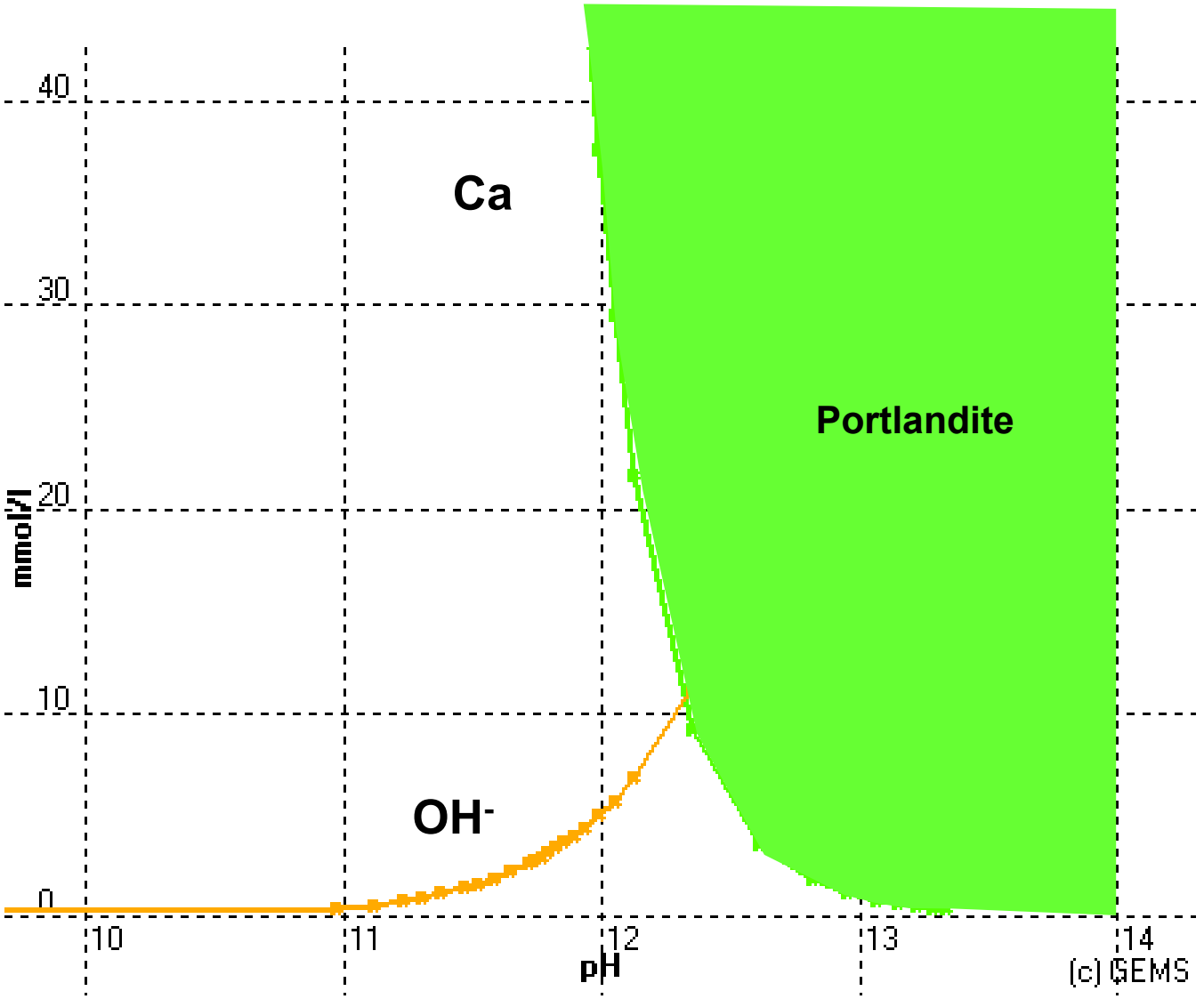
**$Ca_{tot} = SO_{4\ tot} = 17$ mmol/l**

**=> Calculation easier with geochemical softwares**

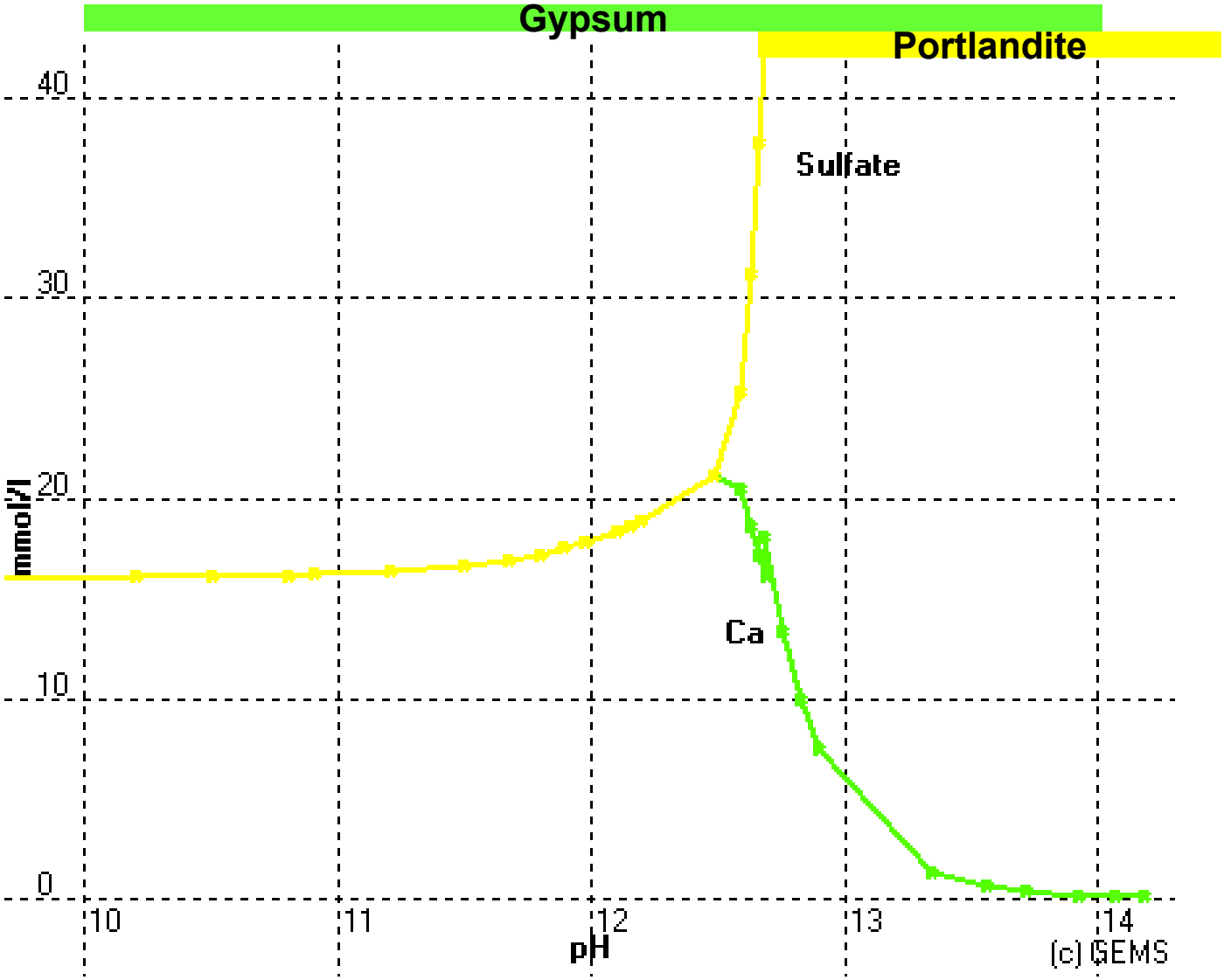
# Solubility of gypsum



# Solubility of portlandite



# Solubility of gypsum



# Codes

Complex systems

Geochemical codes needed for calculation:

- Geochemical database
- User interface: problem formulation
- Problem solving

# Geochemical Codes

**Freeware**

- **GEMS 3.7** http://gems.web.psi.ch/
  *solid solutions, kinetics, fitting, transport modelling*
  ***(Used in this course)***
- PHREEQC http://www.hydrochemistry.eu/
  *transport modelling*
- MINTEQA2 https://www.epa.gov/ceam/minteqa2-equilibrium-speciation-model

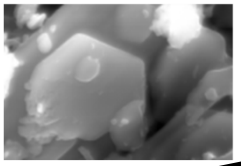
**Commercial products**

- MINEQL+ http://www.mineql.com/
- CHESS

***Comparable results differences in database!***

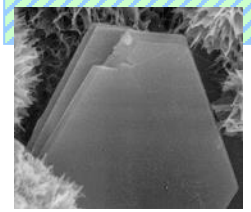
# Thermodynamic database

## Generic data



**PSI/Nagra TDB**

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



**Cemdata07, 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**

$C_3AH_6$

$C_3FS_{0.84}H_{4.32}$ ⇕

$C_3AS_{0.84}H_{4.32}$

**C-S-H**

$Ca_{0.67}SiH_{1.5}$ ⇕

$C_{0.83}S_{0.67}H_{1.8}$ ⇕

$C_{1.3}SH_{2.17}$ ⇕

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

***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 phase characterisation**

# Thermodynamic modelling

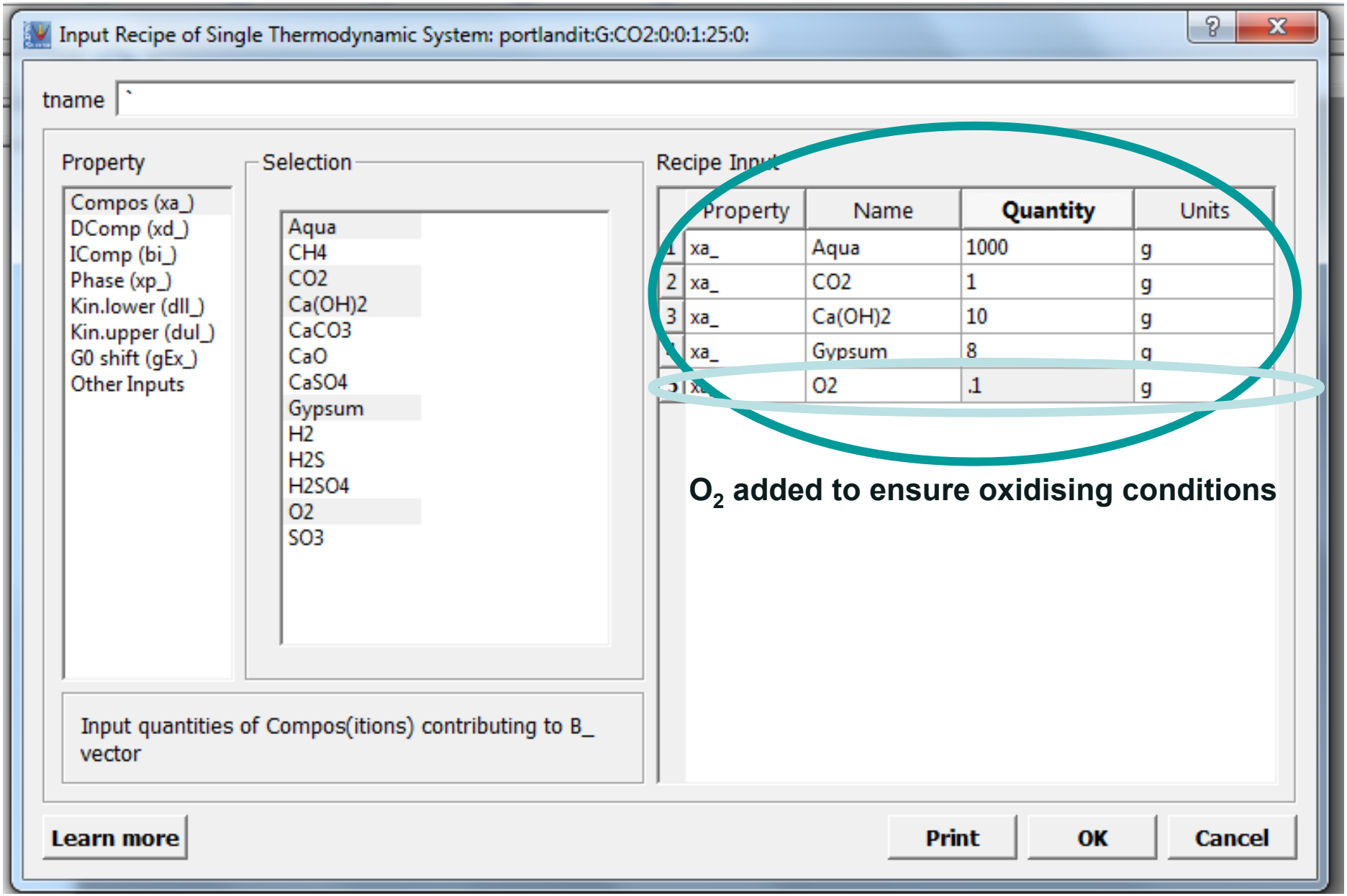
1. Geochemical programme ✓
2. Thermodynamic data ✓
3. Problem formulation:

Define quantities of

- water,
- solids: gypsum, calcite, $C_3A$, $C_3S$,…
- liquids: $H_2SO_4$, …
- gas: $CO_2$, $N_2$, …

