

GEM-Selektor v.3: Thermodynamic Modelling of Aqueous- Solid Solution Systems

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Downloads, technical info, publications: GEMS web site

<http://gems.web.psi.ch/>

Creating a new modeling project

New modeling project:
“CarbSulf:Partitioning&Uptake:”

From Kernel database: take aqueous,
gas, solid phases (skip solid solutions)

First step:

Select parts of the
Default Database;

Select phase types
to include into the
project system
definition

Basis configuration of a new Modelling Project CarbSulf_

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

Phase/DC Filters

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

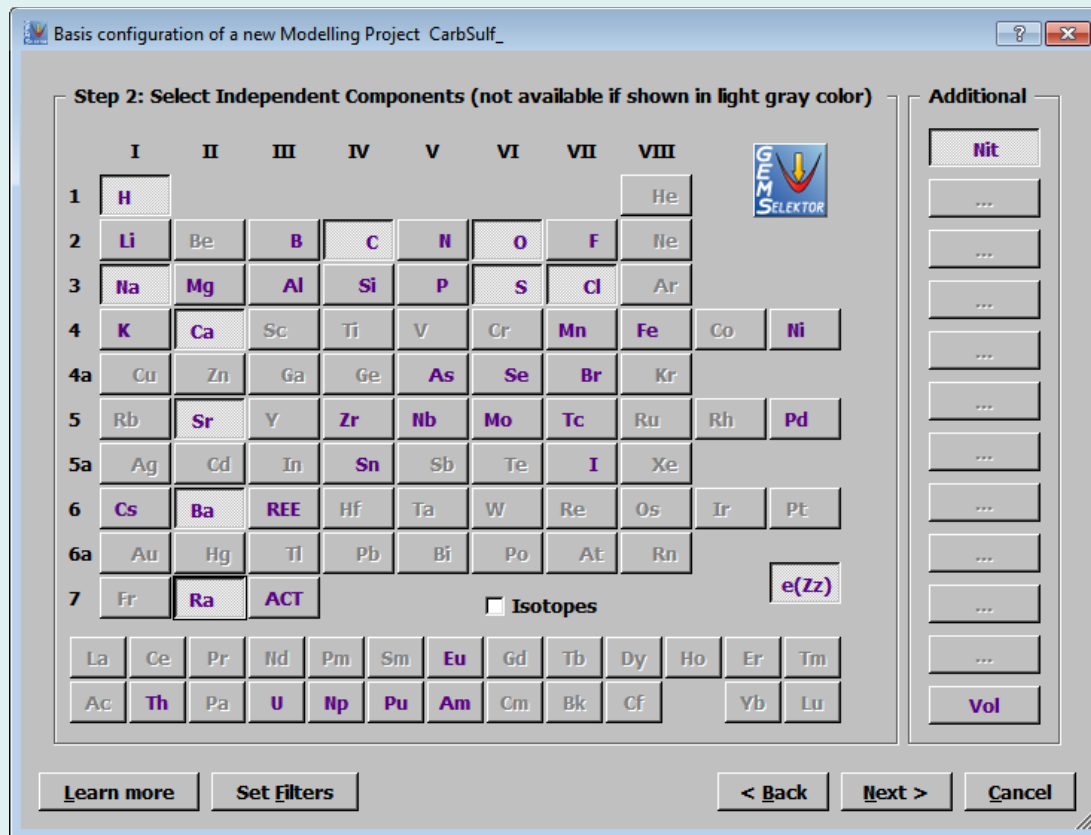
Built-in Database	Version
<input checked="" type="checkbox"/> template	
<input checked="" type="checkbox"/> scripts	not versioned
<input checked="" type="checkbox"/> kernel	
<input checked="" type="checkbox"/> nagra_psi	not versioned
<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> solids	not versioned
<input checked="" type="checkbox"/> secms	not versioned
<input checked="" type="checkbox"/> prods	not versioned
<input checked="" type="checkbox"/> ions	not versioned
<input checked="" type="checkbox"/> gases	not versioned
<input checked="" type="checkbox"/> solutions	not versioned
<input type="checkbox"/> complem	not versioned
<input type="checkbox"/> v_cnst0	not versioned
<input type="checkbox"/> nagra_psi	

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New project: selecting a system basis

New project: “CarbSulf:Partitioning&Uptake:”

Basis: Ba–Ca–Sr–Ra–Na–Cl–C–S–Nit–H–O–e



Autophase Setup:

✧ Davies equation (aq)

✧ Ideal gas mixture

Create a Single System
(SysEq record):

CarbSulf:G:FirstSystem:0:0:1:25:0:

Recipe Input

	Property	Name	Quantity	Units
1	xa_	Aqua	1000	g
2	xa_	AtmAirNit	1000	g
3	xa_	BaSO4	0.1	g
4	xa_	CaSO4	10	g
5	xa_	NaCl	0.1	g
6	xa_	RaSO4	0.001	g
7	xa_	SrSO4	1	g

Setting up a Forward Modeling Problem



Ingredients



Recipe



Cooking



Done

In terms of chemical thermodynamics

at T, P of interest

Feasible
phases and
components



Initial state
(bulk composition, b)



Equilibration,
chemical
mass transfer



Final state
 $n(x)$; stable
speciation

Aqueous-Carbonate Equilibria, Open & Closed

Project “CarbSulf:Partitioning&Uptake”

Using kernel data base, Davies equation for aqueous phase, ideal gas phase



SysEq Recipe 1: ‘calciteAir’ at 1 bar 25 C

Property	Name	Quantity	Units
xa_	AtmAirNit	3000	g
xa_	CaCO3	10	g
xa_	SrCO3	0.01	g
xa_	NaCl	0.001	M
xa_	Aqua	300	g

Check: pH = 8.28; $p\text{CO}_2 = 36 \text{ Pa}$;
 $\text{Ca}_{\text{AQ}} = 0.5 \text{ mm}$; $\text{Sr}_{\text{AQ}} = 80.5 \mu\text{m}$

SysEq Recipe 1: ‘calciteAir’ at 1 bar 75 C

Check: pH = 8.27; $p\text{CO}_2 = 36 \text{ Pa}$;
 $\text{Ca}_{\text{AQ}} = 0.22 \text{ mm}$; $\text{Sr}_{\text{AQ}} = 64.4 \mu\text{m}$

SysEq Recipe 2: ‘calcitesw’ at 400 bar 3 C

Property	Name	Quantity	Units
xa_	AtmAirNit	1	g
xa_	CO2	0.007	M
xa_	CaCO3	10	g
Xa_	SrCO3	0.01	g
xa_	NaCl	35	g
xa_	Aqua	965	g

Check: pH = 7.24; $p\text{CO}_2 = 0.025 \text{ bar}$;
 $\text{Ca}_{\text{AQ}} = 6.32 \text{ mm}$; $\text{Sr}_{\text{AQ}} = 70.2 \mu\text{m}$

No strontianite, no partitioning of Sr

Variant: $\text{dll}_{\text{Str}} = 1\text{e-}5 \text{ mol}$

Take a look at speciation and input data

The Single-System Recipe Wizard

Input Recipe of Single Thermodynamic System: CarbSulf:G:CalciteSW:2:0:400:3:0:

tname Solubility of calcite and strontianite in simplified deep seawater

Property

- Compos (xa_)
- DComp (xd_)
- IComp (bi_)
- Phase (xp_)
- Kin.lower (dll_)
- Kin.upper (dul_)
- G0 shift (gEx_)
- Other Inputs

Selection

AirNit_22	H2
Aqua	H2S
AtmAirNit	H2SO4
BaCO3	HCl
BaSO4	HClO4
BentPWsim	Na2CO3
BentRaBaSr	Na2SO4
CH4	NaCl
CO2	NaClO4
Ca(OH)2	NaOH
CaCO3	O2
CaCl2	RaSO4
CaO	Sr(OH)2
CaSO4	SrCO3
Gypsum	SrSO4

Input quantities of Compos(itions) contributing to B_vector

Recipe Input

	Property	Name	Quantity	Units
1	xa_	Aqua	965	g
2	xa_	AtmAirNit	1	g
3	xa_	CO2	0.007	M
4	xa_	CaCO3	10	g
5	xa_	NaCl	35	g
6	xa_	SrCO3	0.01	g

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Phase stability indices in GEM IPM output

Chemical potential
of j -th compound from \Rightarrow
GEM dual solution u :

$$\hat{\eta}_j = \sum_{i \in N} a_{ij} \hat{u}_i$$



➡ **Stability (saturation) index** for a k -th phase-solution of I_k species:

$$\Omega_k = \sum_{j \in l_k} \hat{x}_j = \sum_{j \in l_k} \exp \left(\hat{\eta}_j - \frac{g_j^o}{RT} - \ln \gamma_j - \Xi_k \right)$$

'dual' estimate of mole fraction

'primal' activity coefficient

Stability (saturation)
index for a k -th pure
phase (j -th species)

$$\Rightarrow \Omega_k = \exp\left(\hat{\eta}_j - \frac{g_j^o}{RT}\right)$$

$\log_{10}\Omega_k$	$< -\varepsilon_\Omega$	$> -\varepsilon_\Omega$ & $< +\varepsilon_\Omega$	$> +\varepsilon_\Omega$
phase:	under-stable	stable	over-stable

SysEq Recipe 2: 'Calcitesw' at 400 bar 3 C

ICnam	u
C ...	-177.14693
Ca ...	-318.71489
Cl ...	-21.618519
H ...	-52.113967
Na ...	-149.752
Nit ...	2.8605319
O ...	1.8574335
Sr ...	-327.7595
Zz ...	35.44269

Calculate stability index of:

Calcite Cal	CaCO_3
Aragonite Arg	CaCO_3
Portlandite	Ca(OH)_2

and compare with 'EqPh' 'Fa'

'Mtparm' window

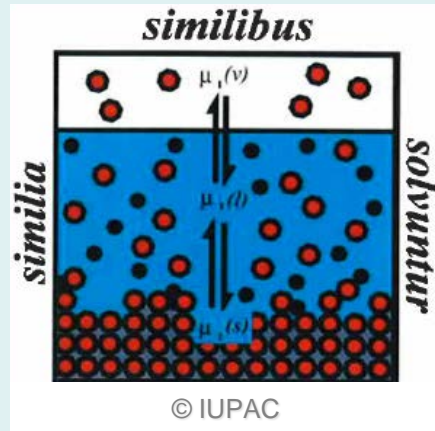
gTP

63	s	CaCO	Arg	...	d	+	-1125074.6
64	s	CaCO	Cal	...	d	+	-1125730.2
65	s	CaOH	Portlandite	...	d	+	-893931.09

'EqPh' page in 'EqDemo' window

	PHnam	Xa	Fa
0	a aq_gen	54.809148	-7.0994752e-012
1	g gas_gen	0	-0.86149778
2	s Graphite	0	-76.996523
3	s Aragonite	0	-0.12401373
4	s Calcite	0.09381742	-2.7511445e-008
5	s Portlandite	0	-12.98278
6	s Strontianite	0	-1.0188954

Aqueous – solid solution systems



Partitioning of an ion (element) M:

- at least two *chemical components* (species) of M,
- present in at least two different *phases*,
- at least one of which is a *solution phase*

Partitioning is closely related to **equilibrium solubility**

Uptake is usually understood as a chemical transfer of minor (trace) element *Tr* from aqueous solution into solid phase(s) upon equilibration of the system.

Measured by solid (solution) – aqueous *Tr* distribution ratios (e.g. in mole fraction)

$$\text{ionic} \quad k_d(Tr) = \frac{x_{TrL}}{m_{Tr^{Z+}}} \quad \text{total} \quad R_d(Tr) = \frac{x_{TrL}}{m_{Tr,tot}}$$

From known chemical speciation, all **distribution ratios** can always be obtained.

Representing uptake in (B,C)L solid solution

Experimentally measurable

Distribution ratios

$$k_{d,B} = \frac{x_{BL}}{m_{B^{z+}}} = \frac{m_{L^{z-}} \gamma_{L^{z-}} \gamma_{B^{z+}}}{K_{BL} \gamma_{BL}}$$

$$k_{d,C} = \frac{x_{CL}}{m_{C^{z+}}} = \frac{m_{L^{z-}} \gamma_{L^{z-}} \gamma_{C^{z+}}}{K_{CL} \gamma_{CL}}$$

subject to speciation and
ligand concentration effects

Fractionation (distribution) coefficient

$$\Delta_{BC} = \frac{k_{d,B}}{k_{d,C}} = \frac{x_{BL} m_{C^{z+}}}{x_{CL} m_{B^{z+}}} = \frac{K_{CL} \gamma_{CL} \gamma_{B^{z+}}}{K_{BL} \gamma_{BL} \gamma_{C^{z+}}}$$

subject to SS K_{SP} ratio
and non-ideality effects

Define $x_{C,aq} = \frac{m_{C^{z+}}}{m_{B^{z+}} + m_{C^{z+}}}$

$$x_{BL} x_{C,aq} = \Delta_{BC} x_{CL} x_{B,aq}$$

$$x_{CL} = x_{C,aq} \frac{1}{\Delta_{BC} - \Delta_{BC} x_{C,aq} + x_{C,aq}}$$

NB: at very *different* end member solubility products, the “ K_{SP} ratio effect” will dominate the effects of non-ideal mixing in solid solution and in aqueous electrolyte

Simple non-ideal mixing in solid solutions

Guggenheim approach (Redlich-Kister model), binary system

Excess
Gibbs
energy:

$$G_m^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) = RTx_1x_2 \sum_r \alpha_r (x_1 - x_2)^r$$

α_r - interaction parameters IP can be $f(T,P)$ but not $f(x)$

Activity
coefficients
(3rd order IP):

$$\ln \gamma_1 = x_2^2 \left(\alpha_0 + \alpha_1 (3x_1 - x_2) + \alpha_2 (x_1 - x_2)(5x_1 - x_2) + \dots \right)$$

$$\ln \gamma_2 = x_1^2 \left(\alpha_0 - \alpha_1 (3x_2 - x_1) + \alpha_2 (x_2 - x_1)(5x_2 - x_1) + \dots \right)$$

Regular model: α_0 non-zero, higher-order parameters are zeros

Subregular model: α_0 and α_1 non-zero

Regular and subregular models

Subregular Margules model (in Thompson-Waldbaum form)

Excess
Gibbs
energy:

$$G_m^E = RT(x_1 \ln f_1 + x_2 \ln f_2) = x_1 x_2 (W_{12} x_2 + W_{21} x_1)$$

W_{12}, W_{21} - interaction parameters ($f(T, P)$)

End-member
activity
coefficients:

$$RT \ln f_1 = (2W_{21} - W_{12})x_2^2 + 2(W_{12} - W_{21})x_2^3$$

$$RT \ln f_2 = (2W_{12} - W_{21})x_1^2 + 2(W_{21} - W_{12})x_1^3$$

Regular model: $W_{12} = W_{21} = W_G$ and $W_G = RT\alpha_0$

Relation to the
Guggenheim model:

$$W_{12} = RT(\alpha_0 - \alpha_1); W_{21} = RT(\alpha_0 + \alpha_1)$$

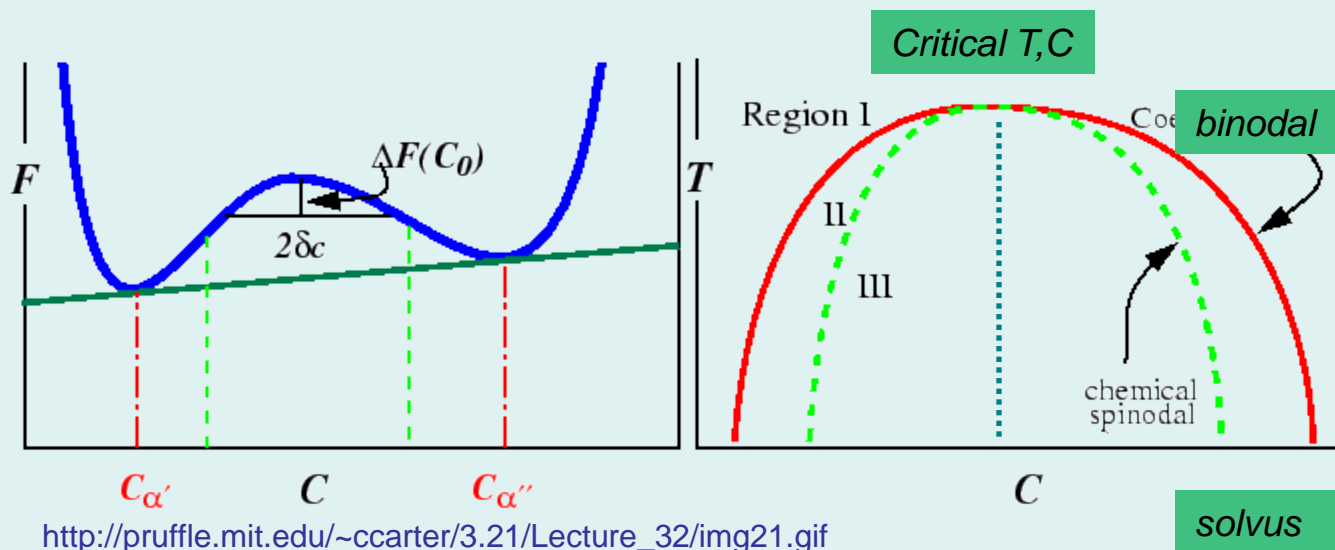
Many more models for complex mixtures have been suggested!

Immiscibility in a binary SS system

If excess Gibbs energy $G^{\text{ex}} > 0$, at some intermediate bulk system composition, two SS phases of different compositions may become stable instead of one

Simple criterion (Glynn, 1991) for the regular SS model $W_G = RT\alpha_0$

Binodal miscibility gap is possible at $\alpha_0 \geq 2.0$



GEM can compute a binodal solvus using two SS phases with the same model

Adding Solid Solutions of M²⁺ Sulfates

Regular (symmetric) mixing model for n -component solid solution (TSolMod library)

$$G_{\text{EX}} = \sum_{i=1}^{n-1} \sum_{j>i}^n \chi_i \chi_j W_{ij}$$

$$W_{ij} = a + bT + cP$$

$$RT \ln \gamma_k = - \sum_{i=1}^{n-1} \sum_{j>i}^n q_i q_j W_{ij}$$

$$q_i = 1 - \chi_i \text{ when } i = k \text{ and } q_i = -\chi_i \text{ when } i \neq k$$

Back to GEMS3 'Database Mode'



'Thermodynamic Phases (Phase)'

Select e.g. 's:CaCO:Aragonite:c:...'



Clone 's:BaRaS:BrtrRaSO4:ss:...'

Set 'R' and 'S' codes (regular built-in); 1 Interaction Param., 3 coeffs



Interaction parameter: (2450 J/mol)

Clone 's:SrBaRaS:ClsBrtrRa:ss:...'



Set 3 Interaction Params., 3 coeffs

GEMS3 coding: M J J J M

Source: V.Vinograd (atomistic prediction),
2013

Interaction parameters:

j	k	a_i	b_i	c_i
0	1	2450	0	0
0	2	8820	0	0
2	1	19900	0	0

The Phase Wizard

Step 1 - Defining the Phase and the Model of Mixing

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

Phase aggregate state code:

s Condensed solid phase, also multi-component solid solution

Select a model of mixing for this phase:

R Regular multicomponent solid-solution model

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

S Activity coefficients will be calculated using a built-in mixing model selected above

Step 2 - Phase Model-Specific Settings

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

Attention! For TSolMod built-in mixing models that use dc_cf and/or ipxT, pc_cf data objects, relevant dimensions will be allocated automatically. Any array will be allocated only if all its dimensions are not zeros.

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

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

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

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

Creating Phase record
's:SrBaRaS:ClsBrtrRa:ss:...'