… at the user interface of the respective programme

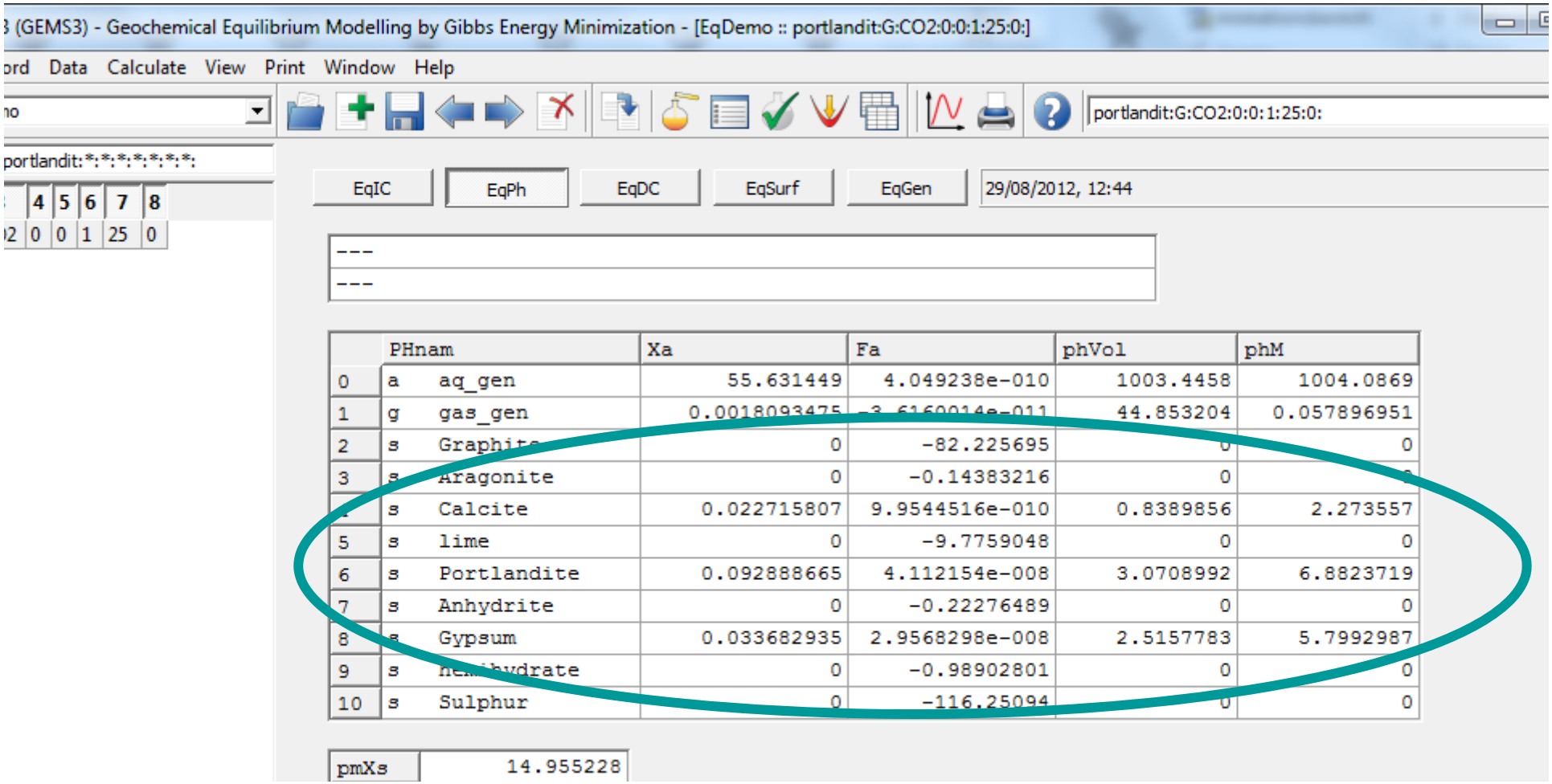
# Input




**$O_2$ added to ensure oxidising conditions**

# Results 1

Solids: amount in g, mol, $cm^3$,…

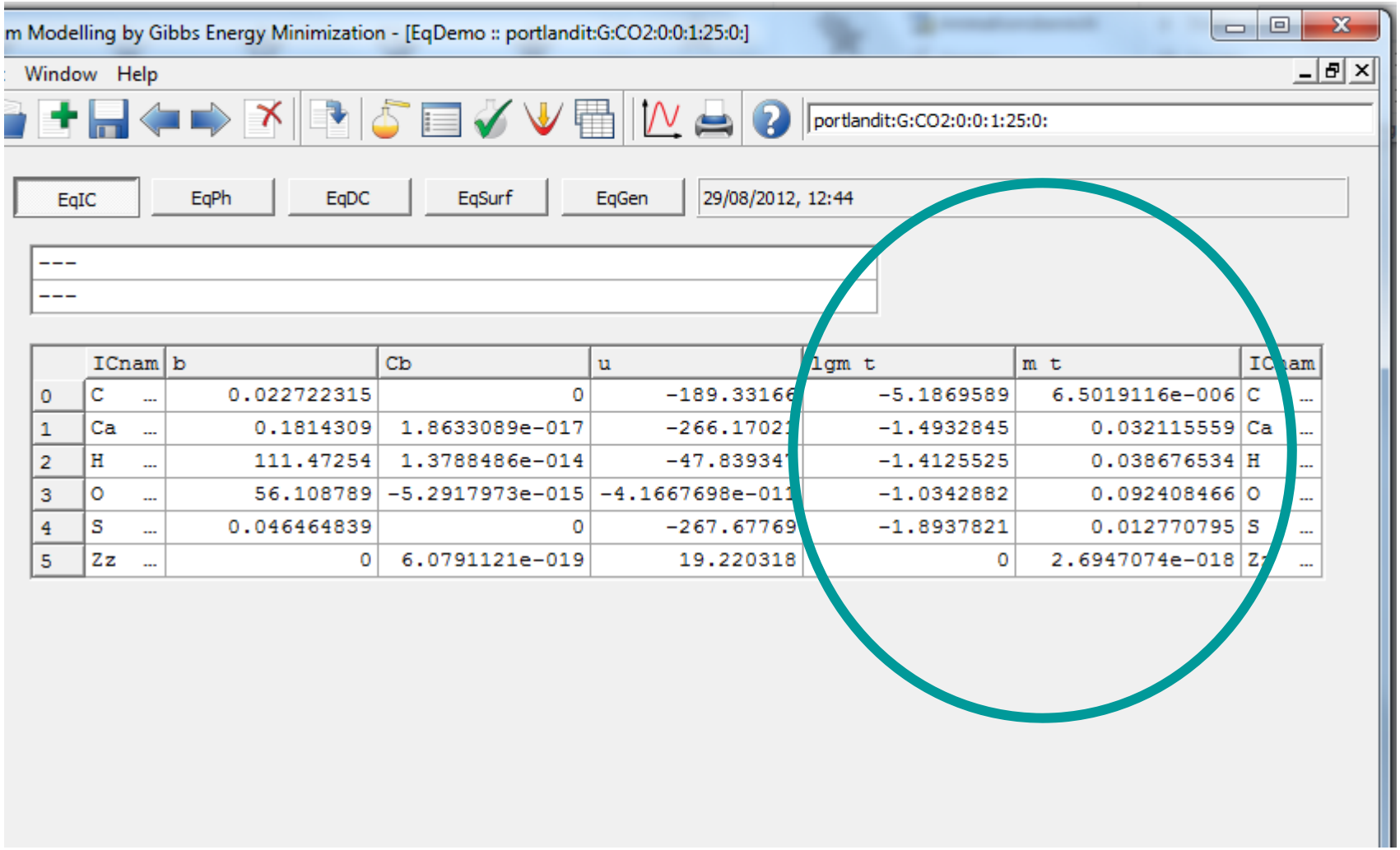



| | PHnam | | Xa | Fa | phVol | phM |
|---|---|---|---|---|---|---|
| 0 | a | aq_gen | 55.631449 | 4.049238e-010 | 1003.4458 | 1004.0869 |
| 1 | g | gas_gen | 0.0018093475 | -3.6160014e-011 | 44.853204 | 0.057896951 |
| 2 | s | Graphite | 0 | -82.225695 | 0 | 0 |
| 3 | s | Aragonite | 0 | -0.14383216 | 0 | 0 |
| 4 | s | Calcite | 0.022715807 | 9.9544516e-010 | 0.8389856 | 2.273557 |
| 5 | s | lime | 0 | -9.7759048 | 0 | 0 |
| 6 | s | Portlandite | 0.092888665 | 4.112154e-008 | 3.0708992 | 6.8823719 |
| 7 | s | Anhydrite | 0 | -0.22276489 | 0 | 0 |
| 8 | s | Gypsum | 0.033682935 | 2.9568298e-008 | 2.5157783 | 5.7992987 |
| 9 | s | hemihydrate | 0 | -0.98902801 | 0 | 0 |
| 10 | s | Sulphur | 0 | -116.25094 | 0 | 0 |

| pmXs | 14.955228 |
|---|---|

# Results 2

Aqueous concentrations (mg/l, mM, …)




| | ICnam | b | Cb | u | lgm t | m t | ICnam |
|---|---|---|---|---|---|---|---|
| 0 | C … | 0.022722315 | 0 | -189.33166 | -5.1869589 | 6.5019116e-006 | C … |
| 1 | Ca … | 0.1814309 | 1.8633089e-017 | -266.17021 | -1.4932845 | 0.032115559 | Ca … |
| 2 | H … | 111.47254 | 1.3788486e-014 | -47.83934 | -1.4125525 | 0.038676534 | H … |
| 3 | O … | 56.108789 | -5.2917973e-015 | -4.1667698e-011 | -1.0342882 | 0.092408466 | O … |
| 4 | S … | 0.046464839 | 0 | -267.67769 | -1.8937821 | 0.012770795 | S … |
| 5 | Zz … | 0 | 6.0791121e-019 | 19.220318 | 0 | 2.6947074e-018 | Zz … |

# 3 GEMS

What is GEMS?

German speakers

Geochemists

English speakers

**Gemstone**

**Gemse** *(chamois)*

GEMS SELEKTOR

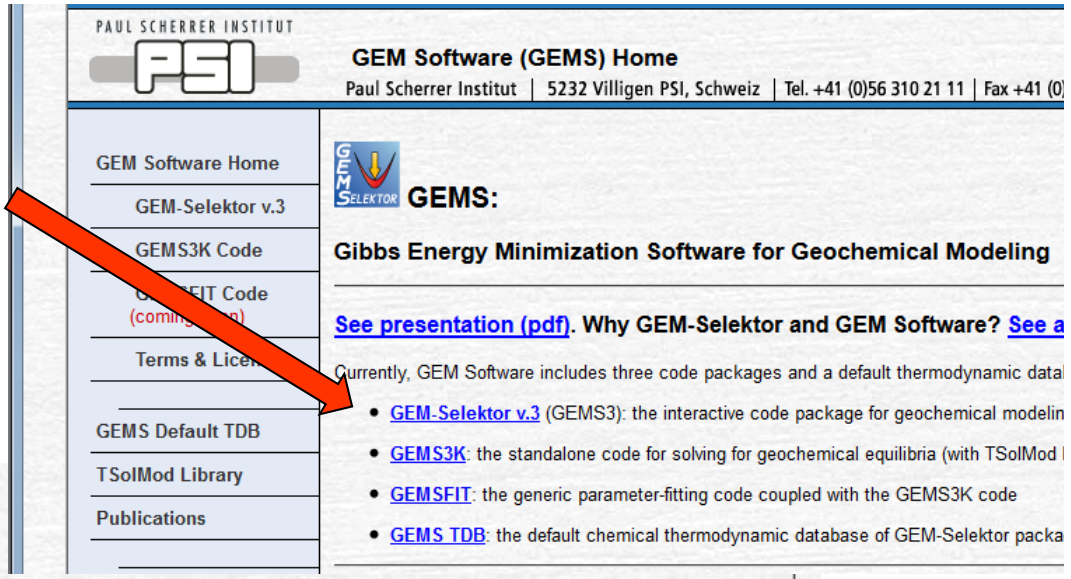
**GEMS TM:**

**Gibbs Energy Minimization Software for Thermodynamic Modelling**

# Installation of GEMS 3

1) http://gems.web.psi.ch/

2)




3) Click on «download», «click here to register…», give your details and

4)

## GEM-Selektor v.3 HTTP Download Page

**Your GEMS3.7.x GEM-Selektor package download registration form has been submitted successfully.**

For more information about installing GEM-Selektor on various operation systems, please download the Installation instructions (pdf) or check the Technical Info page.

Please, use an appropriate direct link below to download the actual revision of the package (to save the installer archive file to disk):

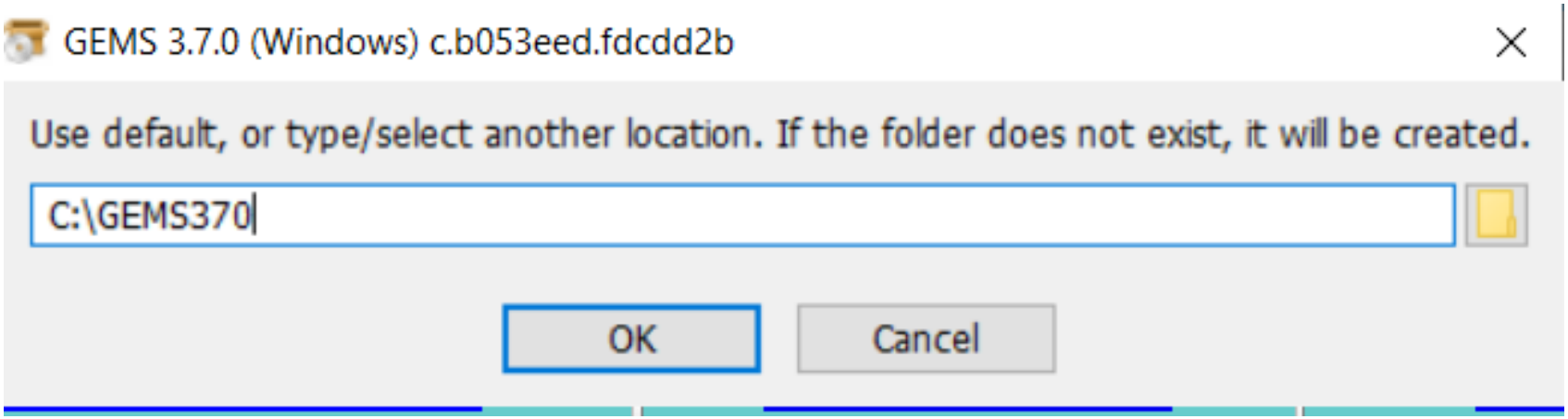
| GEMS3.7.0 for Windows-64 | GEMS3.7.0 for MacOS | GEMS3.7.0 for Ubuntu Linux-64 |
|---|---|---|

**Attention!** There were relavant improvements and functionality additions in GEM-Selektor version 3.7 compared to previous versions. It is recommended to upgrade as soon as possible.

**Attention!** There is a lot of improved functionality in GEM-Selektor v.3.3 or higher compared with v.3.2. For backward compatibility, all modelling projects created in GEM-Selektor v.3.2.x or earlier, will open and work normally in GEM-Selektor v.3.3.x; accordingly, GEMS3K I/O files exported from GEM-Selektor v.3.2.x are readable and will work in coupled codes and examples using GEMS3K v.3.3.x.

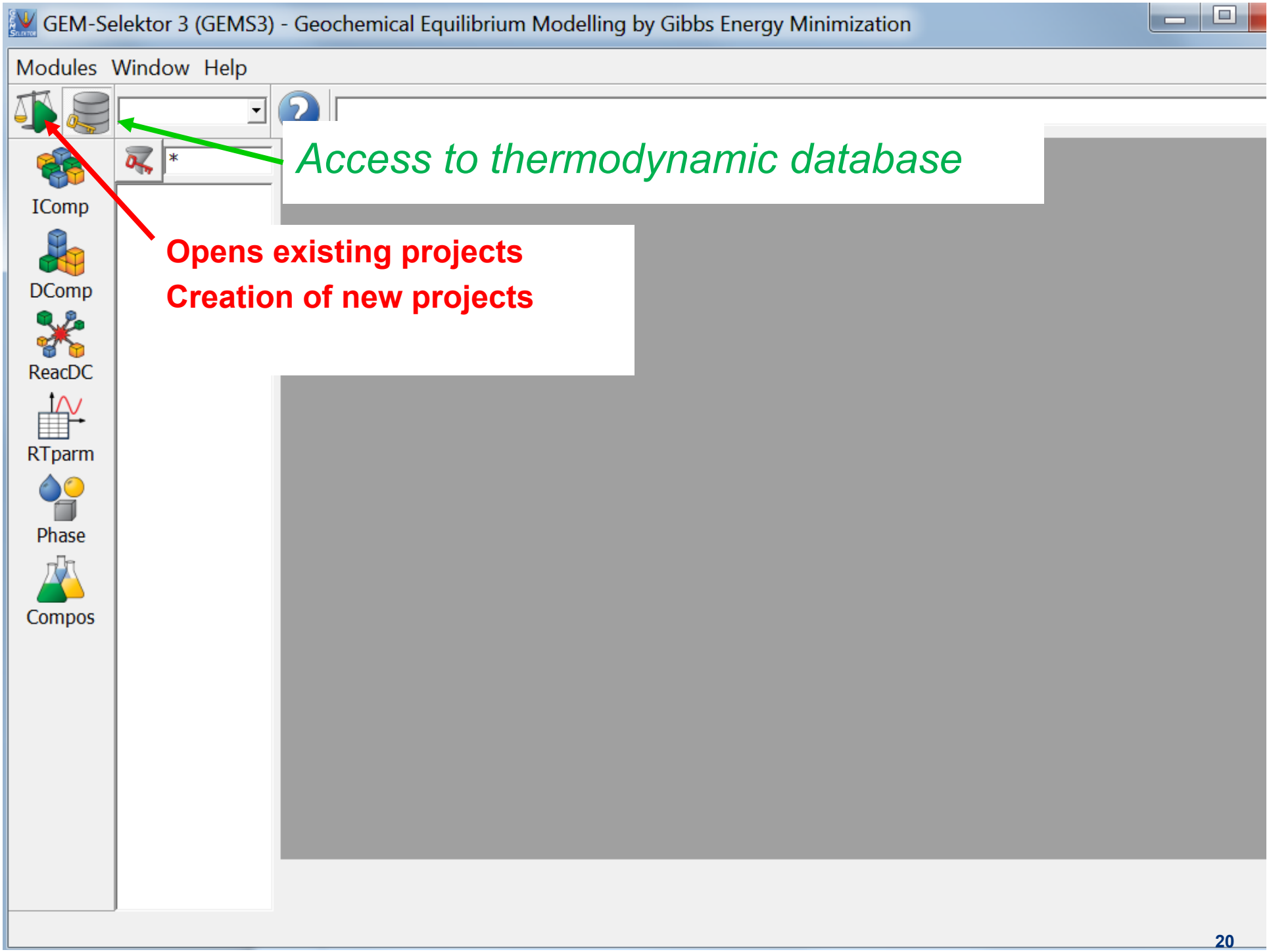
Immediate extension of old modeling projects in GEM-Selektor v.3.3.x with newly created Phase records, remaking existing Phase records, or via Project remake/extension wizard is possible. Before doing that, the user needs only once to open the project; switch to Database Mode; open the Phase window; and remake one-by-one all Phase records available in the project (saving each record back after remake).

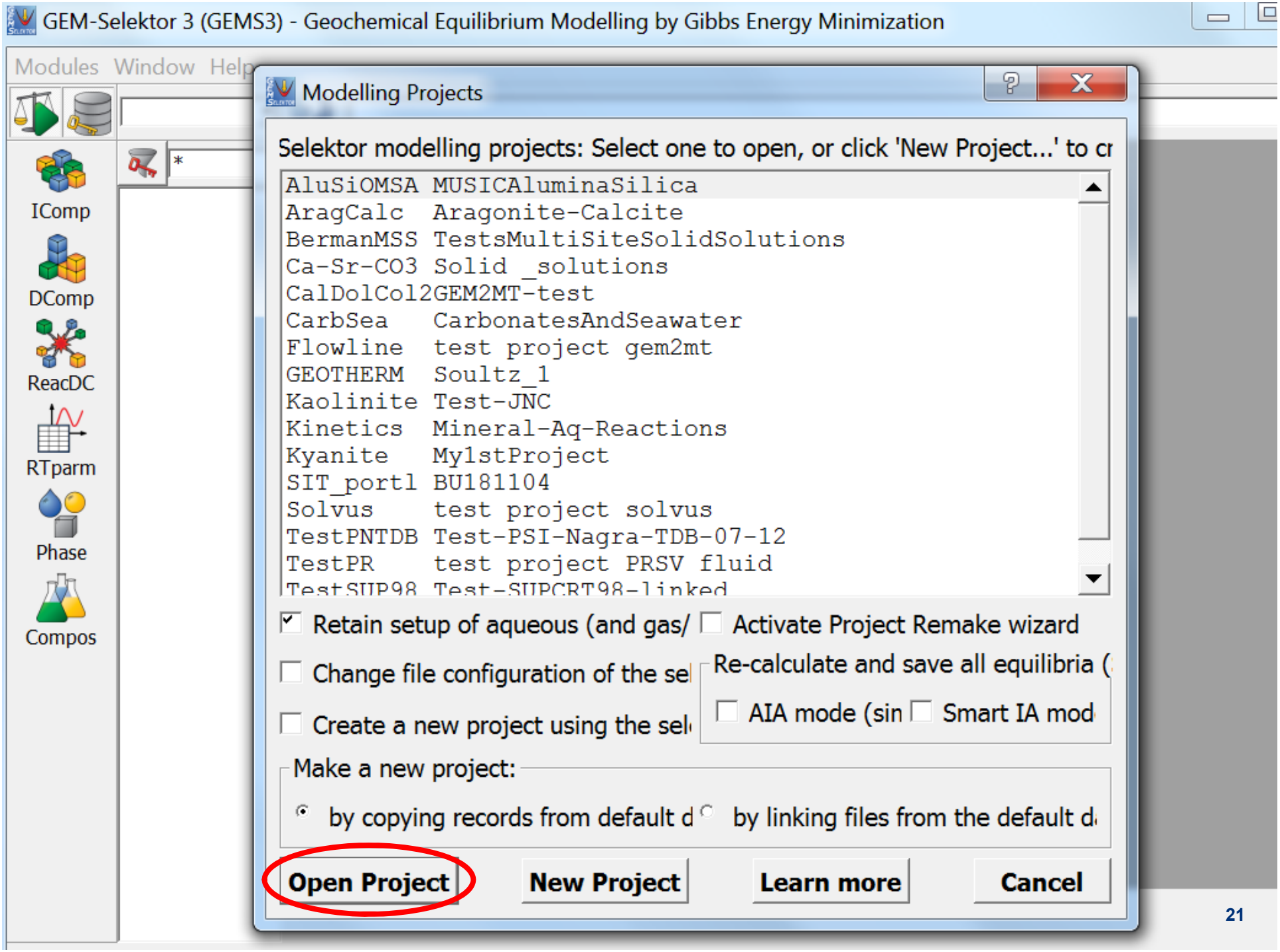
# Installation Windows




- Install the programme in C:\GEMS370
  *The creation of a new folder avoids, for those who had GEMS previously installed, problems with older versions of the thermodynamic databases (tdb).*

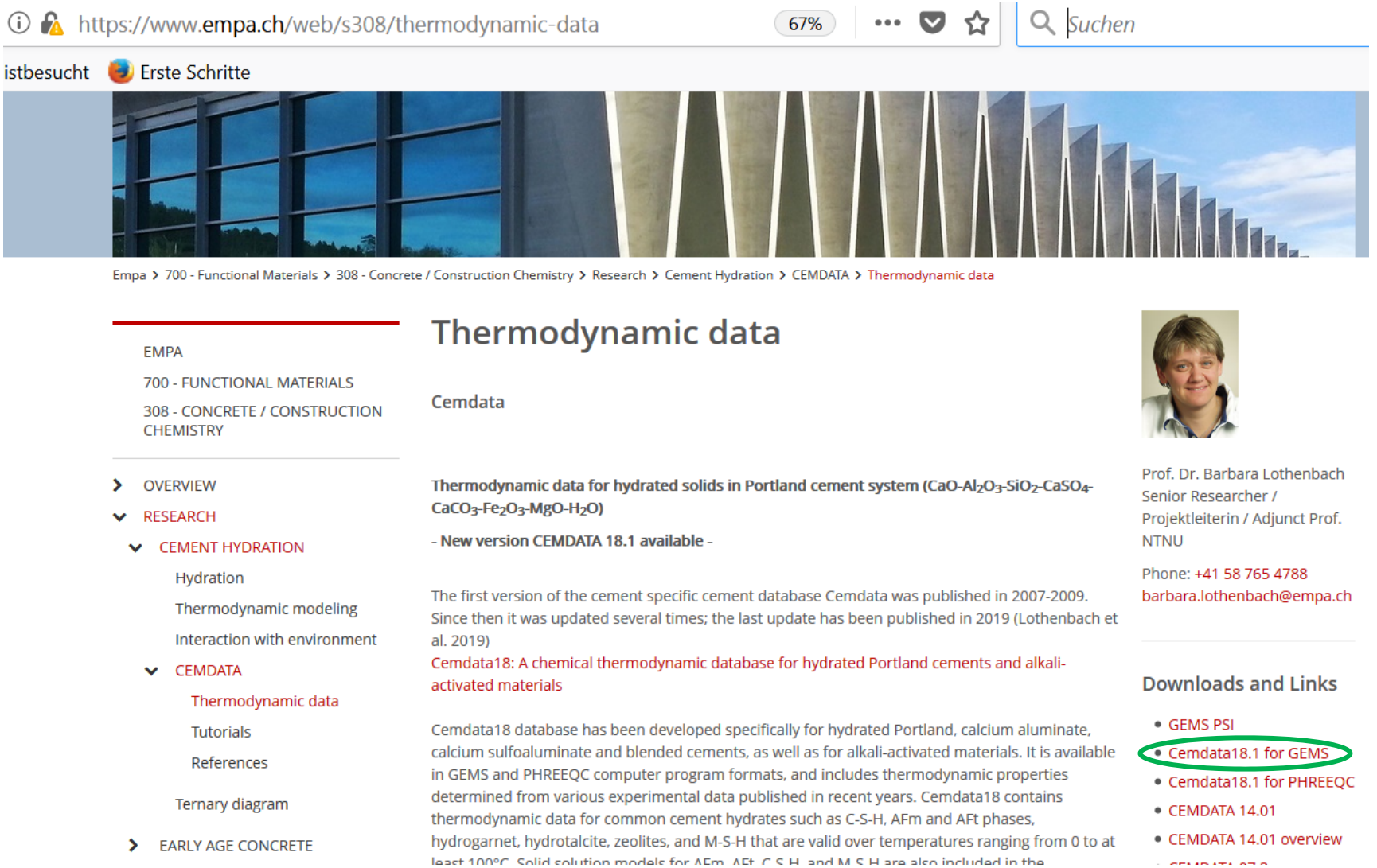
- ! Do **NOT** install it in the programme folder !
  *Problems with administrator rights in windows*


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization
Modules Window Help
IComp
DComp
ReacDC
RTparm
Phase
Compos
*
Access to thermodynamic database
Opens existing projects
Creation of new projects


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization
Modules Window Help
IComp
DComp
ReacDC
RTparm
Phase
Compos
Modelling Projects
Selektor modelling projects: Select one to open, or click 'New Project...' to cr
AluSiOMSA MUSICAluminaSilica
AragCalc Aragonite-Calcite
BermanMSS TestsMultiSiteSolidSolutions
Ca-Sr-CO3 Solid _solutions
CalDolCol2GEM2MT-test
CarbSea CarbonatesAndSeawater
Flowline test project gem2mt
GEOTHERM Soultz_1
Kaolinite Test-JNC
Kinetics Mineral-Aq-Reactions
Kyanite My1stProject
SIT_portl BU181104
Solvus test project solvus
TestPNTDB Test-PSI-Nagra-TDB-07-12
TestPR test project PRSV fluid
Retain setup of aqueous (and gas/
Activate Project Remake wizard
Change file configuration of the sel
Re-calculate and save all equilibria (
Create a new project using the sel
AIA mode (sin
Smart IA mod
Make a new project:
by copying records from default d
by linking files from the default d
Open Project
New Project
Learn more
Cancel

# Installation of cement database

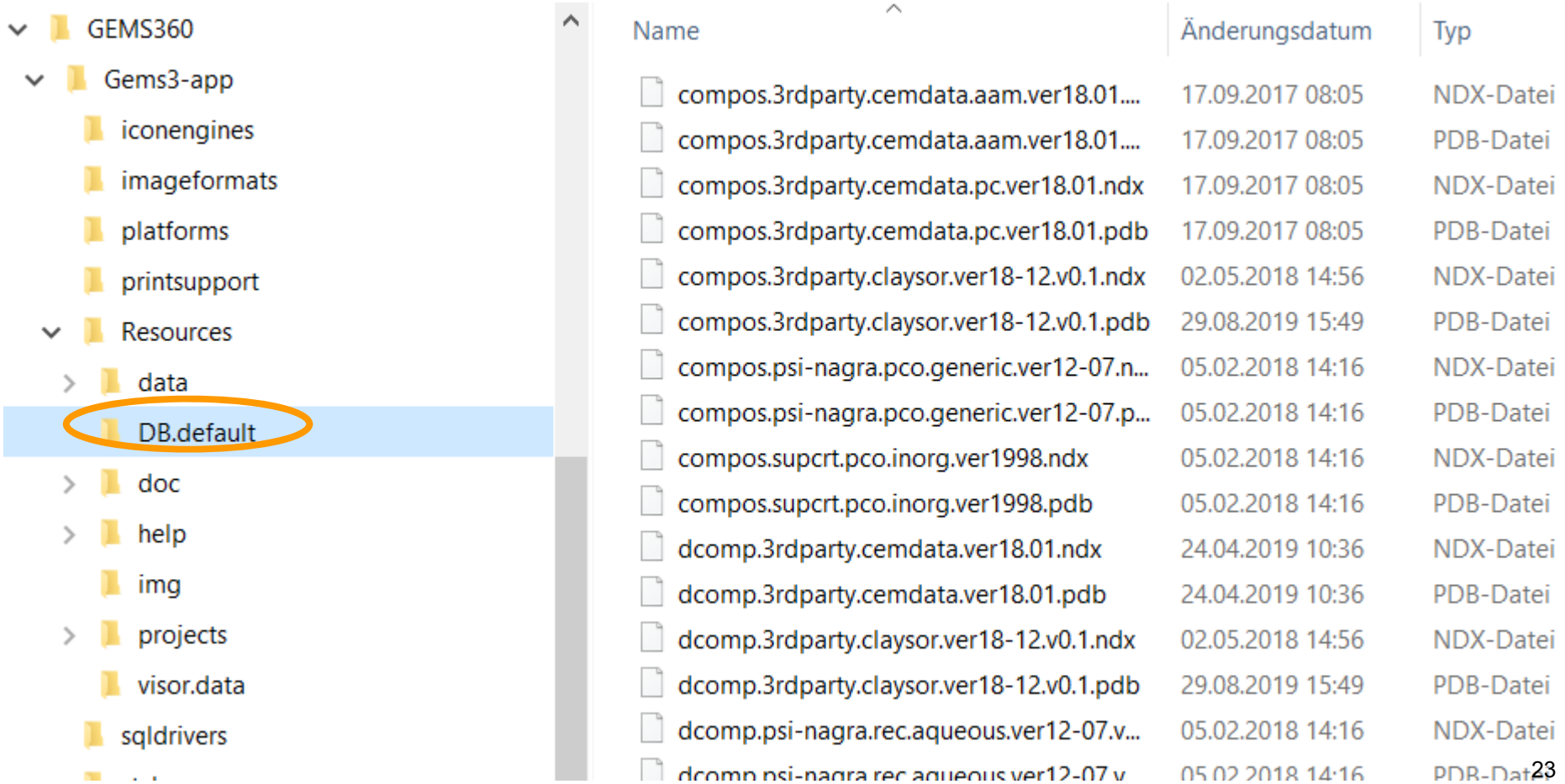
1. **Close GEMS**
2. Get cemdata18 at https://www.empa.ch/web/s308/thermodynamic-data




3. unzip cemdata18 database

# Installation of cement database

1. **Close** GEMS
2. Get cemdata18 and unzip folder
3. Copy all files (*without folder!*) from the folder Cemdata18 into the directory C:\GEMS345/GEMS3-app/Resources/DB.default
4. Open GEMS and cemdatabase will be available for «new projects»

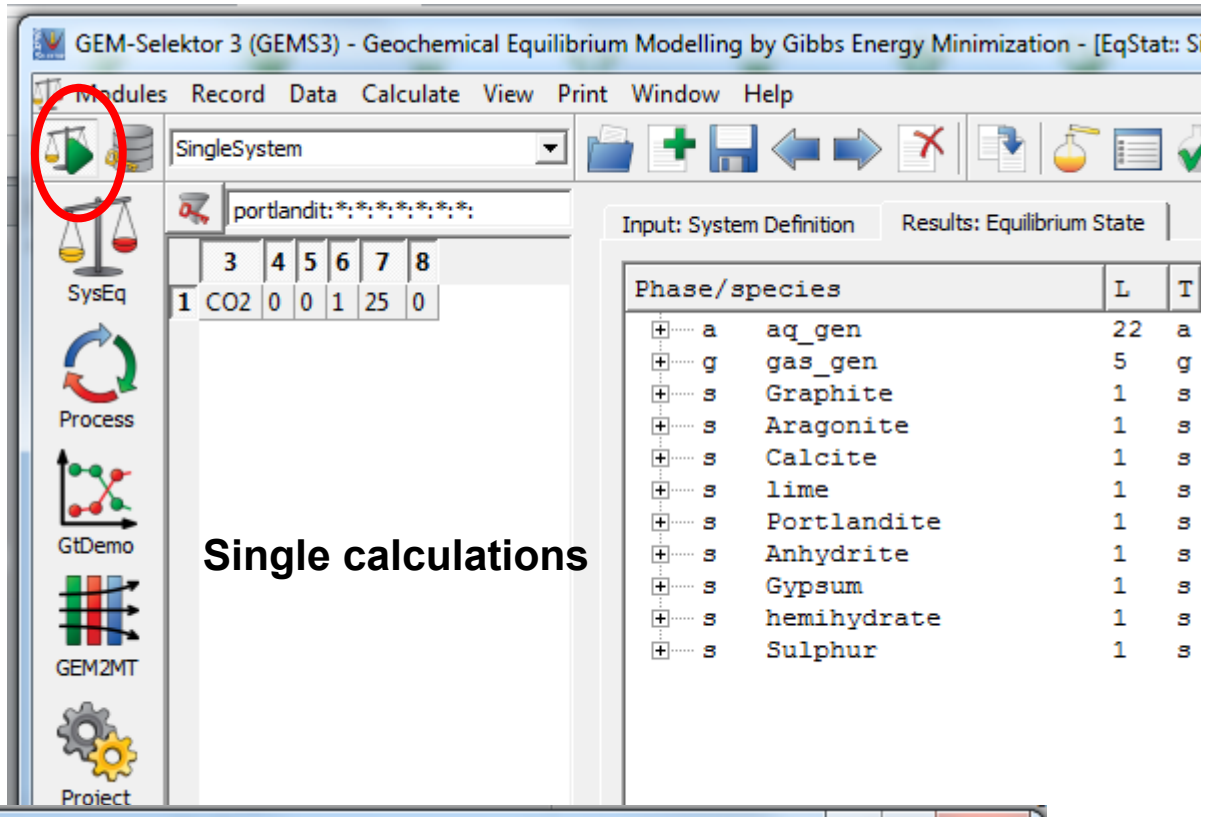


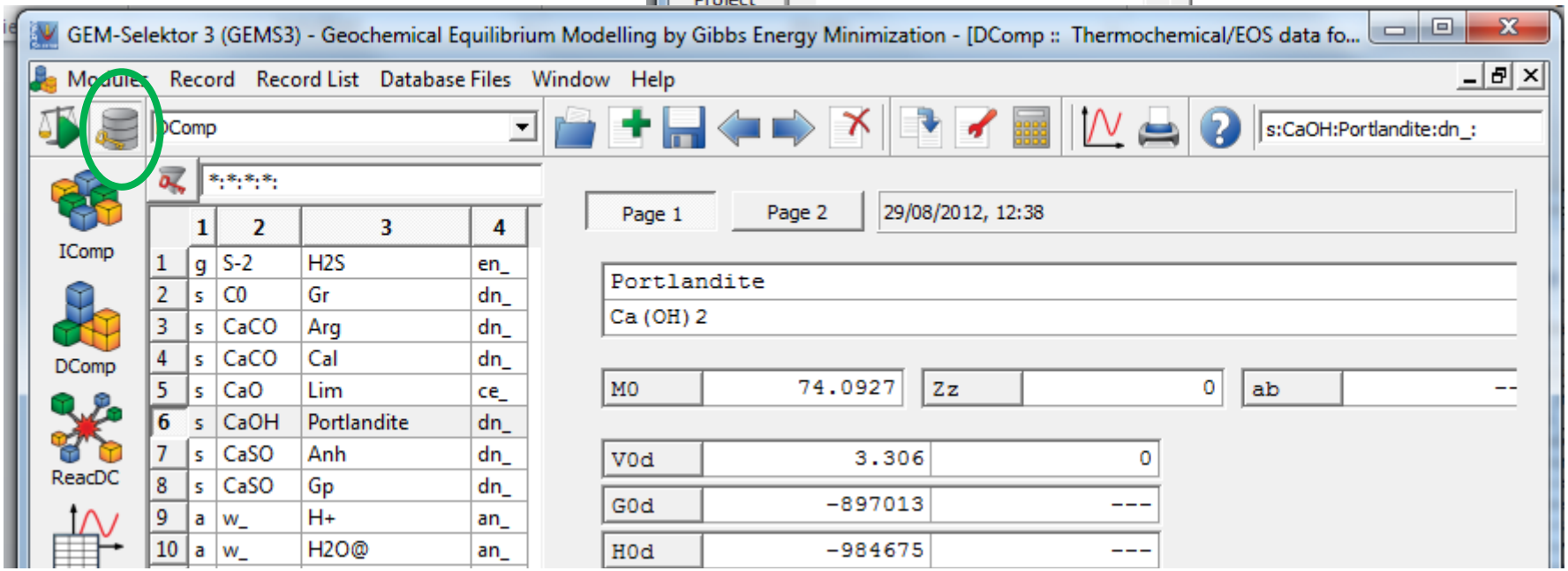
# GEMS structure

**calculations**

**Thermodynamic database**

***for experienced users***



*Access database*

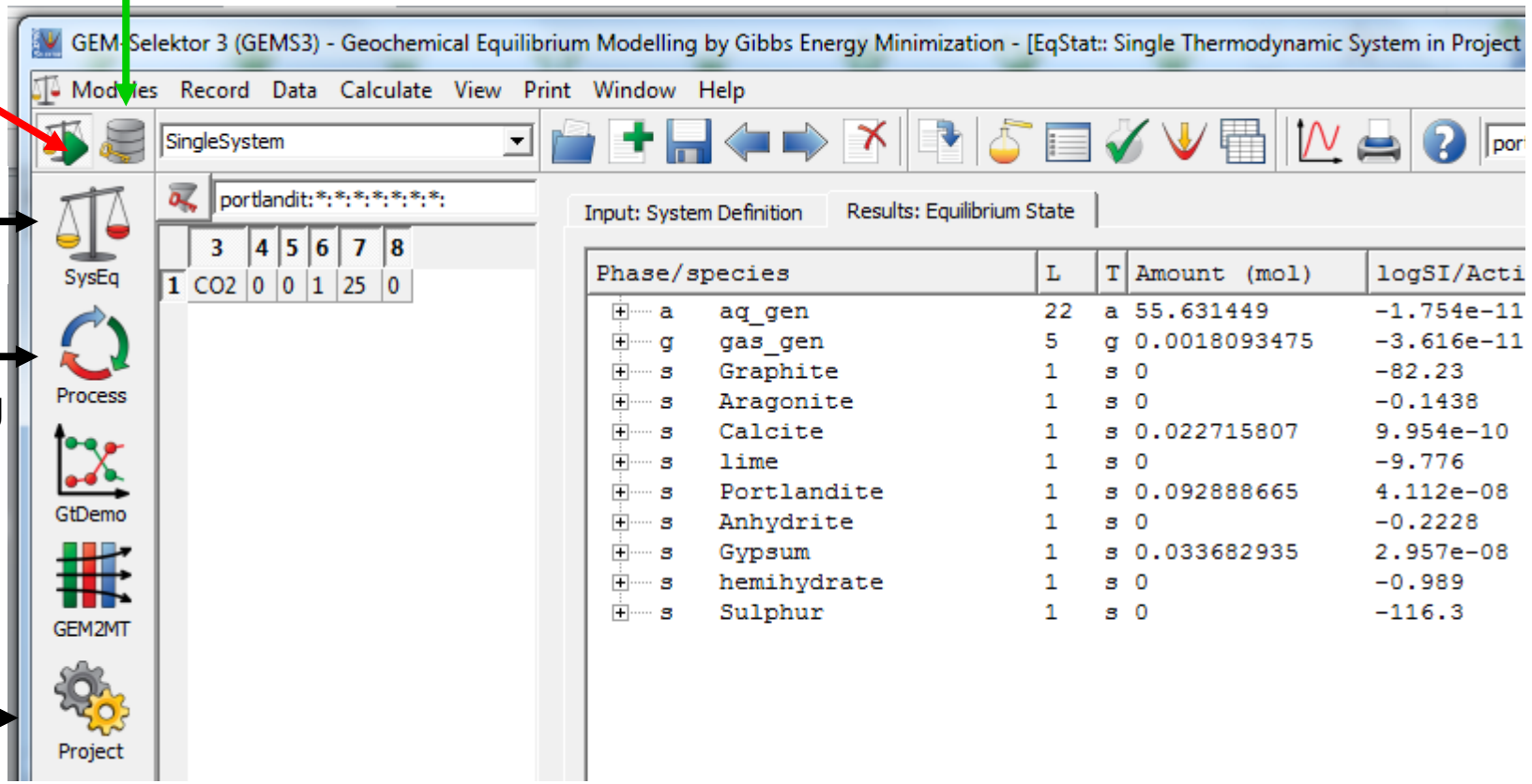
**Opens projects**

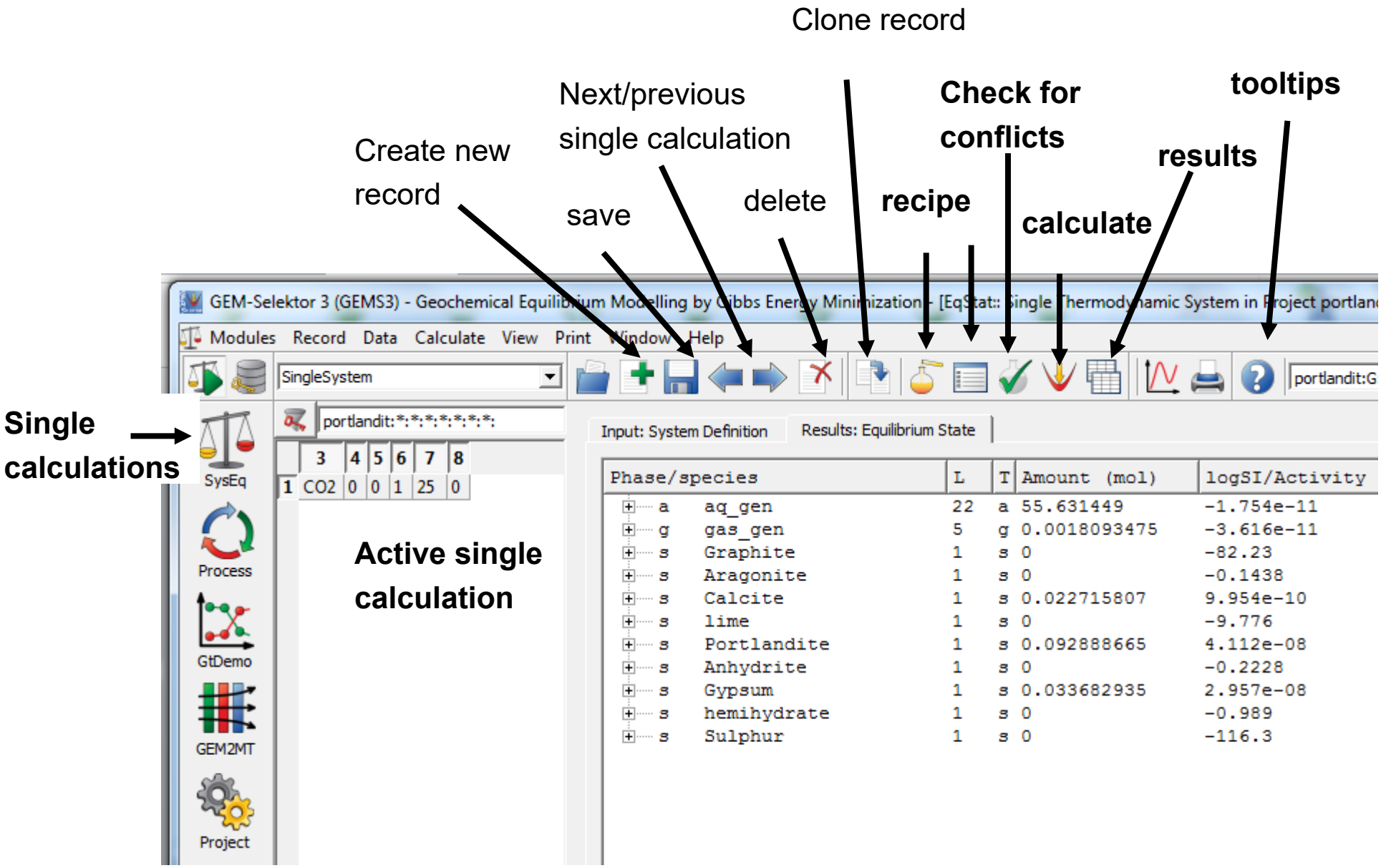
**Single calculations**

**Processes: programming of single calcualtions**

**Numerical settings**

***Normally not used***






**Continue with tutorial C3A**

# First Tutorial – single systems: hydration of $C_3A$

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## Hydration of $C_3A$ ($Ca_3Al_2O_6$)[a]