Please, mark ReacDC/DComp keys to be included into the Phase

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

r	s	BaCO	witherite	dn
r	s	RaCO	RaCO3	dn
r	s	RaSO	RaSO4	dn
d	s	BaSO	Brtr	dn
d	s	CO	Gr	dn
d	s	CaCO	Arg	dn
d	s	CaCO	Cal	dn
d	s	CaOH	Portlandite	dn
d	s	CaSO	Anh	dn
d	s	CaSO	Gp	dn
d	s	SO	Sulfur	dn
d	s	SrCO	Str	dn
d	s	SrSO	Cls	dn

Entering the interaction parameters

in TSolMod convention (Wagner et al., *Can. Miner.* 2012)

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

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Ph ncp 3 3 Ph npx 2 Ph nsi 0 0 nSub 0

a *b* *c*

W_{01} → W_{02} → W_{12} →

	ipxT	ipxT	ph cf[0]	ph cf[1]	ph cf[2]
0	0	1	2450	0	0
1	0	2	8820	0	0
2	2	1	19900	0	0

Regular (symmetric) mixing model for *n*-component solid solution

$$W_{ij} = a + bT + cP$$

0	s	BaSO	Brt	...
1	s	RaSO	RaSO4	...
2	s	SrSO	Cls	...

$$G_{EX} = \sum_{i=1}^{n-1} \sum_{j>i}^n \chi_i \chi_j W_{ij}$$

Partitioning in Aq-SS sulfate systems

- Common-ligand effect on cation solubility: Ba, Sr, Ra sulfates (+- excess CaSO_4)
- Partitioning of cations Ba, Sr, Ra between aqueous and sulfate solid solutions (Lippmann diagrams)
- Impact of non-ideality on Ra, Ba solid solution uptake isotherms

Common-ligand effect on mineral solubility

Calculated k_d and total dissolved molalities of metals and sulfur in presence of various combinations of stable crystalline sulphate phases

Phases	$\log_{10}k_d(\text{Ba})$ eq (31)	$\log_{10}m(\text{S})$	$\log_{10}m(\text{Ba})$	$\log_{10}m(\text{Sr})$	$\log_{10}m(\text{Ca})$	$\log_{10}m(\text{Mg})$	I, m
Aq + barite	4.972	-4.970	-4.970				4.e-5
Aq+barite +celestite	6.560	-3.190	-6.483	-3.190			0.002
Aq+barite+ celestite +gypsum	7.339	-1.781	-7.004	-3.839	-1.785		0.045
Aq+barite +gypsum	7.338	-1.784	-7.0035	-10.00	-1.784		0.045
Aq+barite * +epsomite	8.051	0.3825	-7.388			0.3825	3.633

* Approximate results (DH inappropriate). From Table 2 in Kulik (2010), *EMU Notes in Mineralogy* v.10, p. 65-138.

Solubility of (Sr,Ba,Ra)SO₄ solid solutions

In modeling project “CarbSulf:”

1. Create new

SysEq Recipe 1: ‘sulfass’ at 1 bar 25 C

Property	Name	Quantity	Units
xa_	Aqua	1	G
xa_	AtmAirNit	500	g
xa_	BaSO ₄	0.016	M
xa_	CaSO ₄	2e-6	M
xa_	NaCl	0.01	M
xa_	RaSO ₄	2e-6	M
xa_	SrSO ₄	0.02	M

Disable pure sulfate solid phases of Ba,Ra,Sr

2. Clone

SysEq Recipe 2: ‘sulfass’ at 1 bar 25 C

Add 0.1 mol CaSO₄

Re-compute equilibrium state and
check total dissolved Sr, Ba, Ra

Stable phases

1. Aq + Gas
+ BrtRaSO₄
+ ClsBrtRa

Any change in SS
compositions?

lgm t	m t	ICnam
-6.37999	4.1687902e-007	Ba ...
-4.8261111	1.4924125e-005	C ...
-5.69897	2.0000001e-006	Ca ...
-2	0.01	Cl ...
-5.268222	5.3923489e-006	H ...
-2	0.01	Na ...
-2.9889695	0.001025724	Nit ...
-2.4160977	0.0038362091	O ...
-10.115255	7.6691031e-011	Ra ...
-3.0899711	0.00081288455	S ...
-3.0912643	0.00081046759	Sr ...
0	5.2130643e-018	Zz ...

lgm t	m t	ICnam
-6.9926202	1.0171378e-007	Ba ...
-4.7998613	1.5853994e-005	C ...
-1.7687184	0.017032624	Ca ...
-1.998699	0.010030002	Cl ...
-5.1391075	7.259263e-006	H ...
-1.998699	0.010030002	Na ...
-2.9889696	0.0010257238	Nit ...
-1.1592651	0.069300269	O ...
-10.708009	1.9588062e-011	Ra ...
-1.7650223	0.017178201	S ...
-3.8372089	0.00014547591	Sr ...
0	-2.7786492e-017	Zz ...

The Lippmann diagram: solidus and solutus

Solidus
Curve

$$\Sigma\Pi_{eq} = K_{BL}x_{BL}\gamma_{BL} + K_{CL}x_{CL}\gamma_{CL}$$

Solutus
Curve

$$\Sigma\Pi_{eq} = 1 / \left(\frac{x_{B,aq}}{K_{BL}\gamma_{BL}} + \frac{x_{C,aq}}{K_{CL}\gamma_{CL}} \right)$$

$$\Sigma\Pi = \{L^-\} \left(\{B^+\} + \{C^+\} \right)$$

Lippmann's **total solubility product**

plotted with a common ordinate $\log_{10}\Sigma\Pi_{eq}$ and superimposed abscissas x_{CL} and $x_{C,aq}$

where

$$x_{C,aq} = \frac{\{C^+\}}{\{B^+\} + \{C^+\}}; \quad x_{B,aq} = 1 - x_{C,aq}$$

are the aqueous activity fractions

Case of Raoult
(simple) ideal mixing:

$$K_{BL}x_{BL} + K_{CL}x_{CL} = \Sigma\Pi_{eq} = 1 / \left(\frac{x_{B,aq}}{K_{BL}} + \frac{x_{C,aq}}{K_{CL}} \right)$$

Lippmann diagram of (Ba,Ra)SO₄ system

In project “CarbSulf:” select ‘SulfaSS’:1:...

Clone from this record:

SysEq ... ‘sulfass’:0: at 1 bar 25 C

Set up a recipe:

Property	Name	Quantity	Units
xa_	AtmAirNit	1000	g
xa_	Aqua	1000	g
xd_	BrT	0.5	M
xd_	RaSO4	0.5	M

Check the CSD, accept, then switch off the ‘ClSBrTRa’ SS phase.

Run GEM calculation; check that the ‘BrTRaSO4’ phase is present in equilibrium.

Theoretical details: chapters by M.Prieto, D.Kulik in *EMU Notes in Mineralogy* v.10 (2010); *RiMG* v.70 (2009)

Use this parent system to create a Process

‘CarbSulf:G:SulfaSS:0:0:1:25:Lippmann:L:’

Select ‘L’ type, then use the wizard to make an ‘Ion-activity Lippmann diagram’

by specifying SS phase ‘BrTRaSO4’ and ions SO₄²⁻, Ba⁺², Ra⁺² (in this order); set iTm[2] to 1.

Run without graphics first, then plot the results.

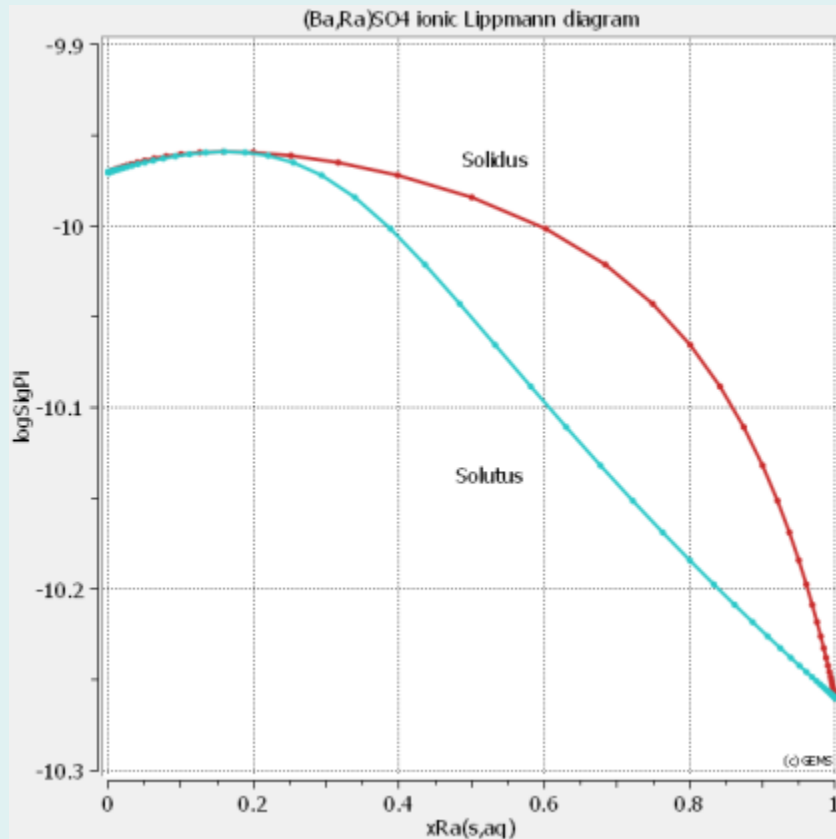
Copy-paste the results to a spreadsheet.

Variants: redo with ideal SS ($W_G=0$);

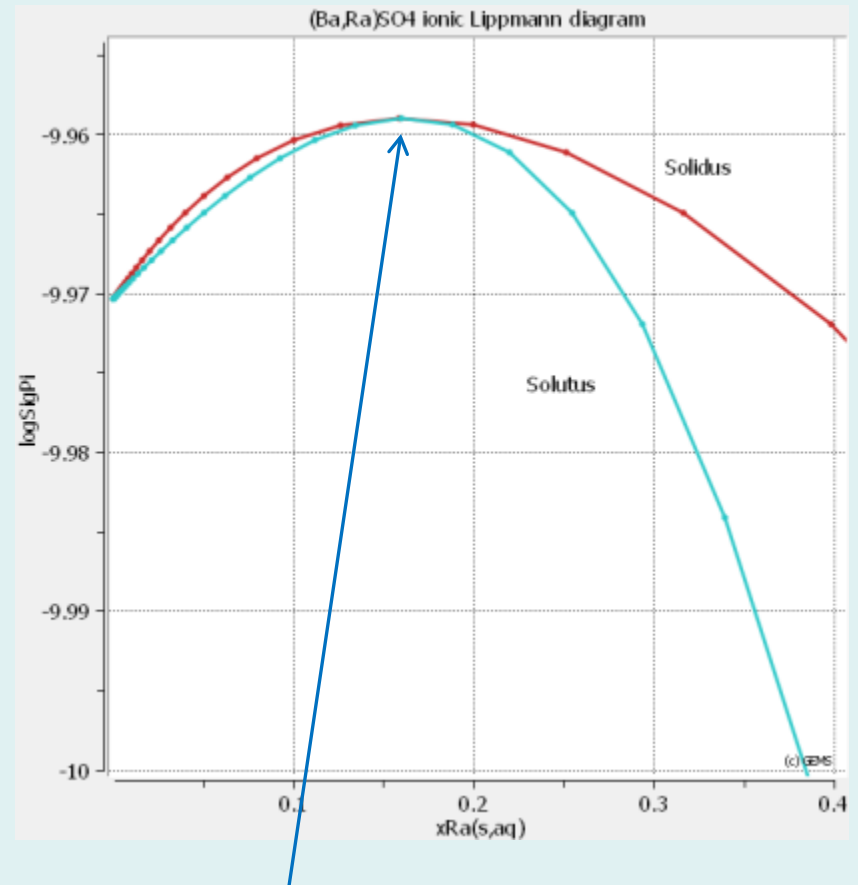
clone a Process producing a total-scale Lippmann diagram.