1) Simulation of reaction $C_3A + CaO + CaSO_4$ Guided tutorial

2) Simulation of reaction $C_3A + CaO + CaCO_3$

3) Simulation of reaction $C_3A + CaCO_3$

4) Simulation of reaction $C_3A + C + CaSO_4 + CaCO_3$

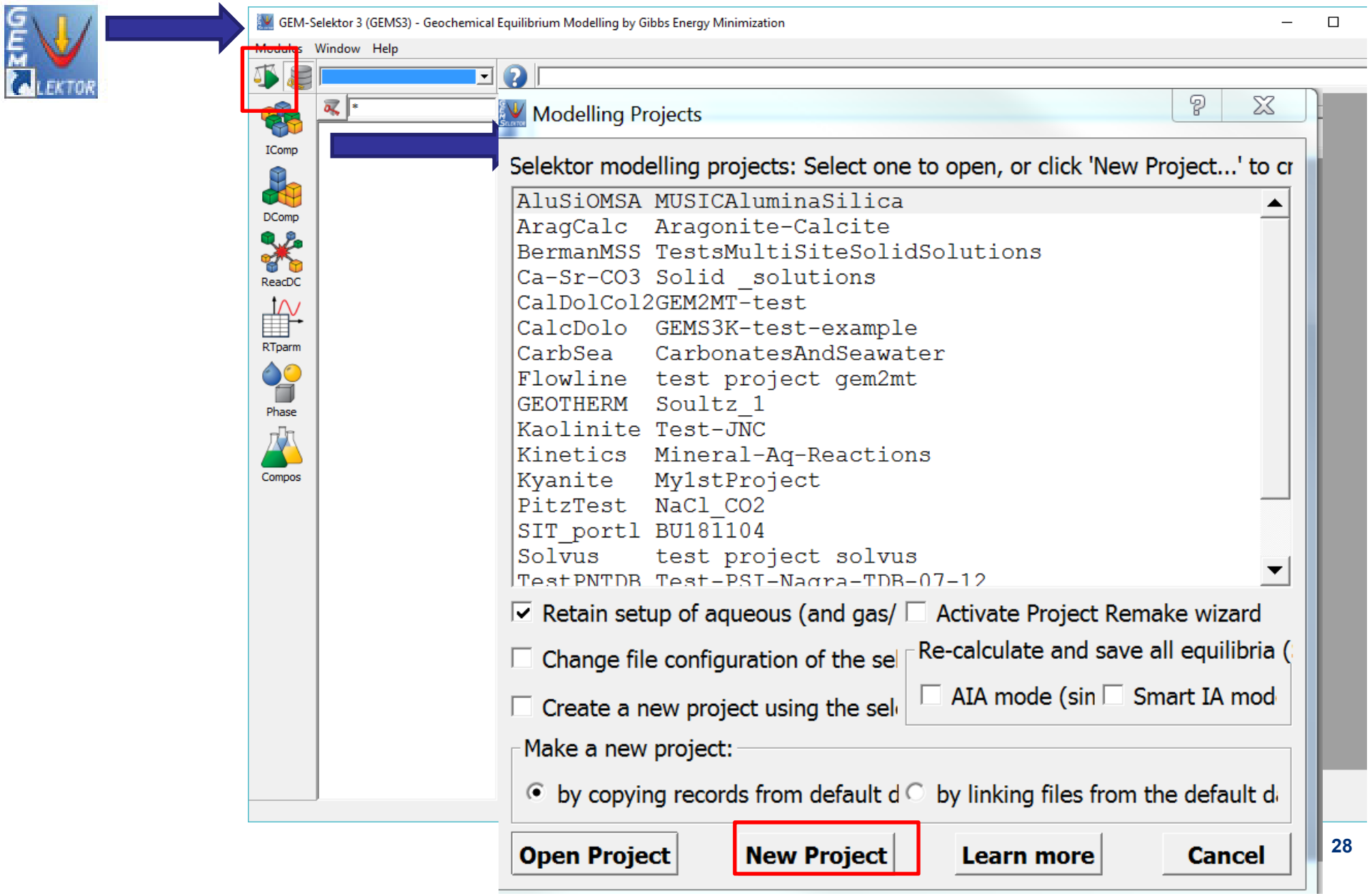
} Individual work

See Seligmann & Greening ICCC 1969 and various papers by Kuzel et al. (Kuzel & Pöllmann CCR 1991, Kuzel et. al CCR 1996) for experimental verification

[a] cement notation

| | |
|---|---|
| C => CaO | A => $Al_2O_3$ |
| S => $SiO_2$ | H => $H_2O$ |
| s => $SO_3$ | c=> $CO_2$ |

# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup



# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup

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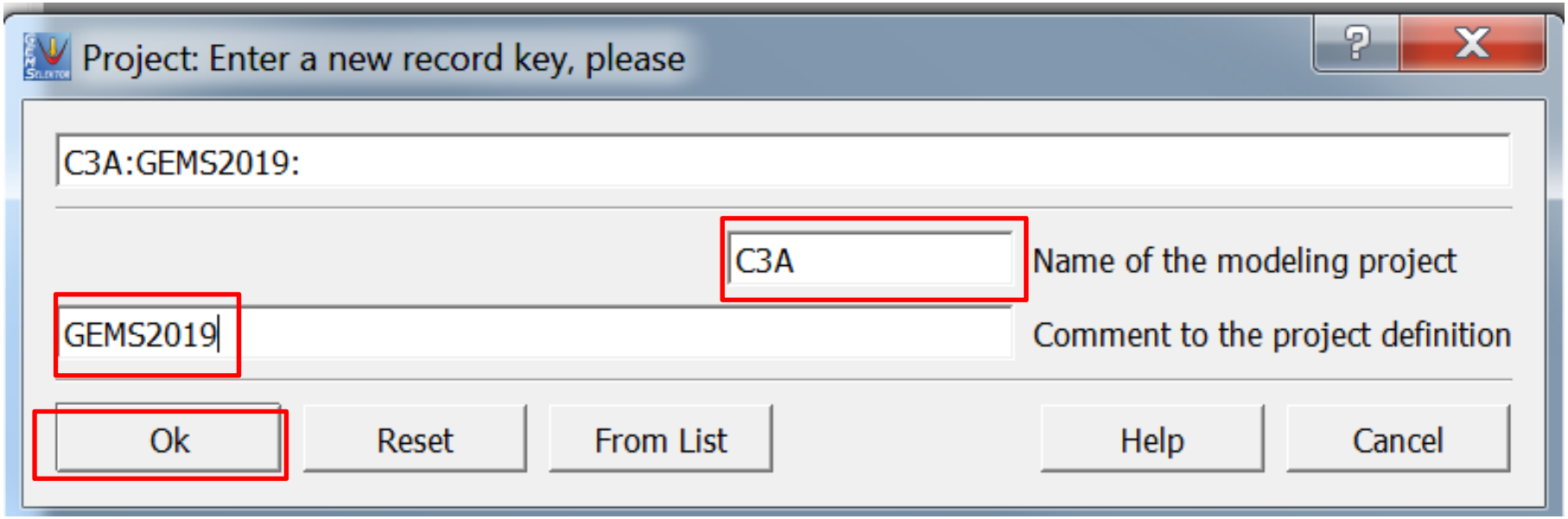
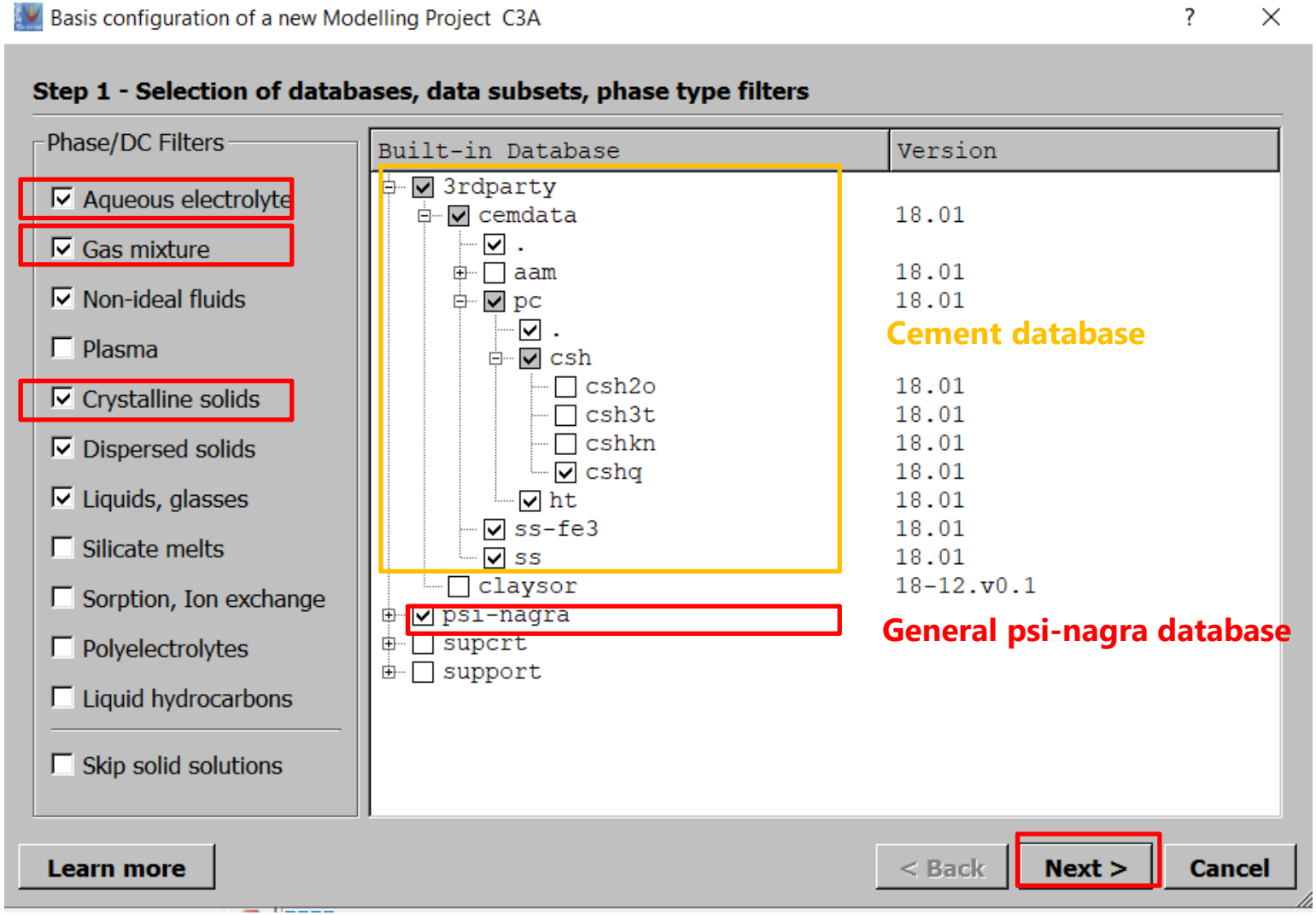


# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup

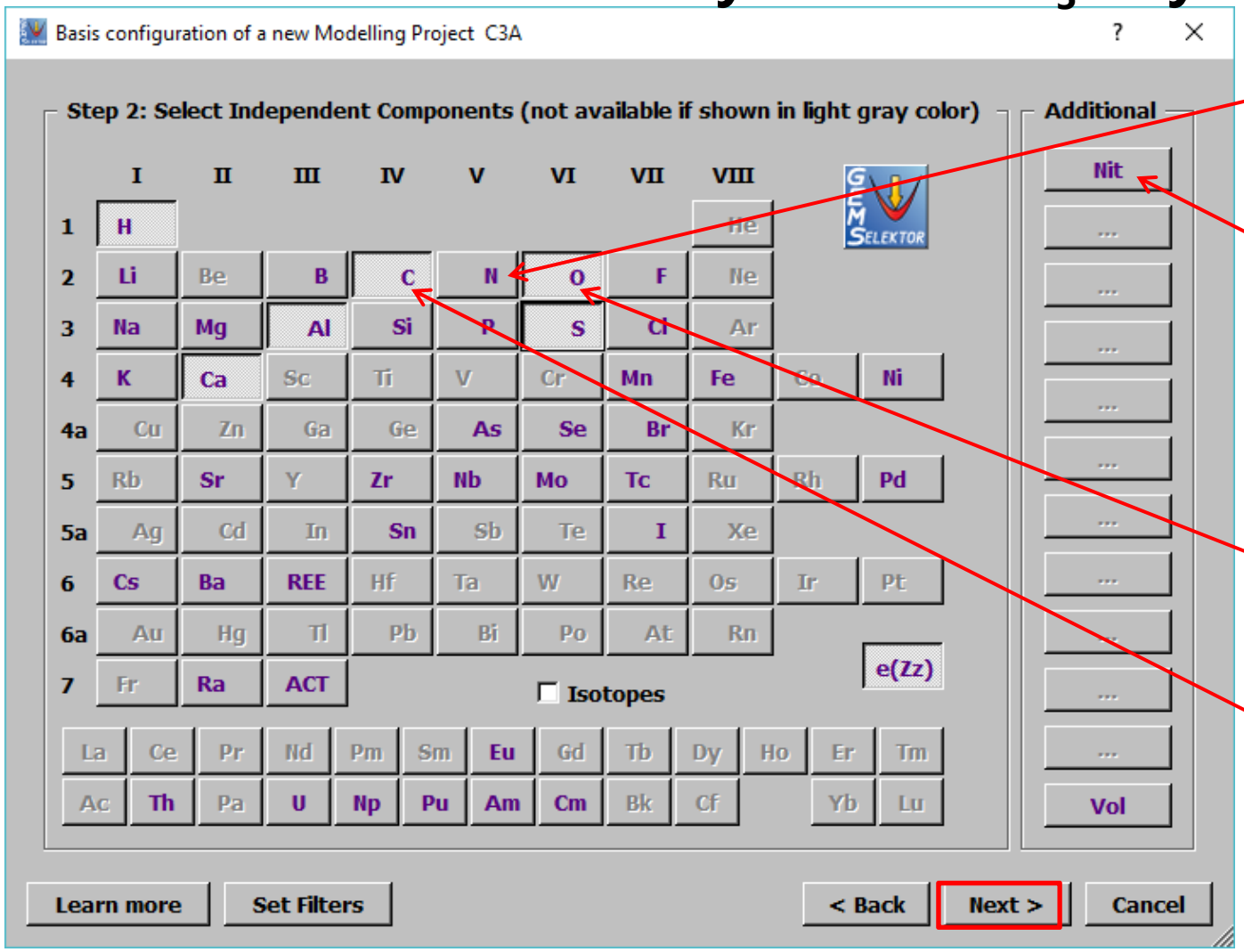
## Select CEMDATA18 (3rd party data base)




**Recommended selection for PC and blended cements**

# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup

## Select elements necessary to model $C_3A$ hydration




„reactive N“ (don‘t use here)

Air: $O_2$, $N_2$, etc. (no reducing conditions, $N_2$ not reactive)

we can also use just oxygen ($O_2$)

needed for parts 2+3 of the tutorial

# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup

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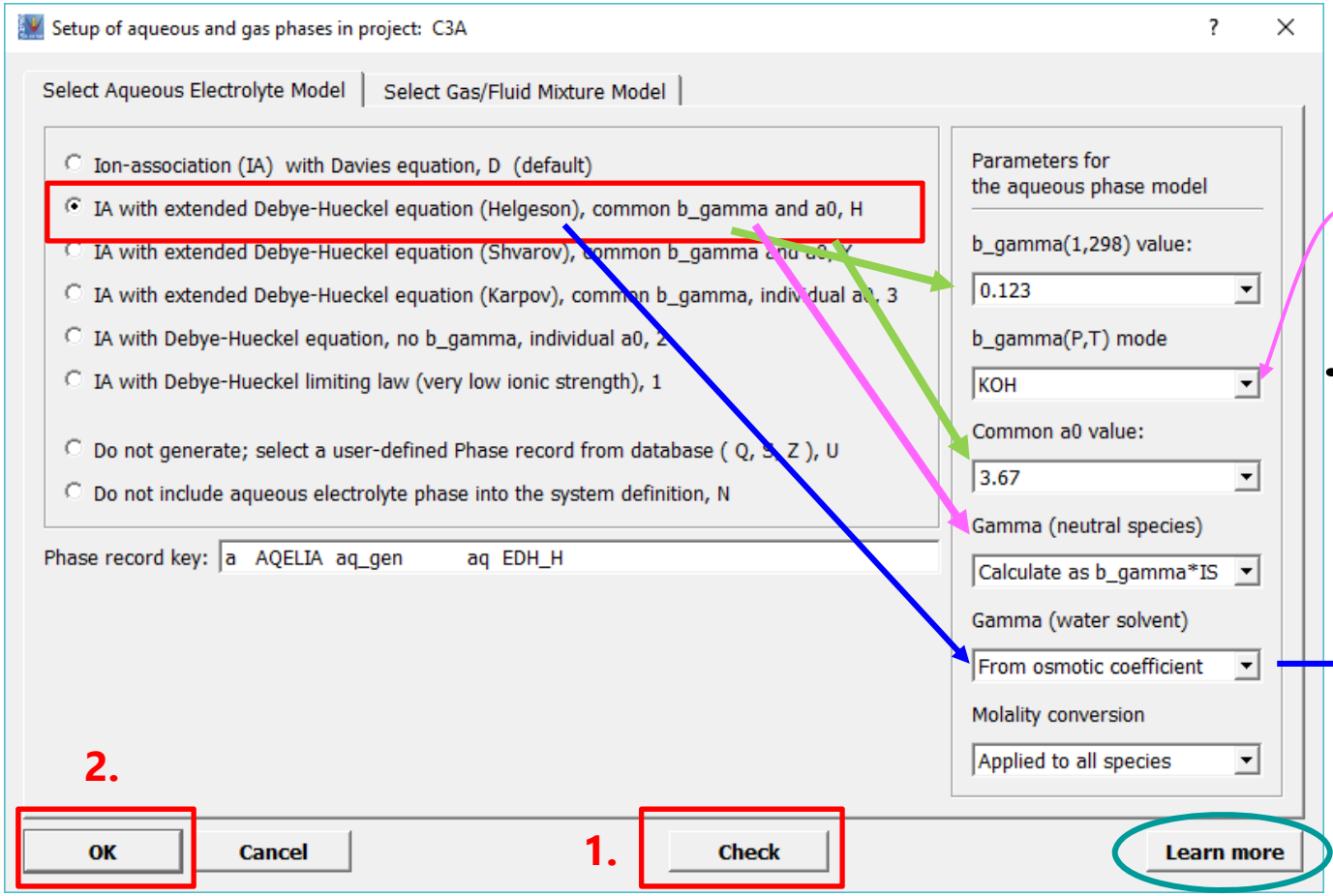
## Select model for calculation of the aqueous phase




1) KOH good for cements

2) f(pressure, temp) -> electrolyte

a0=3.67 for KOH
b0= 0.123

*Calculates activity of water*

More details

# Activity coefficients

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Solubility product e. g. of gypsum

$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\}\cdot\{H_2O\}^2/\{CaSO_4\cdot 2H_2O\}$

$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\} = 10^{-4.58}$

{ } : activity; [ ]: concentration

$\{Ca^{2+}\} = [Ca^{2+}] \cdot \gamma_{Ca2+}$ ← **Activity coefficicient**

Correction of concentrations by activity coefficients, as the ions „feel" their neighbours (other ions, solvent).