In GEMS, Lippmann diagrams come out transposed!

(Ba,Ra) sulfate SS Lippmann diagram



Weak Ra partitioning to aqueous phase;



Alyotropic point (no partitioning)

What about the (Sr,Ba)SO₄ SS system?

(Sr,Ba) sulfate SS Lippmann diagram

In project “CarbSulf:” select ‘SulfaSS:1:...’

Clone from this record:

SysEq ... ‘sulfaSSr’:0: at 1 bar 25 C

Set up a recipe:

Property	Name	Quantity	Units
xa_	AtmAirNit	1000	g
xa_	Aqua	1000	g
xa_	RaSO4	1e-6	M
xd_	Brt	0.5	M
xd_	Cls	0.5	M

Check the CSD, accept, then switch off the ‘BrtRaSO4’ SS phase.

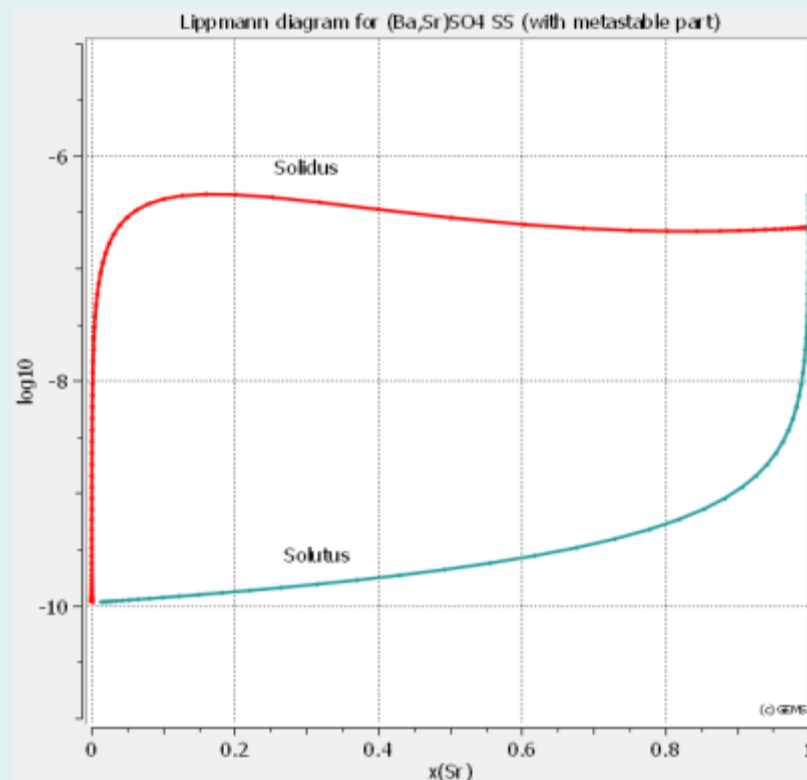
Run GEM calculation; check that the ‘ClsBrtRa’ phase is present in equilibrium. Create a Process:

‘CarbSulf:G:SulfaSSr:0:0:1:25:Lippmann:L:’

Specify the SS phase ‘ClsBrtRa’ and ions SO4-2, Ba+2, Sr+2 (in this order).

Set ipXi: -3.5; 6.5; 0.1

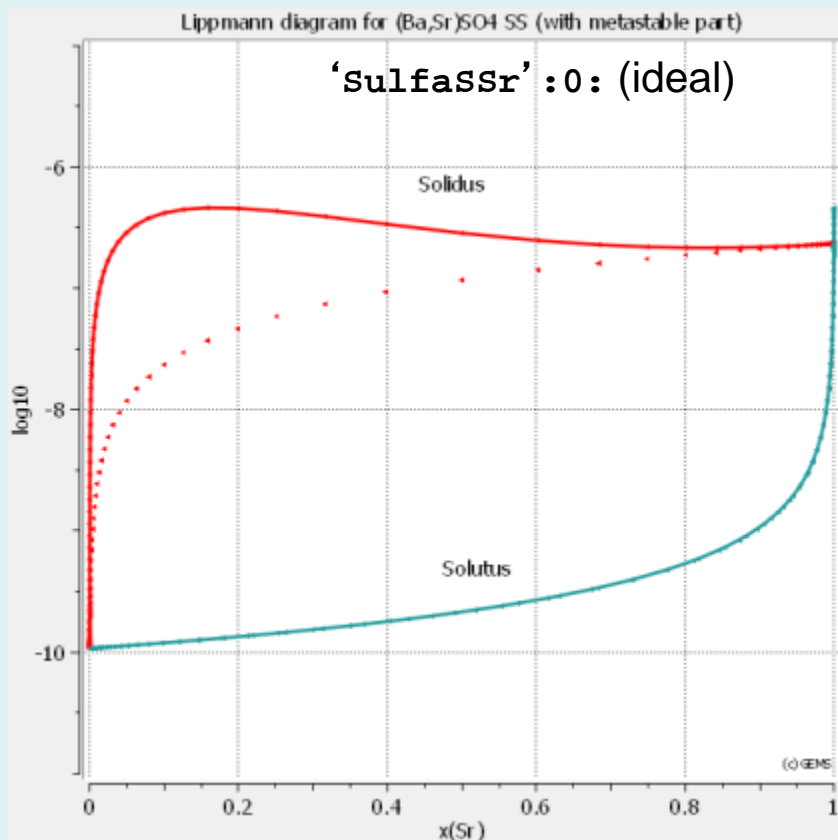
In the Process window, edit both scripts by replacing everywhere {RaSO4} with {Cls}



Strong Ba partitioning to solid phase; peritectic point (to see it, customise for fragment x: -6.8 to -6.3, y: 0.9975 to 1)

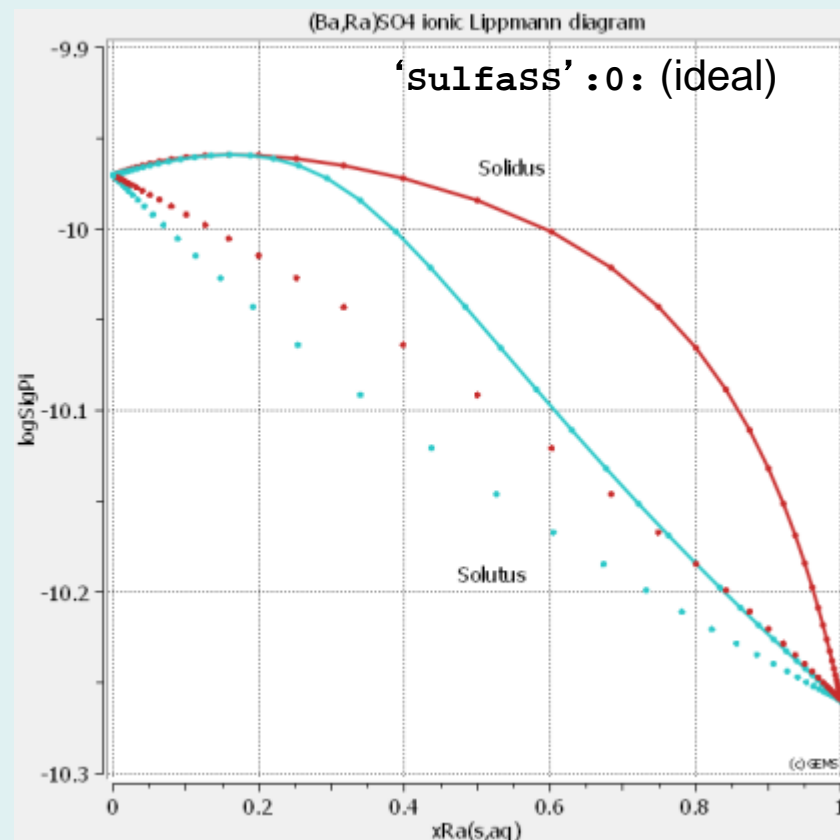
Exploring the effect of (non-)ideality

Go to menu 'Modules' 'Phase'; open ClsBrtrRa and divide all IPs by 10000



Check Fragment: No peritectic point

Go to menu 'Modules' 'Phase'; open BrtRaSO4 and divide all IPs by 10000



No alyotropic point in ideal SS

Aq-SS carbonate systems



- Carbonates are everywhere
- Calcite is the main product of cement degradation

Knowledge of mixing and trace element uptake in carbonate solid solutions is relevant for:

- ✧ diagenetic history of authigenic carbonates;
- ✧ proxies of sea-surface palaeotemperature, water chemistry, and nutrient levels;
- ✧ studies of speleothem geochemistry and palaeo-environments
- ✧ Cement chemistry, toxic and radioactive waste disposal

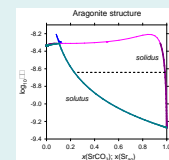
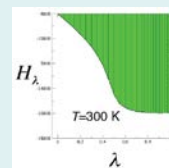
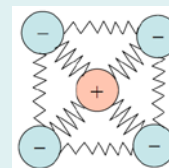
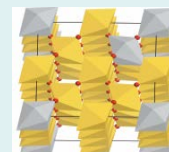
Case study on (Ca,Sr)CO₃ systems

Reference: D.Kulik, V.Vinograd, N.Paulsen, B.Winkler (2010), *Phys.Chem.Earth* 35, 217-232