Activity coefficients depend mainly on:

- ionic strength
- other ionic species
- temperature

# Activity vs. ionic strength – selecting the right aqueous electrolyte model

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**Debye-Hückel** $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}}$ **ionic strength** **I < 0.1 M**

**Extended Debye-Hückel** $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}} + bI$

**common a, common b (Helgeson)** **I < 1-2 M**

individual a, common b (Truesdell-Jones) **I < 1 M**

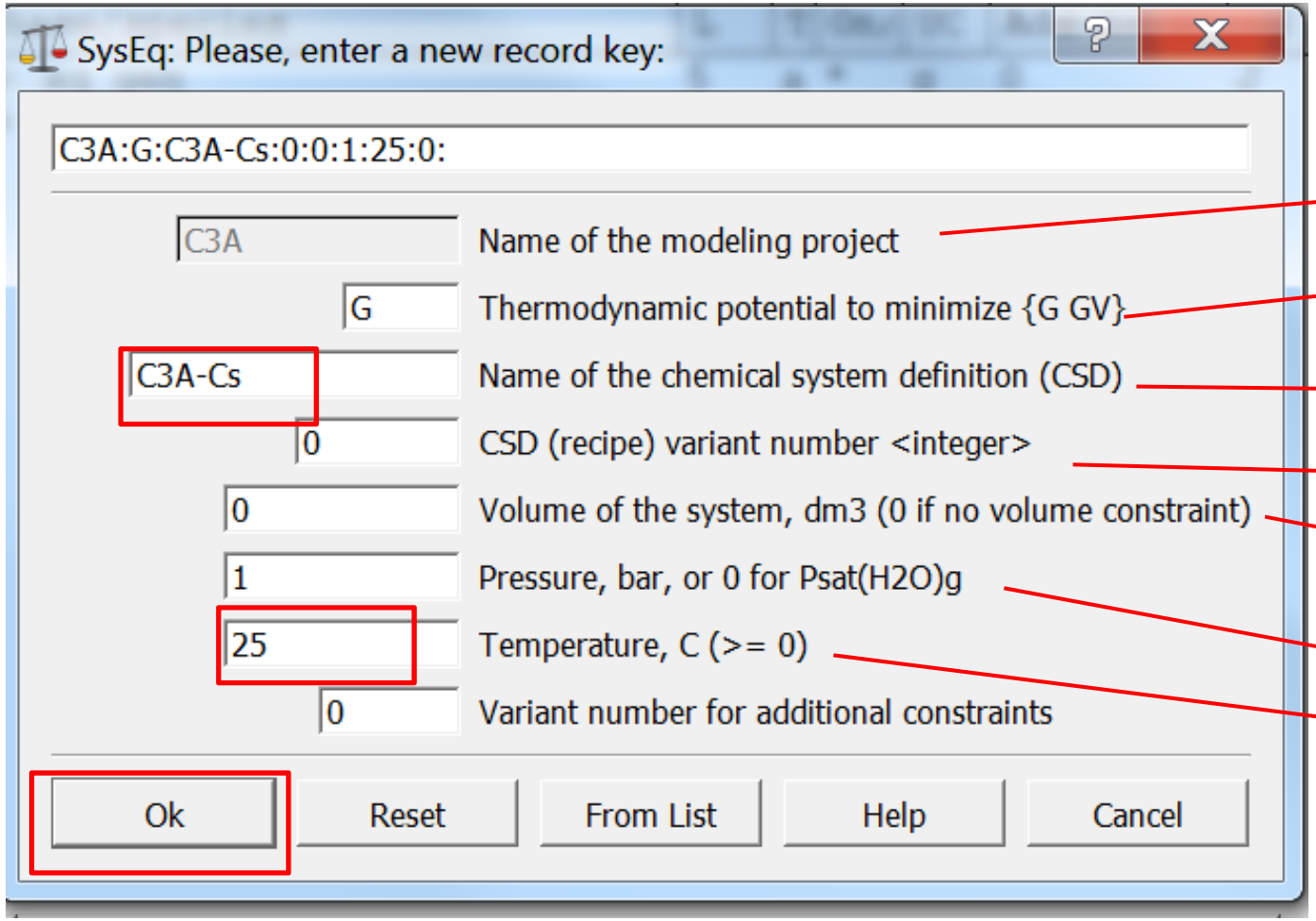
individual a, no b **I < 0.3M**

**Davies** $\log \gamma_{Ca^{2+}} = -AZ^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$ **0.1 < I <0. 5 M**

**SIT** $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+1.5\sqrt{I}} + \sum \varepsilon m_k$ **I < 3 M**

The calculation of activity coefficients is available as built-in function in the GEMS code.
For a detailed overview of different activity coefficients see:
C:\GEMS36\Gems3-app\Resources\doc\pdf\Activity-Coeffs.pdf and references therein

# Hydration of $C_3A$ + CaO + $CaSO_4$ – project setup




**Project name**

**Method (Gibbs energy minimization)**

**System definition**

**Integer (default 0)**

**System volume unconstrained**

**Pressure (bar)**

**Temperature (°C)**

**Avoid special signs such as $ & % ä ö ü æ å ø 好 ...**

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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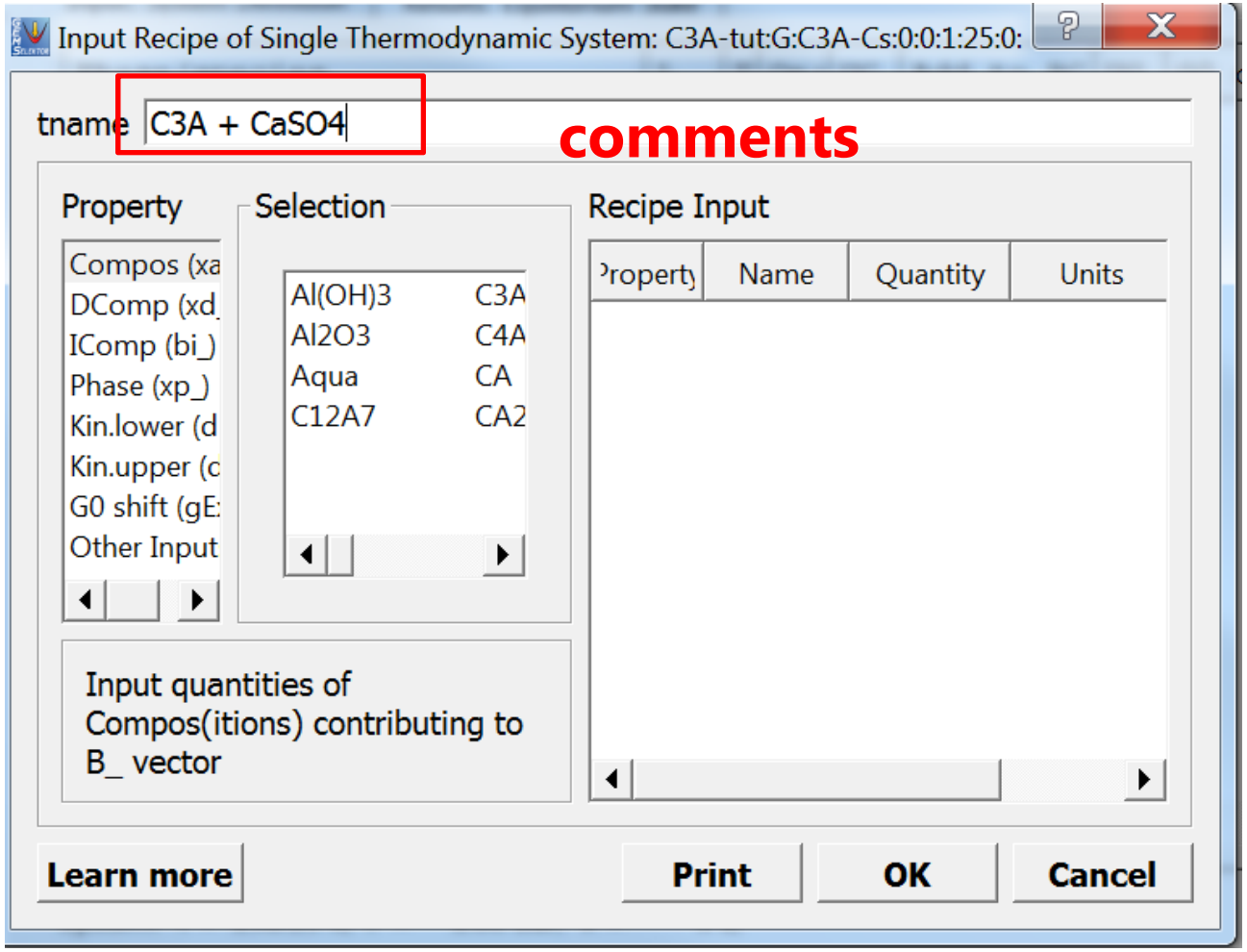
## We need a receipe



# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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## 1 Reaction of $C_3A$ with calcium sulfate

**5 g $C_3A$ + 2.52 g $CaSO_4$ + 2.5 g CaO + 50 g $H_2O$**

*+ 0.1 g $O_2$ (oxidizing conditions, $CO_2$-free = no carbonation)*

molar ratio $SO_3/Al_2O_3$ = 1, molar ratio $CO_2/Al_2O_3$ = 0

Reaction products?

*Expectation: monosulfate*
*$Ca_4Al_2O_6SO_4$ $12H_2O$*
*No ettringite*
*$Ca_6Al_2O_8S_3O_{12}$ $32H_2O$*

> Equilibrium speciation

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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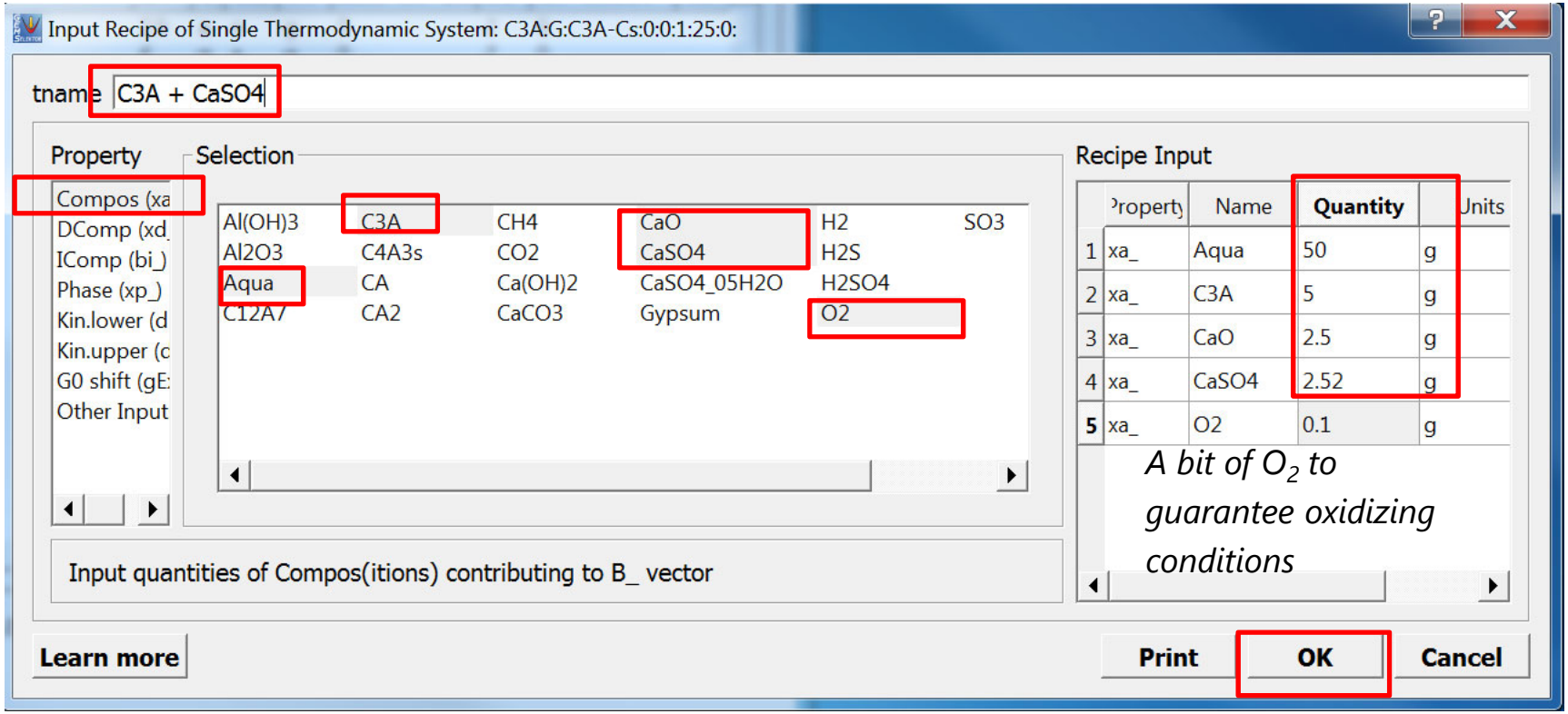

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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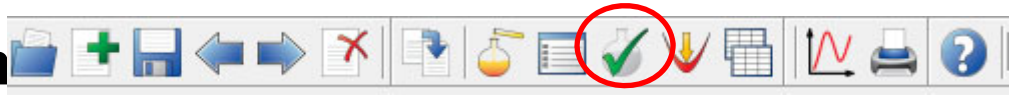
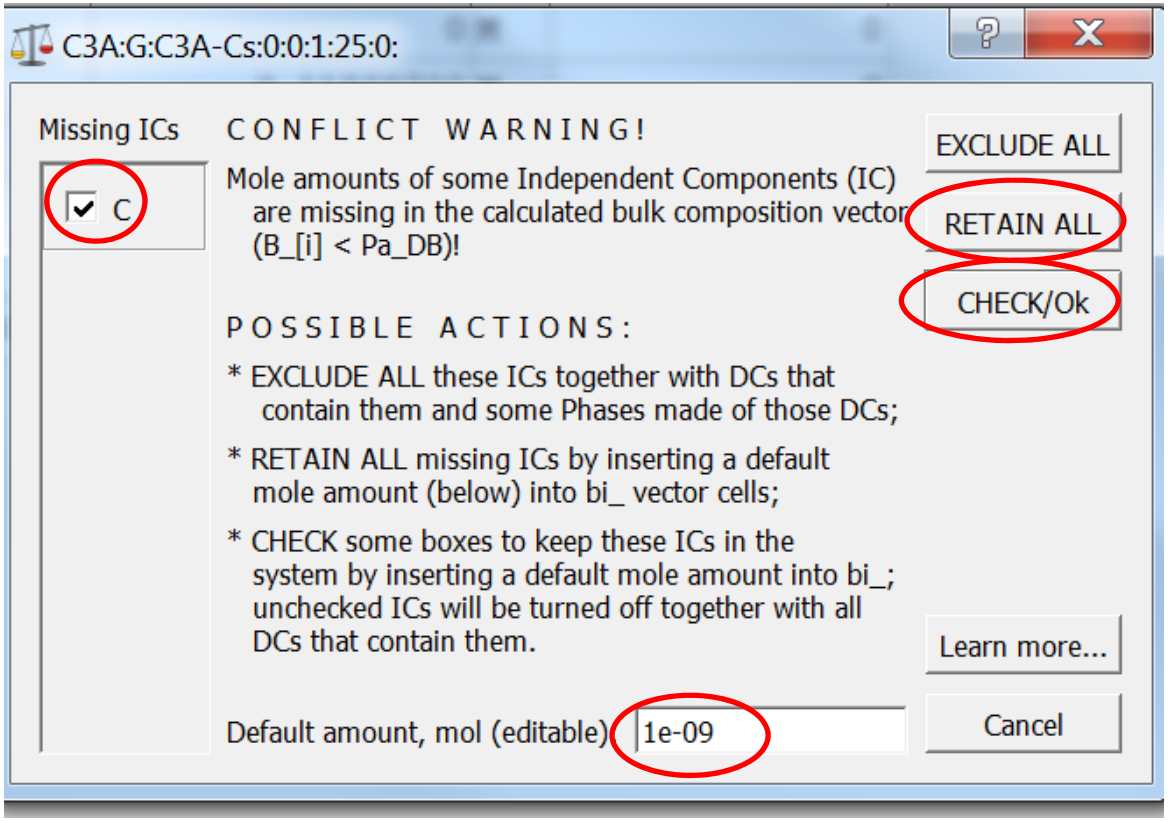
## Check system definition