Aim: To reconcile the available data on (Ca,Sr)CO₃ Aq-SS systems from atomistic simulations to thermodynamic modeling

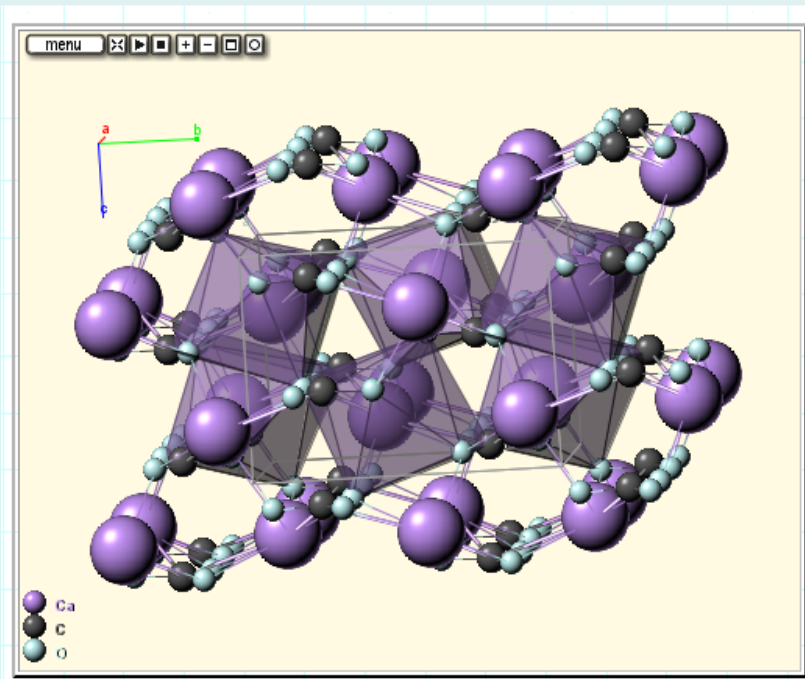
1. Quantum-mechanical calculations of thermodynamic properties of CaCO₃ and SrCO₃ polymorphs, aimed at predictions for a hypothetical pure SrCO₃(R-3c) end member
2. Force-field calculations on supercell structures of the end members using the Double-Defect Method of Cluster Expansion, followed by the Monte Carlo simulations of excess properties of mixing in solid solutions with Pmcn and R-3c structures
3. Thermodynamic modeling of aqueous – solid solution (Aq-SS) systems with SS phases of both structures
4. Interpretation using literature data on strontium partitioning in calcite/ aragonite, energies of mixing, and stability of SrCO₃(R-3c)



Different Ca - Sr carbonate structures

Space group PMCN

orthorhombic



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Aragonite CaCO_3

$G_{298}^{\circ} = -1128.355$
kJ/mol

$V_{298}^{\circ} = 3.415$ J/bar

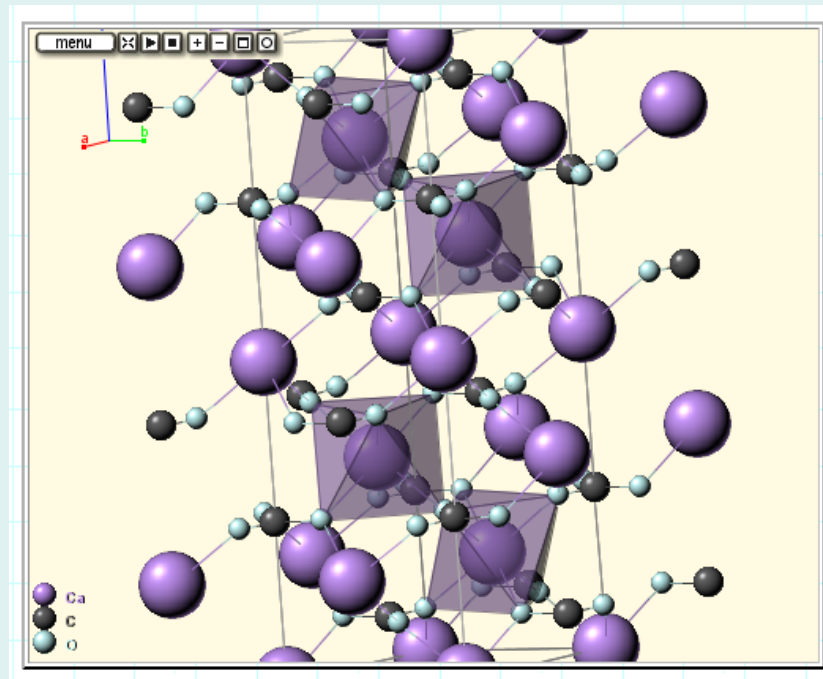
Strontianite SrCO_3

$G_{298}^{\circ} = -1144.735$
kJ/mol

$V_{298}^{\circ} = 3.901$ J/bar

Space group R-3C

rhombohedral



© webmineral.com

Calcite CaCO_3

$G_{298}^{\circ} = -1129.176$
kJ/mol

$V_{298}^{\circ} = 3.6934$ J/bar

$\text{SrCO}_3\text{-RH}$ (hypoth.)

$G_{298}^{\circ} = -1122.82$
kJ/mol

$V_{298}^{\circ} = 4.390$ J/bar

Arg-Str SS: Comparison with experimental data

Regular model:

$$G^{ex} = x_{Arg} x_{Str} W_0$$

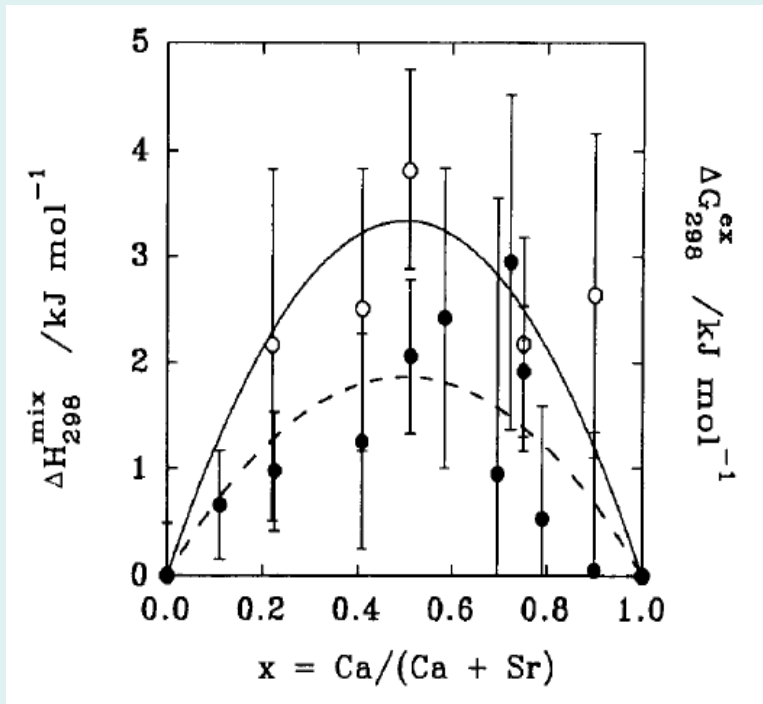


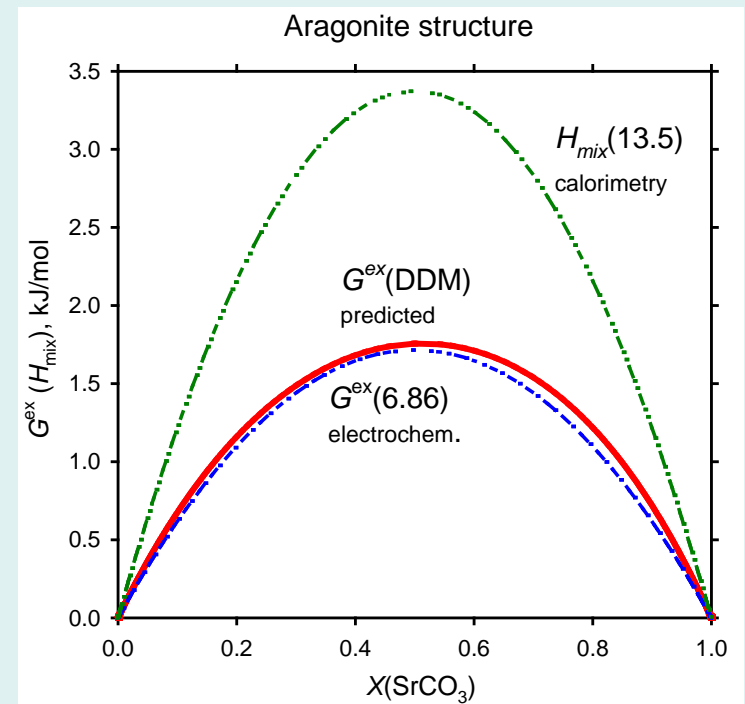
Fig.4 from **Casey et al.**, GCA (1996):

$W_0 = 6.86$ kJ/mol (G^{ex} , electrochemical)

$W_0 = 13.5$ kJ/mol (from H^{ex} , calorimetry)

Atomistic predictions:

$$G^{ex} = x_{Arg} x_{Str} \left(G_0 + G_1 (x_{Arg} - x_{Str}) + G_2 (x_{Arg} - x_{Str})^2 \right)$$



Amazing consistency between atomistic predictions and electrochemical data!

Adding aragonite – strontianite solid solutions

Switch to GEMS3 Database Mode

Select Phase 's:CaCO:Aragonite:c:...' \Rightarrow

Clone Phase 's:CaSrCO:ArgStr:ss:...' \Rightarrow

$$G^{ex} = x_{Arg} x_{Str} \left(G_0 + G_1 (x_{Arg} - x_{Str}) + G_2 (x_{Arg} - x_{Str})^2 \right)$$

Set 'K' and 'S' codes (Redlich-Kister); 1 IP (1 to 0), 16 coeffs per IP (J/mol)

3 interaction parameters each with 4 coefficients

$$G_i = A_i + B_i T + C_i T \ln T + D_i P$$

i	A_i	B_i	C_i	D_i
0	6212.96	3.15903	0	0
1	138.87	0.51069	0	0
2	2429.75	-4.8891	0	0
3	0	0	0	0

Preparations to reproduce a miscibility gap:

Select DComp 's:CaCO:Arg:...' \Rightarrow

Save As DComp 's:CaCO:Arg2:...' \Rightarrow

Select DComp 's:StrCO:Str:...' \Rightarrow

Save As DComp 's:StrCO:Str2:...' \Rightarrow

Select Phase 's:CaSrCO:ArgStr:ss:...' \Rightarrow

Clone Phase 's:CaSrCO:StrArg:ss:...' with end members: Arg2; Str2 instead of Str

J M M J

Adding (Ca,Sr)CO₃ SS with calcite structure

Select DComp 's:SrCO:Str:...'

Clone as DComp 's:SrCO:SrCO3-cal:cn_:'

Set Dcform: 'SrCO3'; V0d[0]: 4.318; H0d[0]: -1215840; S0d[0]: 100.07 (JKb mol)

Page 2: TCint: 0 to 927; aiCpT: 104.516; 0.0219242; -2.5941e6; 0;

Recalculate & save

Select Phase 's:CaCO:Aragonite:c:...' \Rightarrow

Clone Phase 's:CaSrCO:Cal-Sr_cal:ss:...' \Rightarrow

End members:

's:CaCO:Cal:....';

's:SrCO:SrCO3-cal:....'

Set 'K' and 'S' codes (Redlich-Kister);
1 IP (0 to 1), 16 coeffs per IP (J/mol)

3 interaction parameters with 4 coefficients

$$G_i = A_i + B_i T + C_i T \ln T + D_i P$$

i	A_i	B_i	C_i	D_i
0	2798.647	3.74635	0	0
1	-807.403	0.25327	0	0
2	2991.920	-4.27231	0	0
3	0	0	0	0

Save Phase record

$$G^{ex} = x_{Arg} x_{Str} \left(G_0 + G_1 (x_{Arg} - x_{Str}) + G_2 (x_{Arg} - x_{Str})^2 \right)$$

Computing carbonate Aq-SS equilibrium

In project “CarbSulf:”

SysEq Recipe 1:
‘ArgStrss’ at 1 bar 25 C

Property	Name	Quantity
xa_	AtmAirNit	1000
xa_	Aqua	1000
xd_	Arg	0.5
xd_	Str	0.5

Switch off phases:

Cal-Sr_cal; StrArg;

Aragonite, Calcite,
Strontianite

NB: Do not include SS end
members as pure phases!



CarbSulf:G:ArgStrSS:1:0:1:25:0:						
Input: System Definition				Results: Equilibrium State		
Phase/species	L	Ty	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
a aq_gen	18	a	55.510356	1.234e-10		
Ca (CO3) @		S	7.8295671e-006	7.82942e-06	7.8296486e-006	1
Ca (HCO3) +		S	6.3315154e-006	6.04113e-06	6.3315813e-006	0.95416351
Ca+2		S	0.00052266256	0.000433236	0.000522668	0.82887917
CaOH+		S	1.5860199e-008	1.51323e-08	1.5860364e-008	0.95416351
Sr (CO3) @		S	3.4680771e-007	3.46761e-07	3.4681132e-007	1
Sr (HCO3) +		S	8.8280436e-007	8.42343e-07	8.8281355e-007	0.95416351
Sr+2		S	6.0755495e-005	5.03598e-05	6.0756127e-005	0.82887917
SrOH+		S	5.6971101e-010	5.43604e-10	5.6971694e-010	0.95416351
CO2@		S	1.1685806e-005	1.16851e-05	1.1685928e-005	1
CO3-2		S	1.3009608e-005	1.07841e-05	1.3009743e-005	0.82887917
HCO3-		S	0.0011458471	0.00109335	0.001145859	0.95416351
CH4@		S	0	5.13889e-149	0	1
H2@		S	0	4.79465e-45	0	1
N2@		S	0.00051286277	0.000512868	0.00051286811	1
O2@		S	0.00027607085	0.000276072	0.00027607372	1
OH-		S	2.2055466e-006	2.1045e-06	2.2055696e-006	0.95416351
H+		T	4.9824632e-009	4.75382e-09	4.9825151e-009	0.95416351
H2O@		W	55.507796	0.999954	0.99995387	1
g gas_gen	5	g	34.653351	3.957e-10		
CO2		G	0.011888594	0.000343072	0.00034307198	1
CH4		G	0	3.69292e-146	0	1
H2		G	0	6.11964e-42	0	1
N2		G	27.364246	0.789657	0.78965655	1
O2		G	7.2772167	0.21	0.21000037	1
s ArgStr	2	s	0.99940117	-3.994e-09		
Arg		M	0.49946316	1.01307	0.49976243	2.0271057
Str		M	0.49993801	1.01267	0.50023757	2.0243878
s Graphite	1	s	0	-71.88		
Gr		O	0	1.31491e-72	0	1
s Portlandite	1	s	0	-9.517		
Portlandite		O	0	3.04248e-10	0	1

System: T = 298.15 K; P = 1.00 bar; V = 860.1 L; Aqueous: built-in Davies; pH = 8.323; pe = 12.284; IS = 0.002 m

Lippmann diagram: solidus and solutus

$$\Sigma\Pi = \{L^-\}(\{B^+\} + \{C^+\})$$

Lippmann's **total solubility product**

Solidus
Curve

$$\log_{10} \Sigma\Pi = f(x_{BL})$$

Solutus
Curve

$$\log_{10} \Sigma\Pi = f(x_{B,aq})$$

plotted with a common ordinate $\log_{10}\Sigma\Pi_{eq}$ and superimposed abscissas x_{CL} and $x_{C,aq}$

where

$$x_{C,aq} = \frac{\{C^+\}}{\{B^+\} + \{C^+\}}; \quad x_{B,aq} = 1 - x_{C,aq}$$

are the aqueous activity or total dissolved fractions

In case of simple ideal mixing:

$$K_{BL}x_{BL} + K_{CL}x_{CL} = \Sigma\Pi_{eq} = 1 / \left(\frac{x_{B,aq}}{K_{BL}} + \frac{x_{C,aq}}{K_{CL}} \right)$$

Creating a Lippmann diagram

Get SysEq “CarbSulf:ArgStrSS:1:...:” clone
SysEq Recipe 0: ‘Argstrss’ at 1 bar 25 C

Property	Name	Quantity	Units
xa_	AtmAirNit	1000	g
xa_	Aqua	1000	g
xd_	Arg	0.5	M
xd_	Str	0.5	M

Use this parent system to create a Process

‘CarbSulf:G:ArgStrSS:0:0:1:25:Lippmann:L:’

Select ‘L’ type, then use the wizard to make an
‘Ion-activity Lippmann diagram’

by specifying SS phase ‘ArgStr’ and ions CO3-2,
Ca+2, Sr+2 (in this order); set iTm[2] to 1.

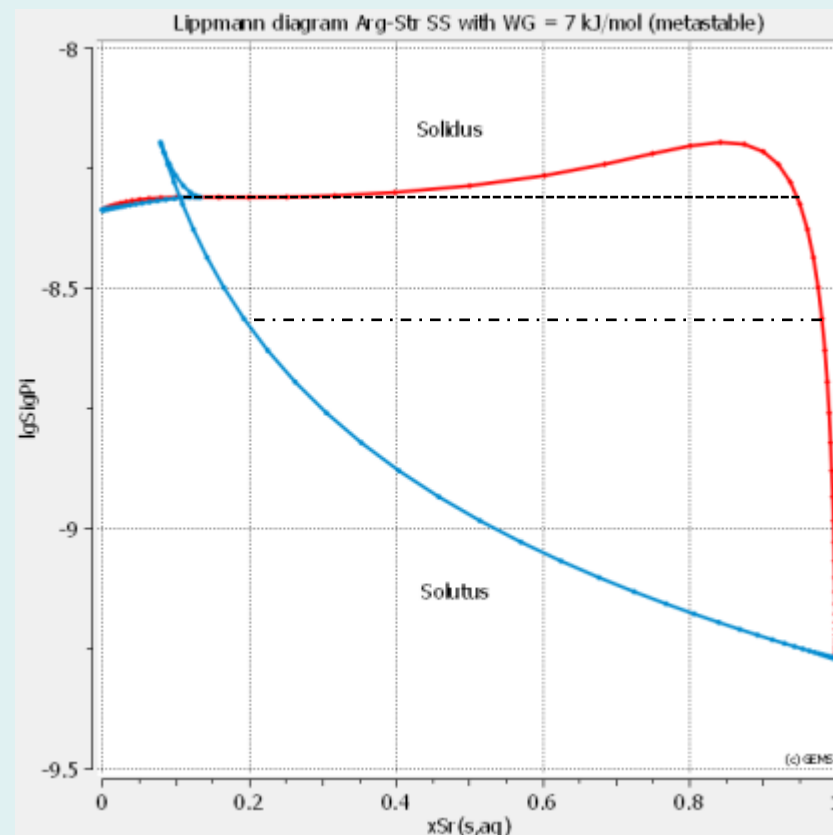
Run without graphics first, then plot the results.

Copy-paste the results to a spreadsheet.

Variants: redo with ideal SS ($W_G=0$);

clone a Process producing a total-scale Lippmann
diagram. Try also the effect of temperature.