we keep carbonate in this example

=> adds a very small amount of C ($10^{-9}$ M), has a negligible effect



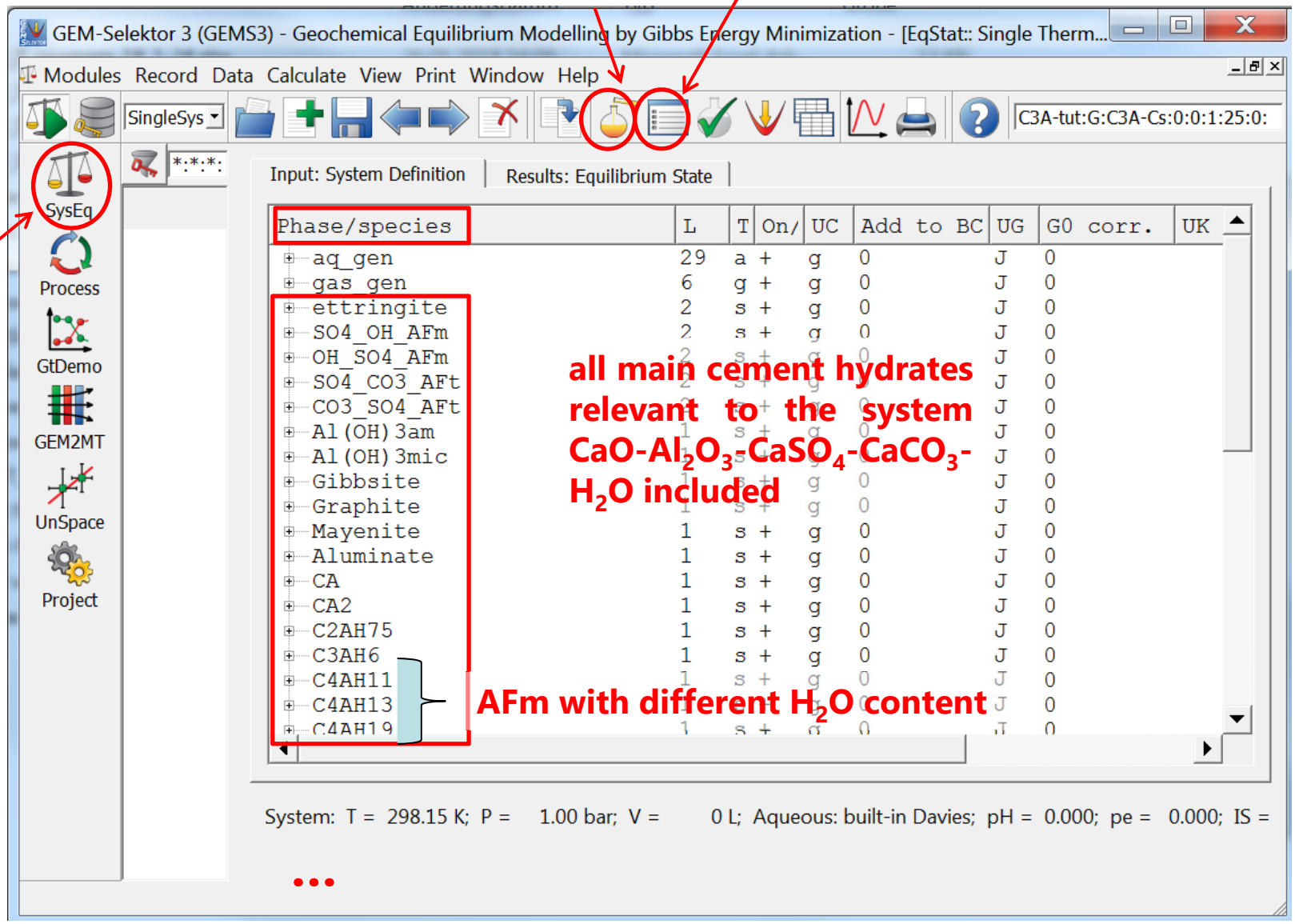
# GEMS interface

**2 equivalent input options**

Recipe wizard (previous page)

Detailed input recipe

Brings you always back to this screen



# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (input)

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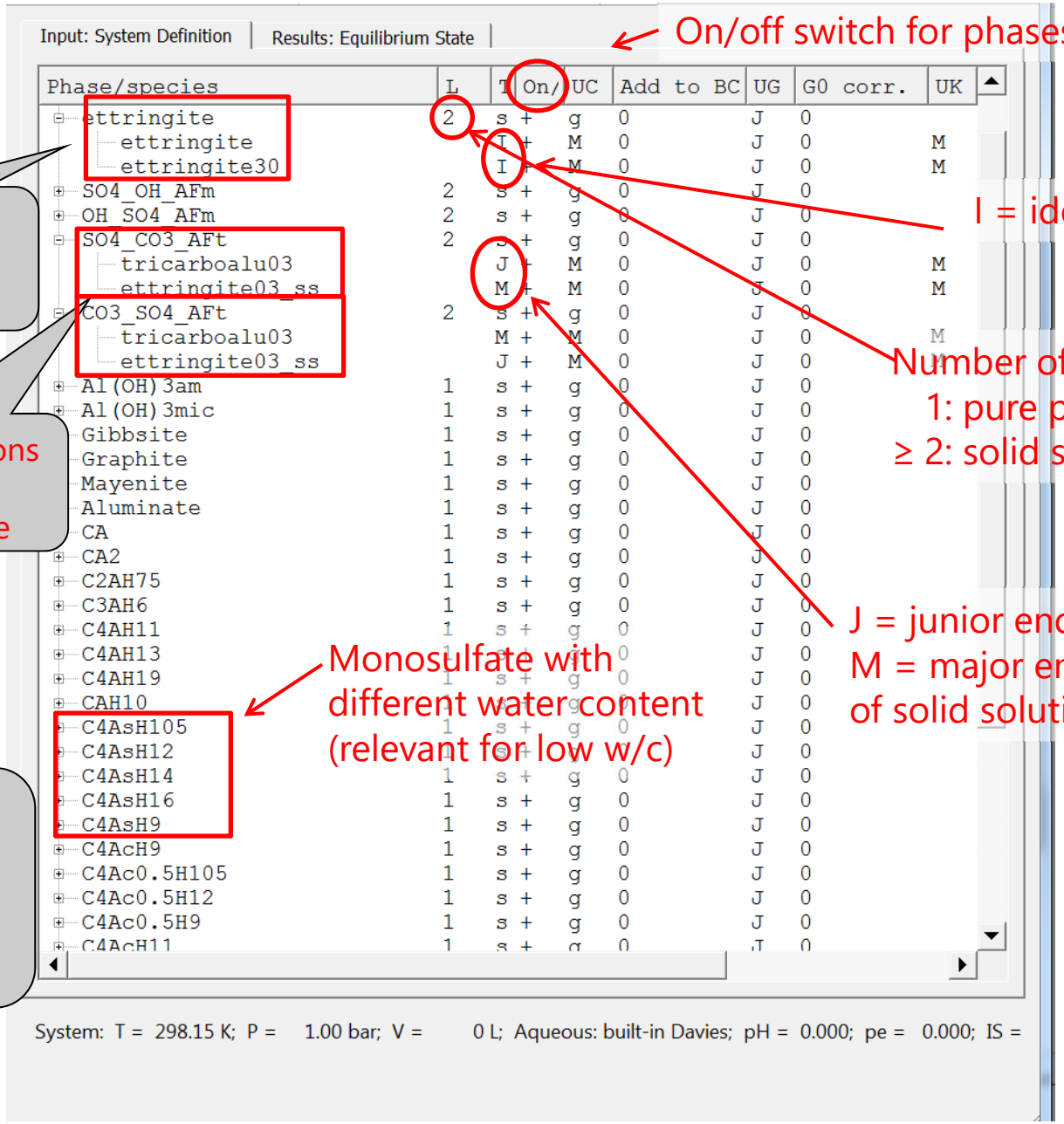



$SO_4$-AFt solid solution 30-32 $H_2O$

2 AFt solid solutions containing sulfate+carbonate

$SO_4$-AFt with less water (metaettringite; for low water content

Monosulfate with different water content (relevant for low w/c)

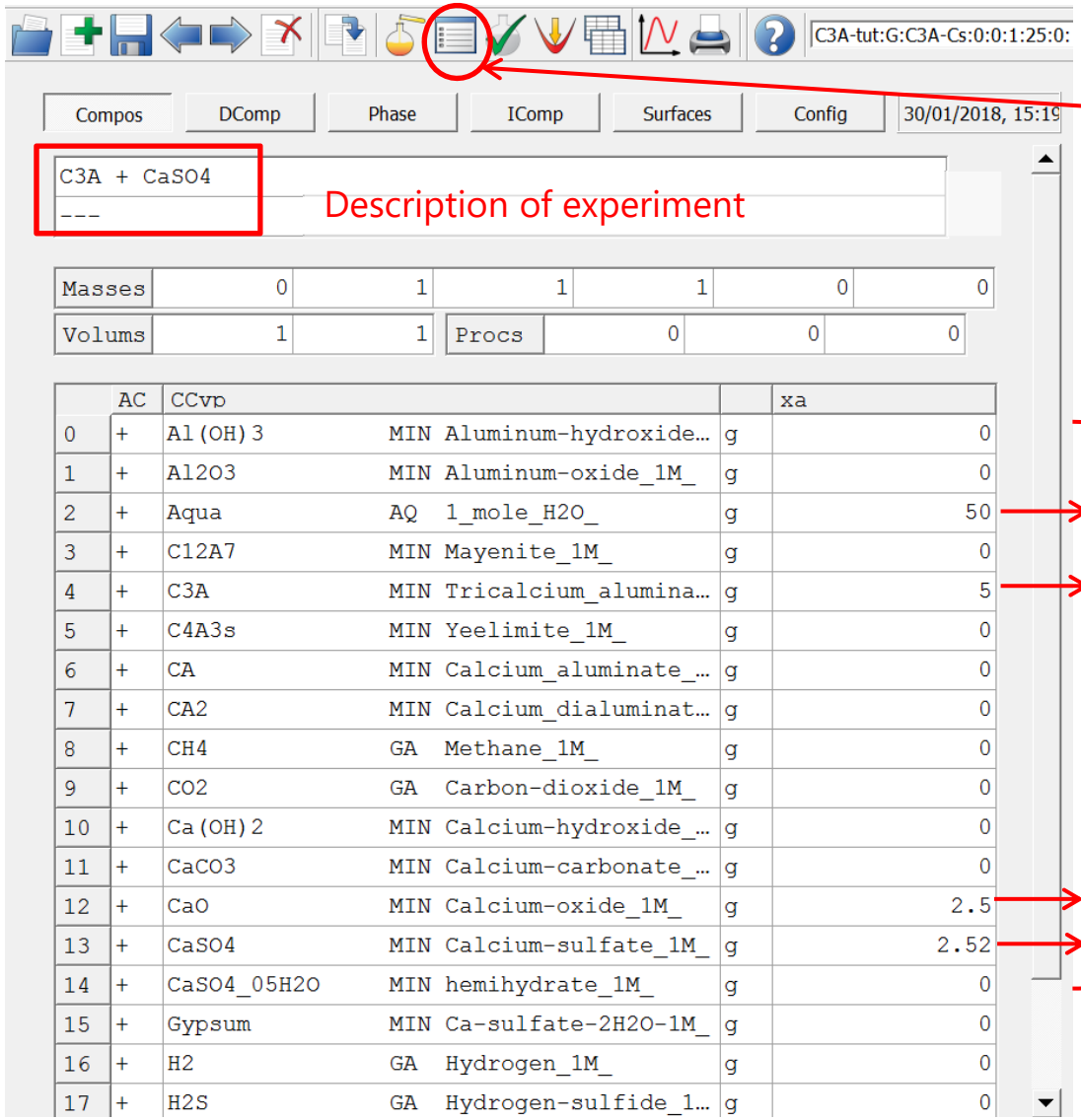
I = ideal solid solution

Number of components
1: pure phase
≥ 2: solid solutions

J = junior end-member
M = major end-member of solid solution

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

**<u>Experimental conditions:</u> React 5 g $C_3A$, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g $O_2$ to simulate gas phase)**




| | AC | CCvp | | | xa |
|---|---|---|---|---|---|
| 0 | + | Al(OH)3 | MIN Aluminum-hydroxide… | g | 0 |
| 1 | + | Al2O3 | MIN Aluminum-oxide_1M_ | g | 0 |
| 2 | + | Aqua | AQ 1_mole_H2O_ | g | 50 |
| 3 | + | C12A7 | MIN Mayenite_1M_ | g | 0 |
| 4 | + | C3A | MIN Tricalcium_alumina… | g | 5 |
| 5 | + | C4A3s | MIN Yeelimite_1M_ | g | 0 |
| 6 | + | CA | MIN Calcium_aluminate_… | g | 0 |
| 7 | + | CA2 | MIN Calcium_dialuminat… | g | 0 |
| 8 | + | CH4 | GA Methane_1M_ | g | 0 |
| 9 | + | CO2 | GA Carbon-dioxide_1M_ | g | 0 |
| 10 | + | Ca(OH)2 | MIN Calcium-hydroxide_… | g | 0 |
| 11 | + | CaCO3 | MIN Calcium-carbonate_… | g | 0 |
| 12 | + | CaO | MIN Calcium-oxide_1M_ | g | 2.5 |
| 13 | + | CaSO4 | MIN Calcium-sulfate_1M_ | g | 2.52 |
| 14 | + | CaSO4_05H2O | MIN hemihydrate_1M_ | g | 0 |
| 15 | + | Gypsum | MIN Ca-sulfate-2H2O-1M_ | g | 0 |
| 16 | + | H2 | GA Hydrogen_1M_ | g | 0 |
| 17 | + | H2S | GA Hydrogen-sulfide_1… | g | 0 |

Detailed input recipe

Input generated before by the input wizard => 2 equivalent options to input data

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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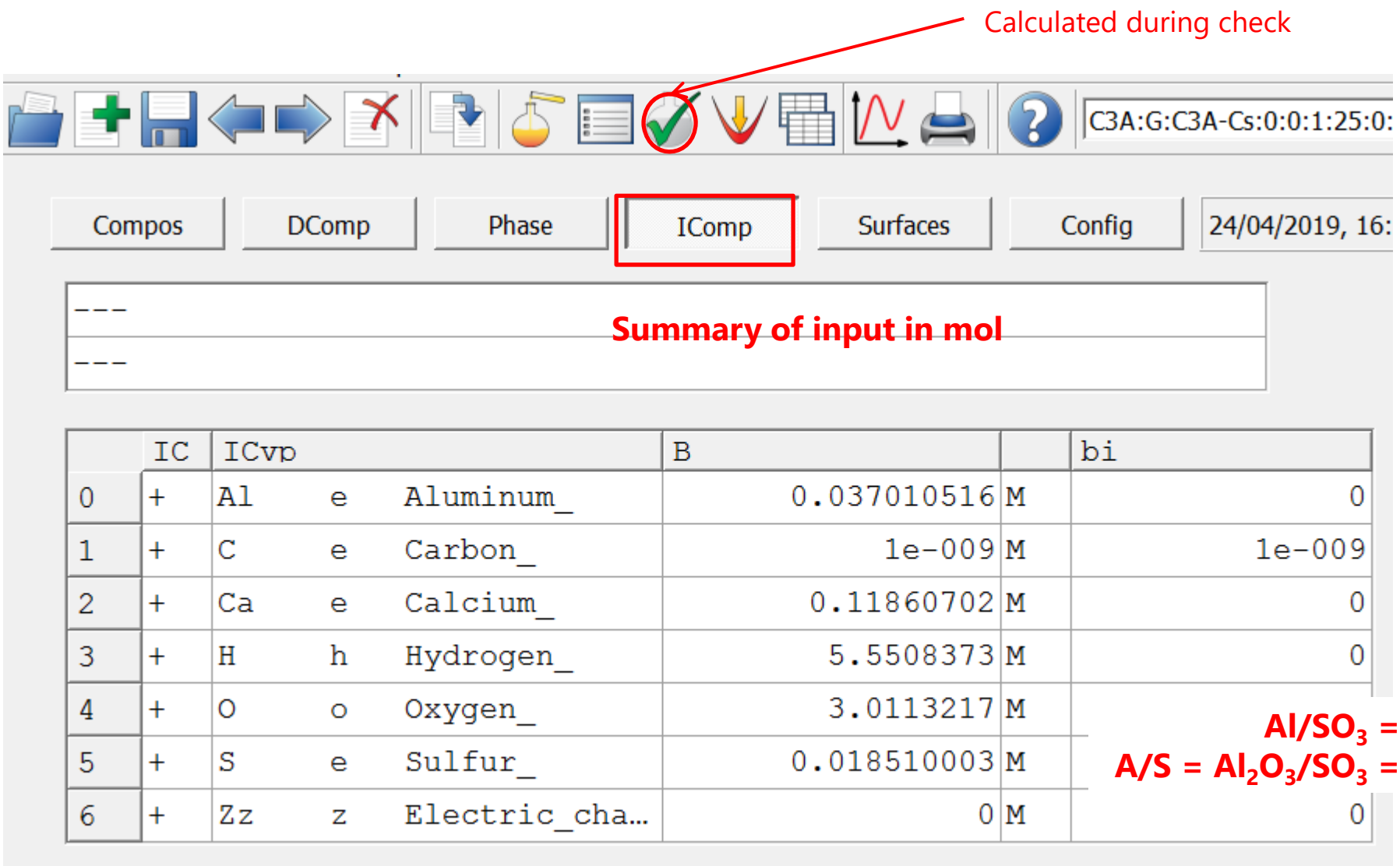
**<u>Experimental conditions:</u> React 5 g $C_3A$, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g $O_2$ to simulate gas phase)**



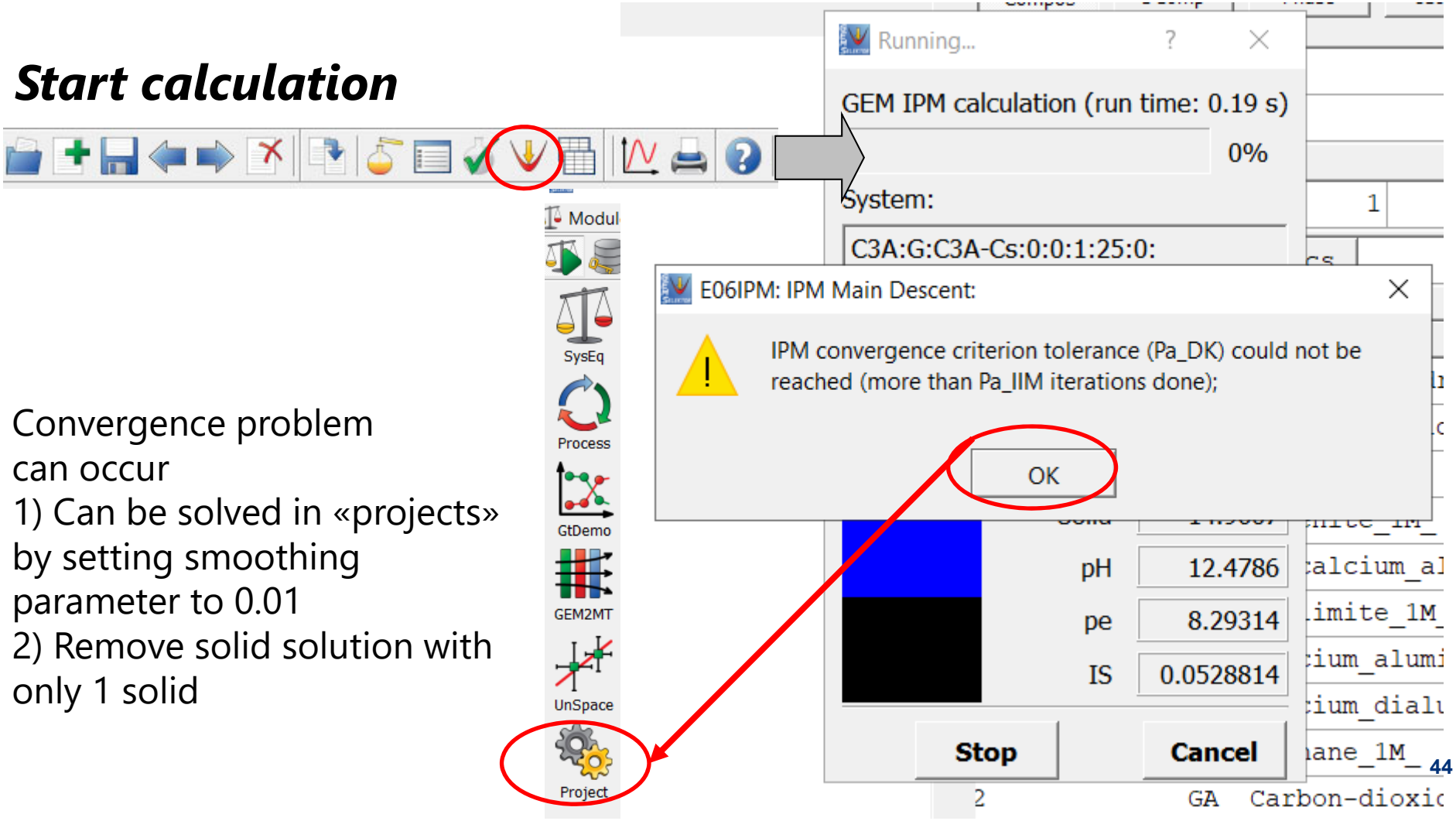

| | IC | ICvp | | | B | | bi |
|---|---|---|---|---|---|---|---|
| 0 | + | Al | e | Aluminum_ | 0.037010516 | M | 0 |
| 1 | + | C | e | Carbon_ | 1e-009 | M | 1e-009 |
| 2 | + | Ca | e | Calcium_ | 0.11860702 | M | 0 |
| 3 | + | H | h | Hydrogen_ | 5.5508373 | M | 0 |
| 4 | + | O | o | Oxygen_ | 3.0113217 | M | |
| 5 | + | S | e | Sulfur_ | 0.018510003 | M | |
| 6 | + | Zz | z | Electric_cha… | 0 | M | 0 |

**$Al/SO_3$ = 2**
**$A/S = Al_2O_3/SO_3$ = 1**

# Hydration of $C_3A$ + CaO + $CaSO_4$ – calculation of equilibrium

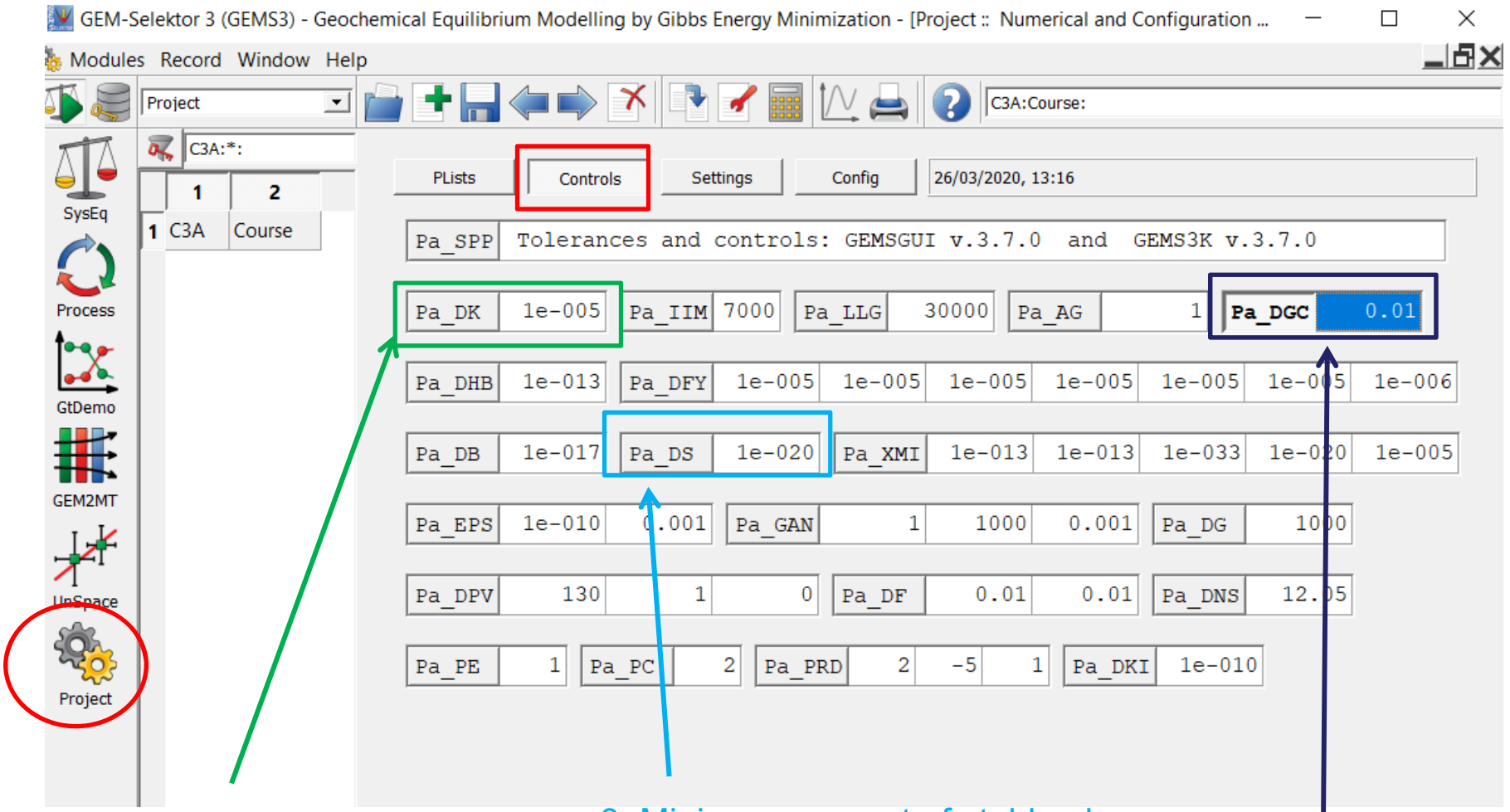
**<u>Experimental conditions:</u> React 5 g $C_3A$, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g $O_2$ to simulate gas phase)**

## *Start calculation*




Convergence problem can occur
1) Can be solved in «projects» by setting smoothing parameter to 0.01
2) Remove solid solution with only 1 solid

# Convergence problem - workaround




2. Covergence tolerance parameter:
use higher value, e.g. 1e-004,
maximum seems to be 5e-003

3. Minimum amount of stable phases:
use lower value, e.g. 1e-023

1. Smoothing parameter:
use low positive value, e.g. 0.01

**=> 0.01 works**

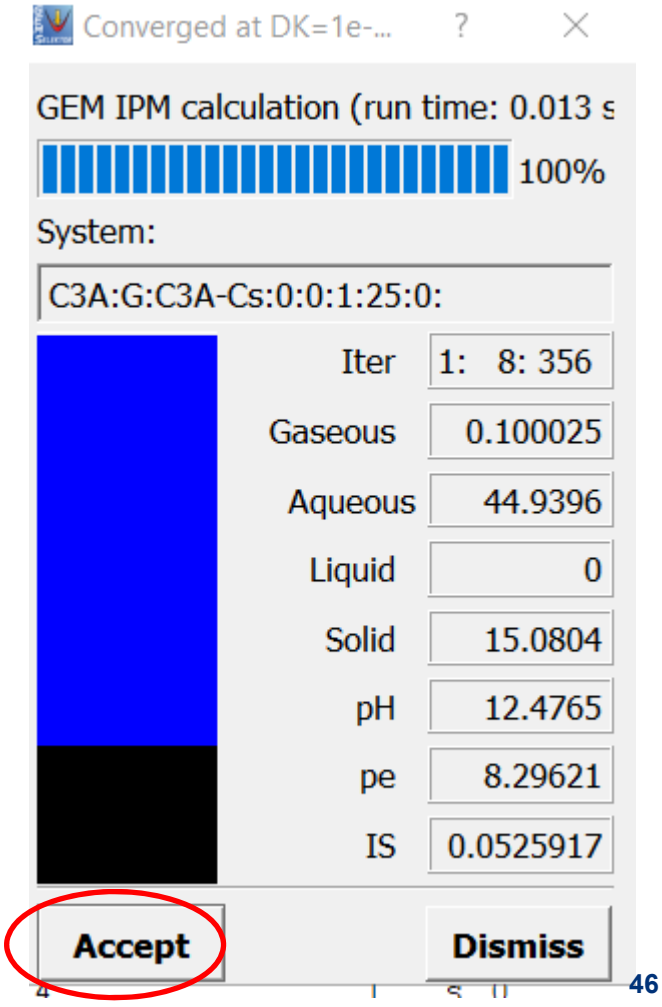
**Do not touch the other values !!!**

# Hydration of $C_3A$ + CaO + $CaSO_4$ – calculation of equilibrium

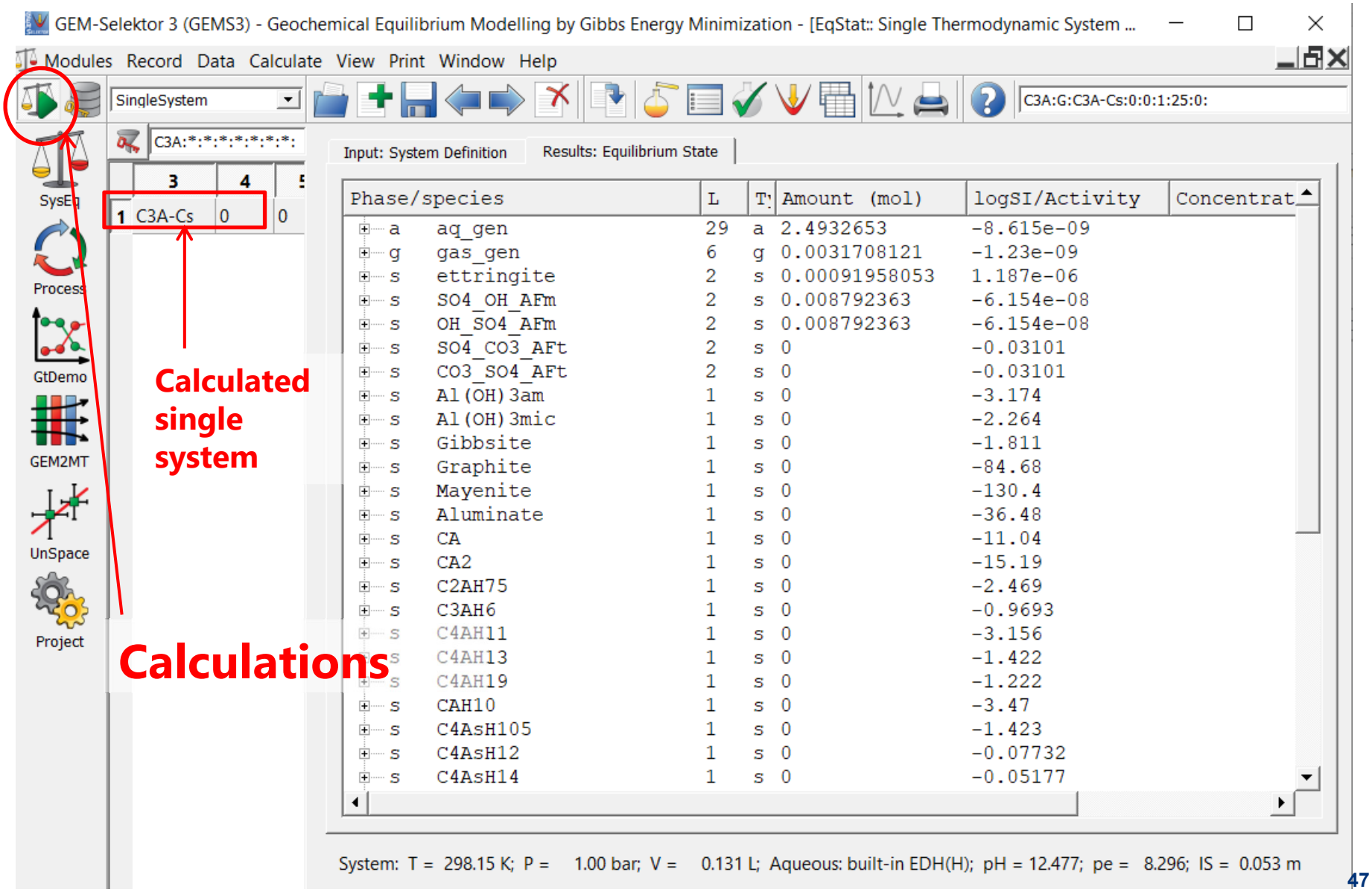
d Technology

**<u>Experimental conditions:</u>** **React 5 g $C_3A$, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g $O_2$ to simulate gas phase)**

***Start calculation***



# Hydration of $C_3A$ + CaO + $CaSO_4$ – results



# Hydration of $C_3A$ + CaO + $CaSO_4$ – results

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Name of single system

2.5 mol aqueous phase (water + dissolved ions)

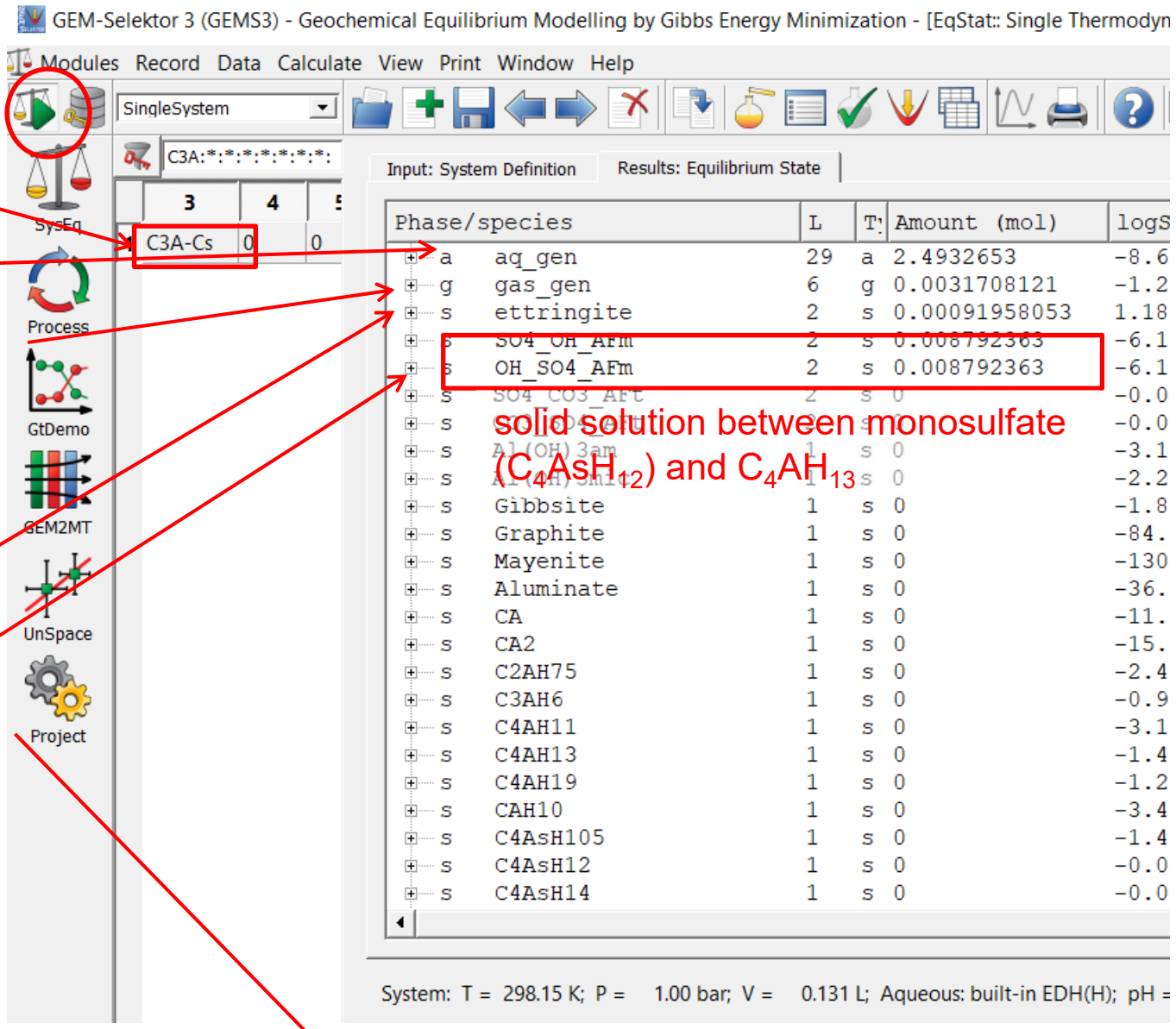
0.0032 mol gaseous phase

*Solid products:*

0.0009 mol ettringite

0.0176 mol monosulfate

0.0418 mol portlandite



# Hydration of $C_3A$ + CaO + $CaSO_4$ – results

## Solid solutions

| Phase/species | L | T | Amount (mol) | logSI/Activity | Concentrat |
|---|---|---|---|---|---|
| a aq_gen | 29 | a | 2.4932653 | -8.615e-09 | |
| g gas_gen | 6 | g | 0.0031708121 | -1.23e-09 | |
| s ettringite | 2 | s | 0.00091958053 | 1.187e-06 | |
| ettringite | | I | 0.00073534039 | 0.79965 | 0.79964763 |
| ettringite30 | | I | 0.00018424014 | 0.200353 | 0.20035237 |
| s SO4_OH_AFm | 2 | s | 0.008792363 | -6.154e-08 | |
| C4AH13 | | J | 0.00091690195 | 0.0378465 | 0.10428391 |
| monosulphate12 | | M | 0.007875461 | 0.836918 | 0.89571609 |
| s OH_SO4_AFm | 2 | s | 0.008792363 | -6.154e-08 | |
| C4AH13 | | M | 0.00091690195 | 0.0378465 | 0.10428391 |
| monosulphate12 | | J | 0.007875461 | 0.836918 | 0.89571609 |
| s SO4_CO3_AFt | 2 | s | 0 | -0.03101 | |
| tricarboalu03 | | J | 0 | 0.00244367 | 0 |
| ettringite03_ss | | M | 0 | 0.929907 | 0 |
| s CO3_SO4_AFt | 2 | s | 0 | -0.03101 | |
| tricarboalu03 | | M | 0 | 0.00244367 | 0 |
| ettringite03_ss | | J | 0 | 0.929907 | 0 |
| s Al(OH)3am | 1 | s | 0 | -3.174 | |
| AlOHam | | O | 0 | 0.000669392 | 0 |

**ideal solid solution:**

**80 mol-% ettringite-32$H_2O$**
**20 mol-% ettringite-30 $H_2O$**

**Non ideal solid solution:**

**10 mol-% $C_4AH_{13}$**
**90 mol-% $C_4AsH_{12}$**

**Incomplete solid solution (hardly any $CO_3$ endmember; normally not stable, can be deactivated:**

# Hydration of $C_3A$ + CaO + $CaSO_4$ – system creation (recipe)

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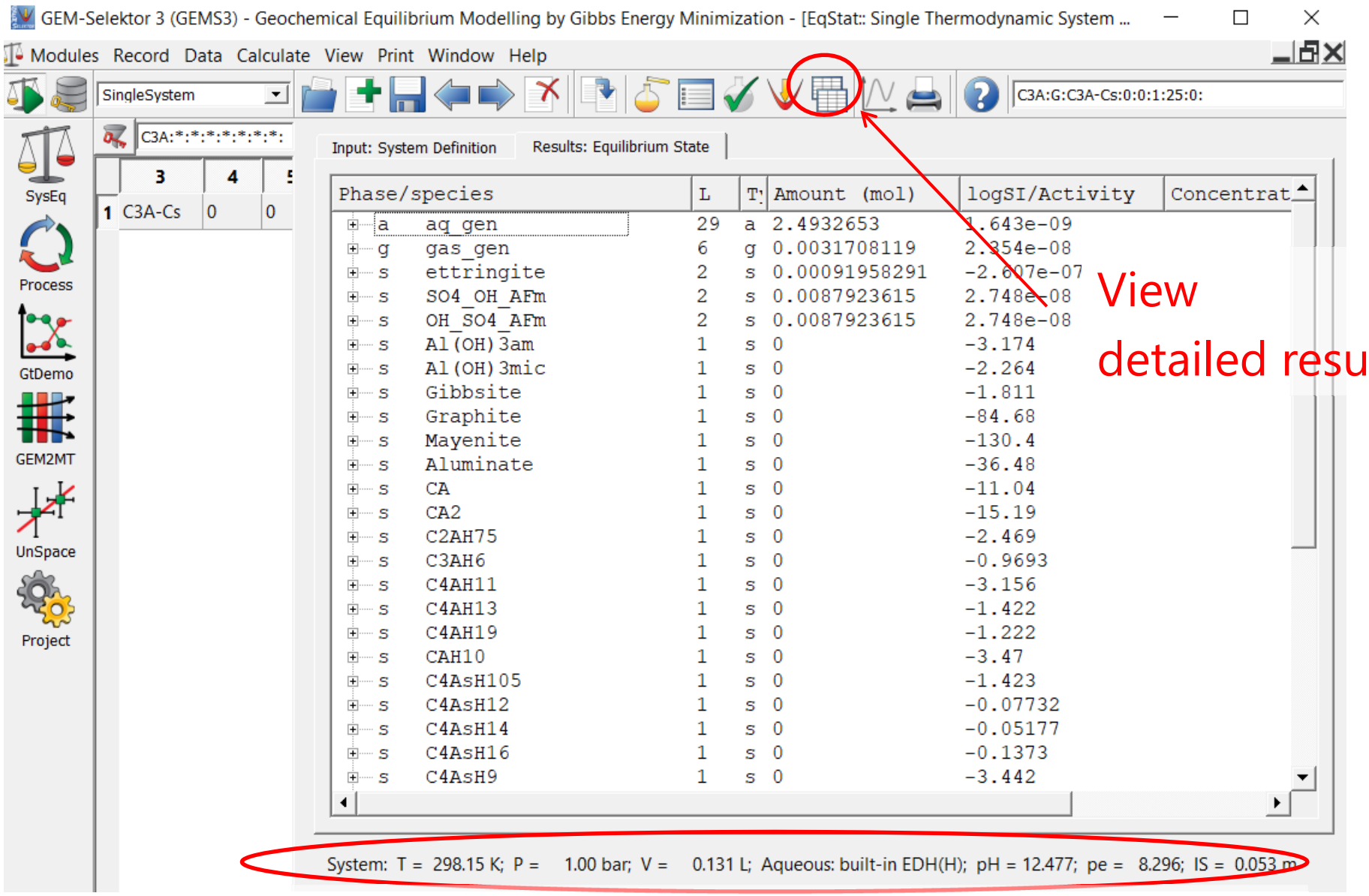
Input: System Definition | Results: Equilibrium State

| Phase/species | L | T | On/ | UC | Add to BC | UG | G0 corr. | UK | Lower_KC | Upper_KC | KC type |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ettringite | 2 | s | + | g | 0 | J | 0 | | | | |
| SO4_OH_AFm | 2 | s | + | g | 0 | J | 0 | | | | |
| OH_SO4_AFm | 2 | s | + | g | 0 | J | 0 | | | | |
| SO4_CO3_AFt | 2 | s | – | g | 0 | J | 0 | | | | |
| tricarboalu03 | | J | – | M | 0 | J | 0 | M | 0 | 1000000 | B |
| ettringite03_ss | | M | – | M | 0 | J | 0 | M | 0 | 1000000 | B |
| CO3_SO4_AFt | 2 | s | – | g | 0 | J | 0 | | | | |
| tricarboalu03 | | M | – | M | 0 | J | 0 | M | 0 | 1000000 | B |
| ettringite03_ss | | J | – | M | 0 | J | 0 | M | 0 | 1000000 | B |
| Al(OH)3am | 1 | s | + | g | 0 | J | 0 | | | | |
| Al(OH)3mic | 1 | s | + | g | 0 | J | 0 | | | | |
| Gibbsite | 1 | s | + | g | 0 | J | 0 | | | | |

**As we have very little carbonate in the system in the first calculation we may switch off the carbonate-sulfate AFt solid solutions**

**(In the input page)**

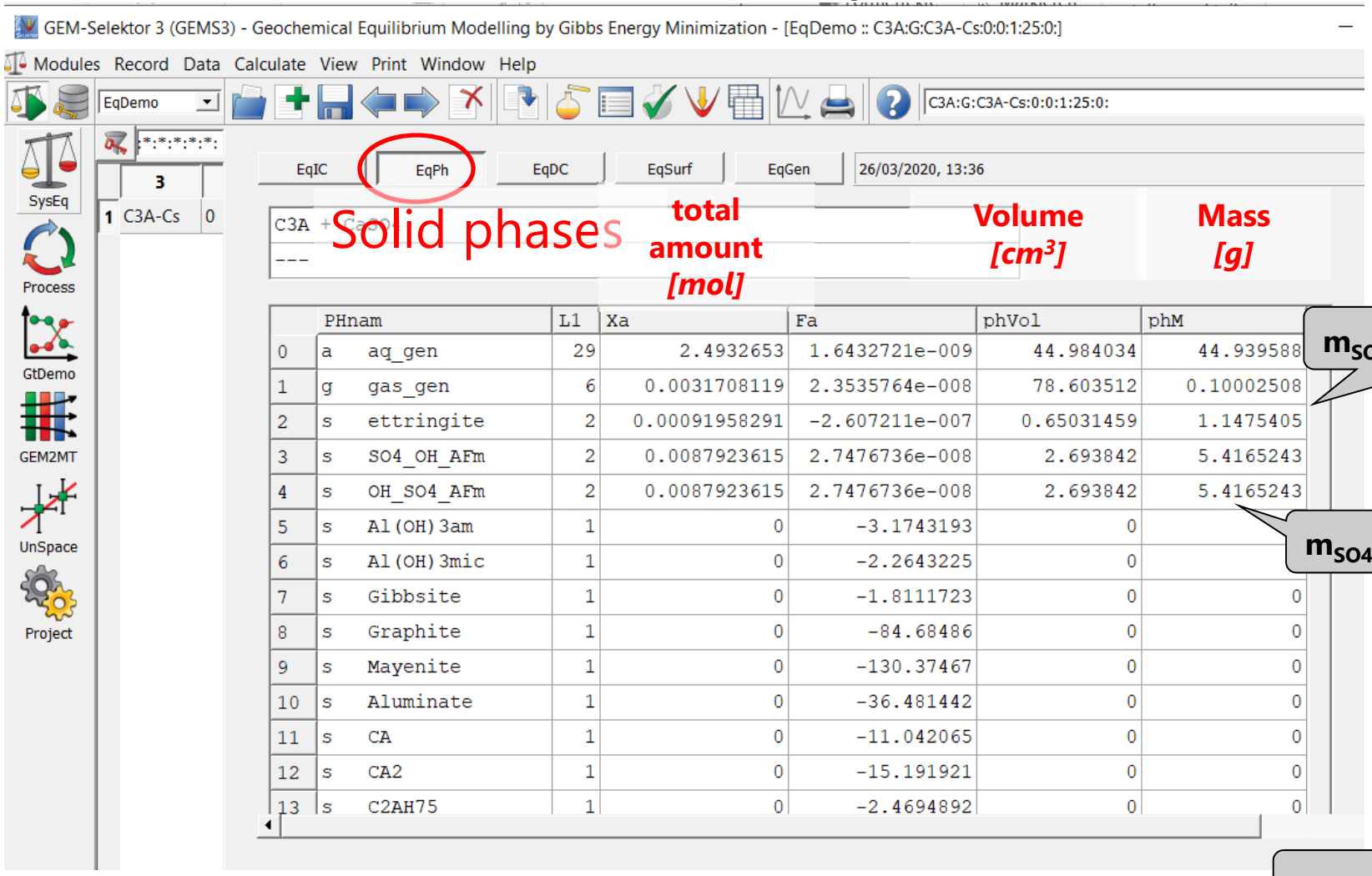
# Hydration of $C_3A$ + CaO + $CaSO_4$ – results




General information: pH, ionic strength, redox, …

# Hydration of $C_3A$ + CaO + $CaSO_4$ – results

*Detailed information about composition of aqueous, gaseous and solid phases*




| | | PHnam | L1 | Xa | Fa | phVol | phM |
|---|---|---|---|---|---|---|---|
| 0 | a | aq_gen | 29 | 2.4932653 | 1.6432721e-009 | 44.984034 | 44.939588 |
| 1 | g | gas_gen | 6 | 0.0031708119 | 2.3535764e-008 | 78.603512 | 0.10002508 |
| 2 | s | ettringite | 2 | 0.00091958291 | -2.607211e-007 | 0.65031459 | 1.1475405 |
| 3 | s | SO4_OH_AFm | 2 | 0.0087923615 | 2.7476736e-008 | 2.693842 | 5.4165243 |
| 4 | s | OH_SO4_AFm | 2 | 0.0087923615 | 2.7476736e-008 | 2.693842 | 5.4165243 |
| 5 | s | Al(OH)3am | 1 | 0 | -3.1743193 | 0 | |
| 6 | s | Al(OH)3mic | 1 | 0 | -2.2643225 | 0 | |
| 7 | s | Gibbsite | 1 | 0 | -1.8111723 | 0 | 0 |
| 8 | s | Graphite | 1 | 0 | -84.68486 | 0 | 0 |
| 9 | s | Mayenite | 1 | 0 | -130.37467 | 0 | 0 |
| 10 | s | Aluminate | 1 | 0 | -36.481442 | 0 | 0 |
| 11 | s | CA | 1 | 0 | -11.042065 | 0 | 0 |
| 12 | s | CA2 | 1 | 0 | -15.191921 | 0 | 0 |
| 13 | s | C2AH75 | 1 | 0 | -2.4694892 | 0 | 0 |

$m_{SO4\text{-}AFt}$ = 1.15 g

$m_{SO4\text{-}AFm}$ = 10.83 g

$m_{Portlandite}$ = 3.10 g

# Hydration of $C_3A$ + CaO + $CaSO_4$ – results

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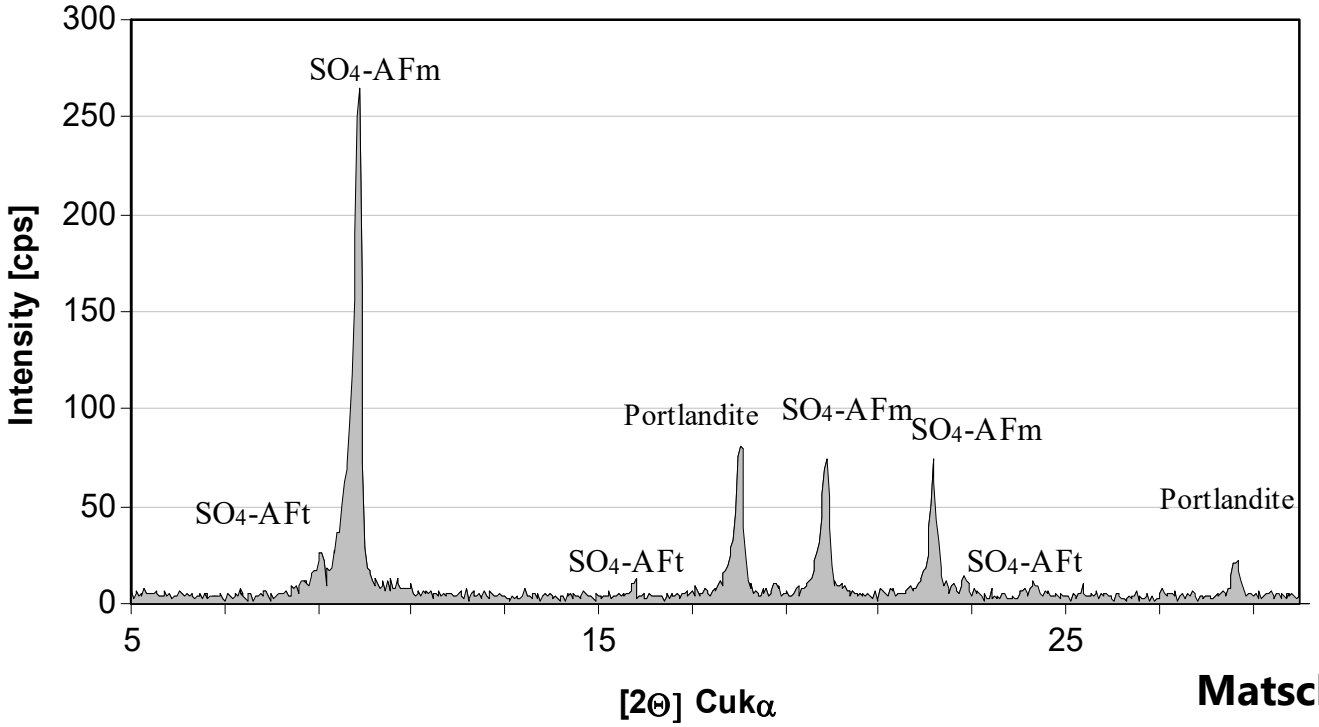
## Comparison to experiments:

Hydration of $C_3A$ at $SO_3/Al_2O_3$ = 1, cured 28 d at 25°C, solid phases by XRD




**Matschei 2007**

*Qualitatively very good agreement between experimental and calculated results*
Phase assemblage $SO_4$-AFm - $SO_4$-AFt - portlandite - aq. predicted and observed.
Quantification with help of GEMS possible.

# Hydration of $C_3A$ + CaO + $CaSO_4$ – results

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## Composition of aqueous phase

EqIC | EqPh | EqDC | EqSurf | EqGen | 26/03/2020, 13:36

C3A + CaSO4
---

Output: total molalities in aqueous phase (mol/kg $H_2O$)

| | ICnam | b | Cb | u | lgm t | m t | ICnam |
|---|---|---|---|---|---|---|---|
| 0 | Al … | 0.037010516 | 1.3578917e-017 | -324.92795 | -4.3723484 | 4.2427904e-005 | Al … |
| 1 | C … | 1e-009 | -2.6864406e-026 | -194.9941 | -7.6519556 | 2.2286631e-008 | C … |
| 2 | Ca … | 0.11860702 | -1.5518762e-017 | -266.15404 | -1.6910673 | 0.020367266 | Ca … |
| 3 | H … | 5.5508373 | 1.241501e-016 | -47.83096 | -1.390652 | 0.040676917 | H … |
| 4 | O … | 3.0113217 | -9.3112574e-017 | -0.016474237 | -1.3631496 | 0.043336159 | O … |
| 5 | S … | 0.018510003 | 0 | -275.13628 | -5.1208648 | 7.5706847e-006 | S … |
| 6 | Zz … | 0 | 2.0011687e-020 | 19.102731 | 0 | -6.3290455e-019 | Zz … |

total mol in system (input)

$Log_{10}$ of total molalities

# Tutorial – single systems: hydration of $C_3A$

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Hydration of $C_3A$ ($Ca_3Al_2O_6$)[a]

1) Simulation of reaction $C_3A$ + CaO + $CaSO_4$ **Guided tutoria**

2) Simulation of reaction $C_3A$ + CaO + $CaCO_3$

3) Simulation of reaction $C_3A$ + $CaCO_3$

4) Simulation of reaction $C_3A$ + C + $CaSO_4$ + $CaCO_3$

**Individual work**

See Seligmann & Greening ICCC 1969 and various papers by Kuzel et al. (Kuzel & Pöllmann CCR 1991, Kuzel et. al CCR 1996) for experimental verification

# Hydration of $C_3A$ + $CaCO_3$

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***Experimental problem part 2:***

Reaction of $C_3A$ with CaO plus calcium carbonate

**5 g $C_3A$ + 1.86 g $CaCO_3$ + 2.5 g CaO + 50 g $H_2O$**

*+ 0.1 g $O_2$ (oxidizing conditions, $CO_2$-free = no carbonation)*

molar ratio $SO_3/Al_2O_3$ = 0, molar ratio $CO_2/Al_2O_3$ = 1

***Experimental problem part 3:***

Reaction of $C_3A$ with calcium carbonate (no surplus of CaO)

**5 g $C_3A$ + 1.86 g $CaCO_3$ + 50 g $H_2O$**

*+ 0.1 g $O_2$ (oxidizing conditions, $CO_2$-free = no carbonation)*

molar ratio $SO_3/Al_2O_3$ = 0, molar ratio $CO_2/Al_2O_3$ = 1

# Hydration of $C_3A$ + $CaCO_3$ + $CaSO_4$

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***Experimental problem part 4:***

Reaction of $C_3A$ with CaO, calcium carbonate, calcium sulfate

5 g $C_3A$ + + 1.86 g $CaCO_3$ + 2.52 g $CaSO_4$ + 2.5 g CaO
+ 50 g $H_2O$
*+ 0.1 g $O_2$ (oxidizing conditions, $CO_2$-free = no carbonation)*

molar ratio $SO_3/Al_2O_3$ = 1, molar ratio $CO_2/Al_2O_3$ = 1

# Hydration of $C_3A$ + $CaCO_3$ and/or $CaSO_4$

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## ***Experimental problem part 2 - 4***

Hints:

- Create new system for part 2
- Keep carbonate solid solutions switched on
- For part 3 + 4 it might be convenient to clone the system from part 2 (only if we keep S in the system)