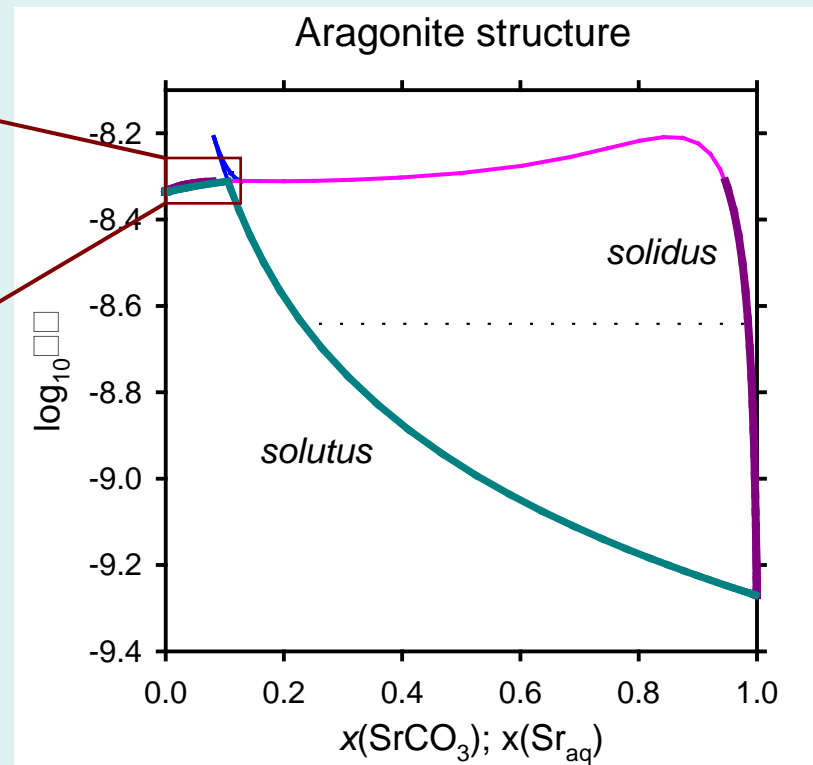
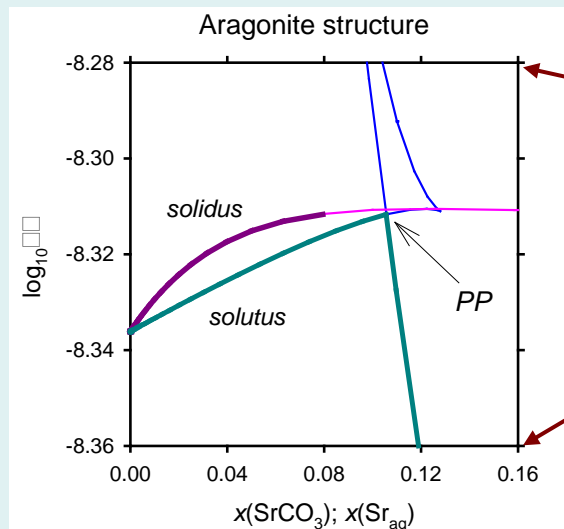
Theoretical details: chapters by M.Prieto, D.Kulik in *EMU Notes in Mineralogy* v.10 (2010); *RiMG* v.70 (2009)



? Where are metastable part and miscibility gap?

Lippmann diagram for the Arg-Str Aq-SS system

25 C,
1 bar



Lippmann's total solubility product

$$\Sigma\Pi = \{\text{CO}_3^{2-}\}(\{\text{Ca}^{2+}\} + \{\text{Sr}^{2+}\})$$

Solutus curve:

plot of $\log\Sigma\Pi$ vs

$$x_{\text{Sr},\text{aq}} = \frac{\{\text{Sr}^{2+}\}}{\{\text{Ca}^{2+}\} + \{\text{Sr}^{2+}\}}$$

Solidus curve:

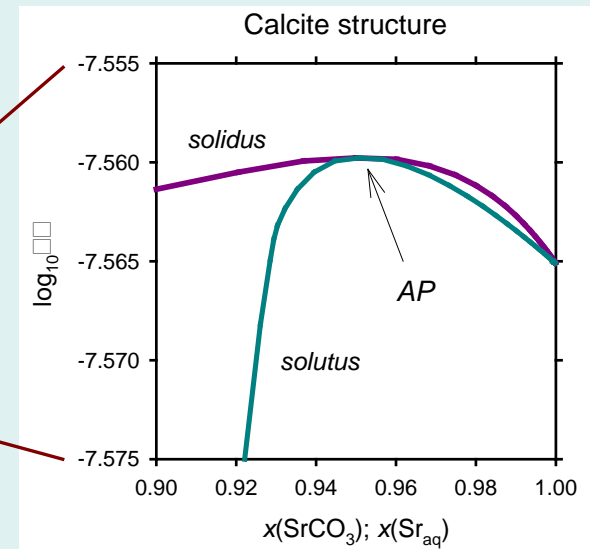
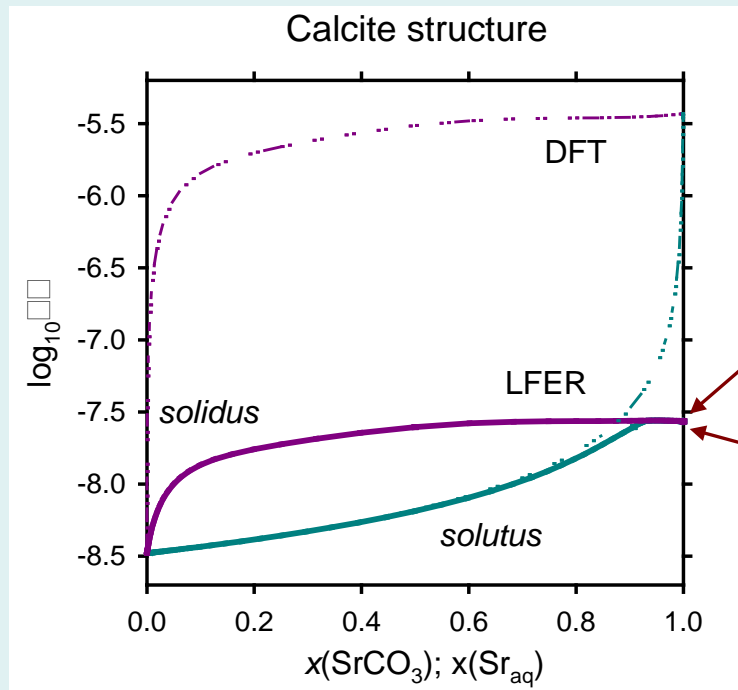
plot of $\log\Sigma\Pi$ vs bulk solid

$$x_{\text{SrCO}_3}$$

- Thick lines: stable part (two SS phases included, a miscibility gap is formed)
- Thin lines: metastable part (only one SS phase included)
- PP: Peritectic/eutectic point: defines a constant composition of aqueous solution within the miscibility gap

Lippmann diagram for $(\text{Ca,Sr})\text{CO}_3$ with calcite structure

One R-3c SS phase + Aq solution



25 C,
1 bar

Thick lines: Stable (no miscibility gap), LFER G^0_{298} of $\text{SrCO}_3(\text{R-3c})$

Thin lines: Variant with the DFT-predicted G^0_{298} of $\text{SrCO}_3(\text{R-3c})$ end member: Strontium always stays in aqueous solution (infeasible?)

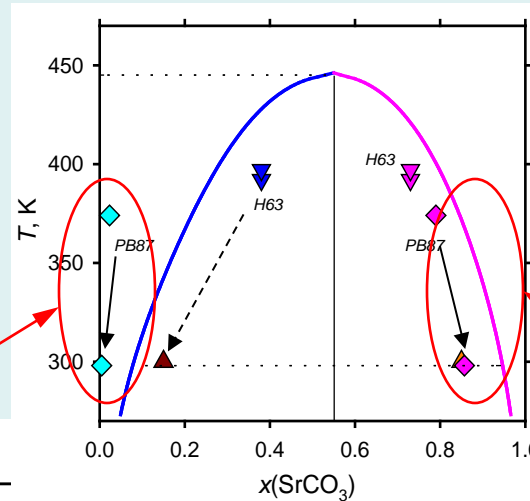
AP: Alyotropic point: $K_{\text{D,Sr}} = 1$ (no preference in partitioning)

Homework with GEMS3:
Create a process to produce Lippmann diagrams using the 'Cal-Sr_cal' SS phase

Two SS with different structures in the system

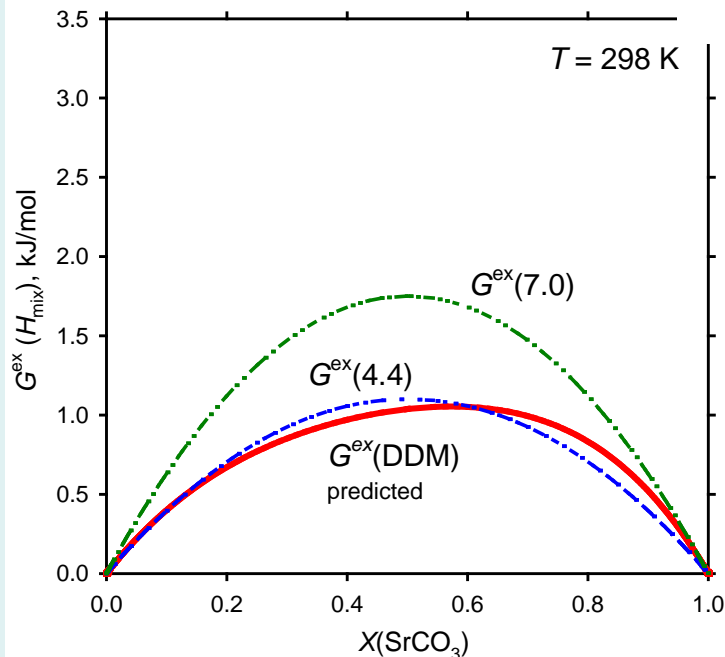
Sr-calcite phase
(Ca,Sr)CO₃ (R-3c)

Ca-strontianite phase
(Ca,Sr)CO₃ (Pmcn)



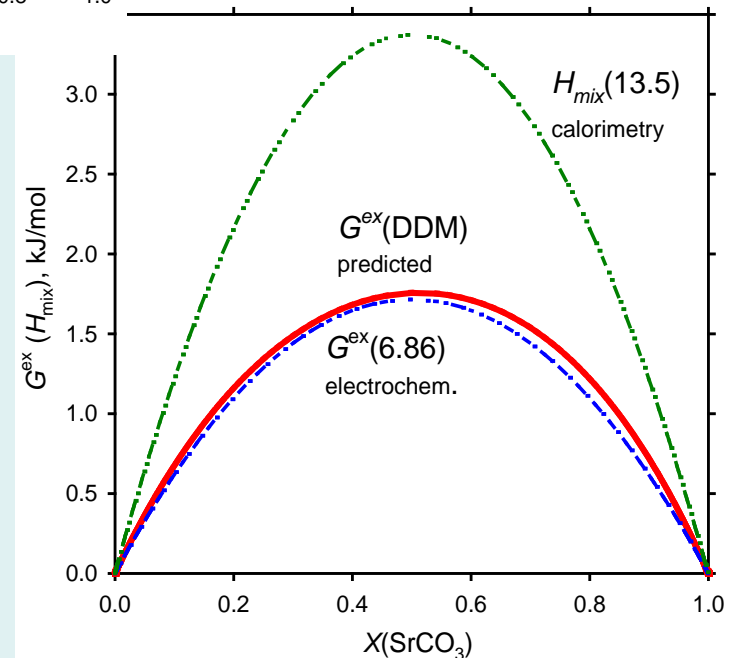
Calcite structure

Aragonite structure



Equilibrium:

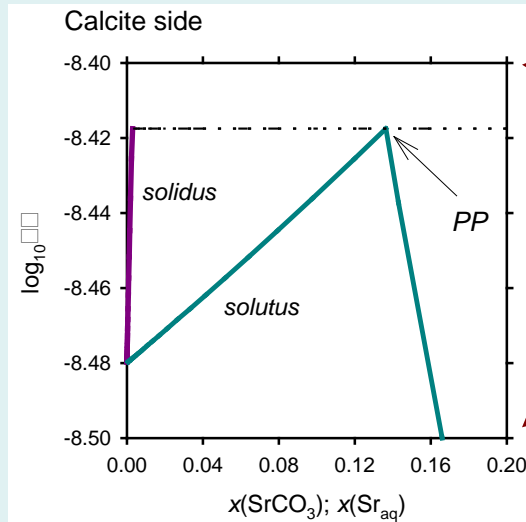
Phases co-exist
within an
asymmetric
“miscibility gap”



Analog of Lippmann diagram for “stable case” of 2 SS

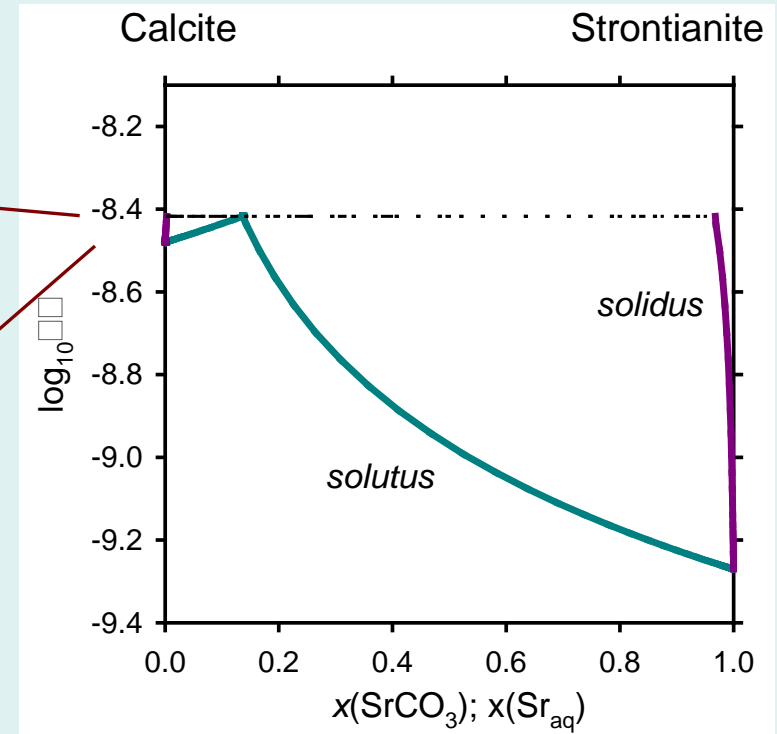
One R-3c SS phase (calcite structure)
+ one Pmcn SS phase (aragonite structure)
+ Aq solution

25 C,
1 bar



Sr in calcite: predicted $K_{d,\text{aq}} = 0.02$
as in good experimental data!

LFER value of G°_{298} of $\text{SrCO}_3(\text{R3c})$



Thick lines:

Stable phase diagram; note a broad and asymmetric “miscibility gap”

PP:

Peritectic/eutectic point: aqueous composition in equilibrium with both SS phases

Thin dashed line:

“Peritectic line” connecting stable $x_{\text{Sr-in-Cal}} = 0.003$ and $x_{\text{Sr-in-Str}} = 0.968$

Suggestions for further reading

- Glynn, P. (2000). *Solid solution solubilities and thermodynamics: Sulfates, carbonates and halides*. In: Sulfate minerals: Crystallography, geochemistry and environmental significance. *RIMG*, 40: 481-511.
- Gamsjäger, H. and E. Königsberger (2003). *Solubility of sparingly soluble ionic solids in liquids*. In: The Experimental Determination of Solubilities. (eds. G. T. Hefer and R. P. T. Tomkins), Wiley: 315-358.
- Anderson, G. M. (2005). Thermodynamics of Natural Systems. Cambridge Univ. Press.
- Nordstrom, D. K. and J. L. Munoz (1994). Geochemical thermodynamics. Palo Alto, CA, Blackwell Scientific.
- Powell, R. (1987). *Darken's quadratic formalism and the thermodynamics of minerals*. American Mineralogist, 72: 1-11.
- Kulik D.A., Vinograd V.L., Paulsen N., Winkler B. (2010): *(Ca,Sr)CO₃ aqueous–solid solution systems: From atomistic simulations to thermodynamic modeling*. Physics and Chemistry of the Earth, 35, 217-232.
- Kulik D.A. (2010): *Geochemical thermodynamic modelling of ion partitioning*. Chapter 3 in: Ion-partitioning in ambient-temperature aqueous systems (eds. M. Prieto, H. Stoll), EMU Notes in Mineralogy, 10, 65-138.

GtDemo of changes in aq composition

Open GtDemo: OPCalterat:PR:MS-blending:2:Aq_el_conc:

Clone GtDemo:

OPCalterat:PR:Carbonation:3:Aq_el_conc:

Go through Wizard with no changes except at Step 4: Enter '*' into Process record key (template)

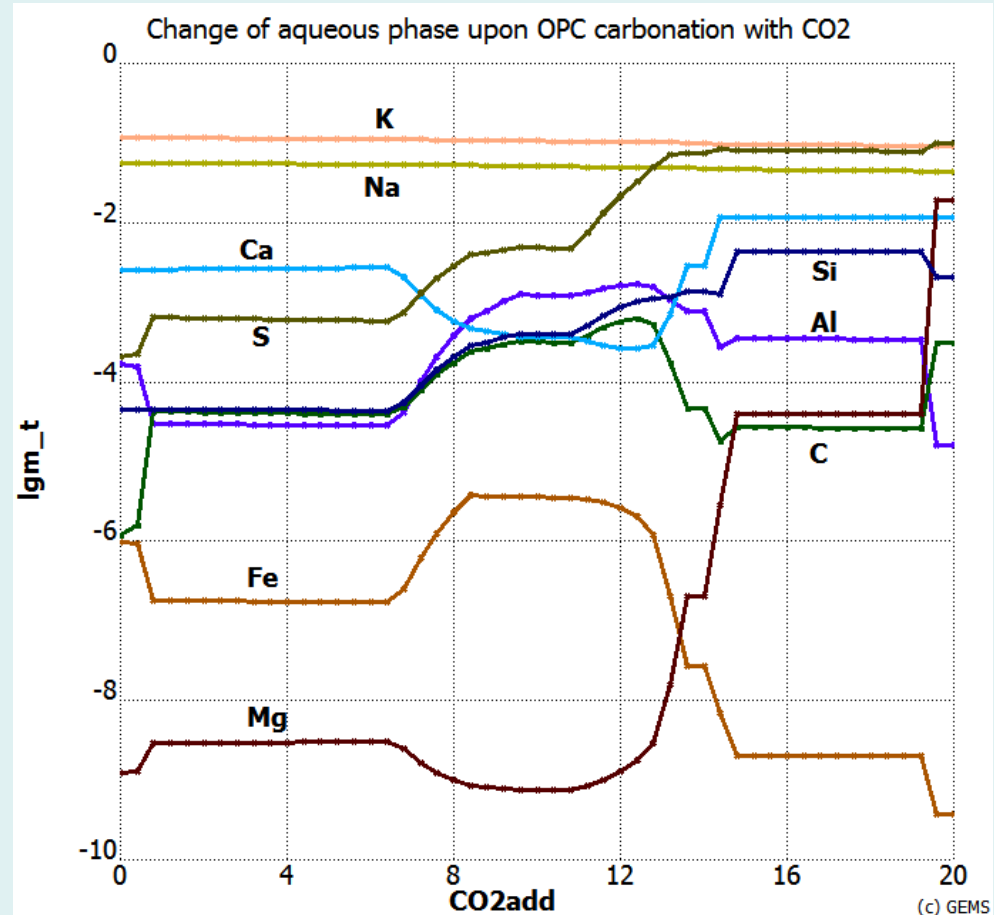
Afterwards, Select Proces record

OPCalterat:G:OPCpar:0:0:1:25:0:Carbonation:S:

From the appearing SysEq record list, 'Select All'

Type title: Change of C-S-H composition upon OPC carbonation with CO2

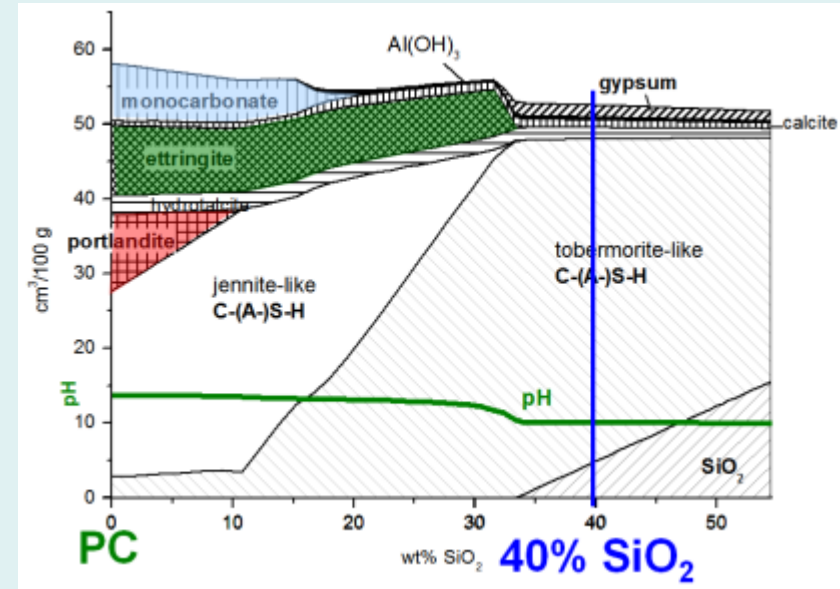
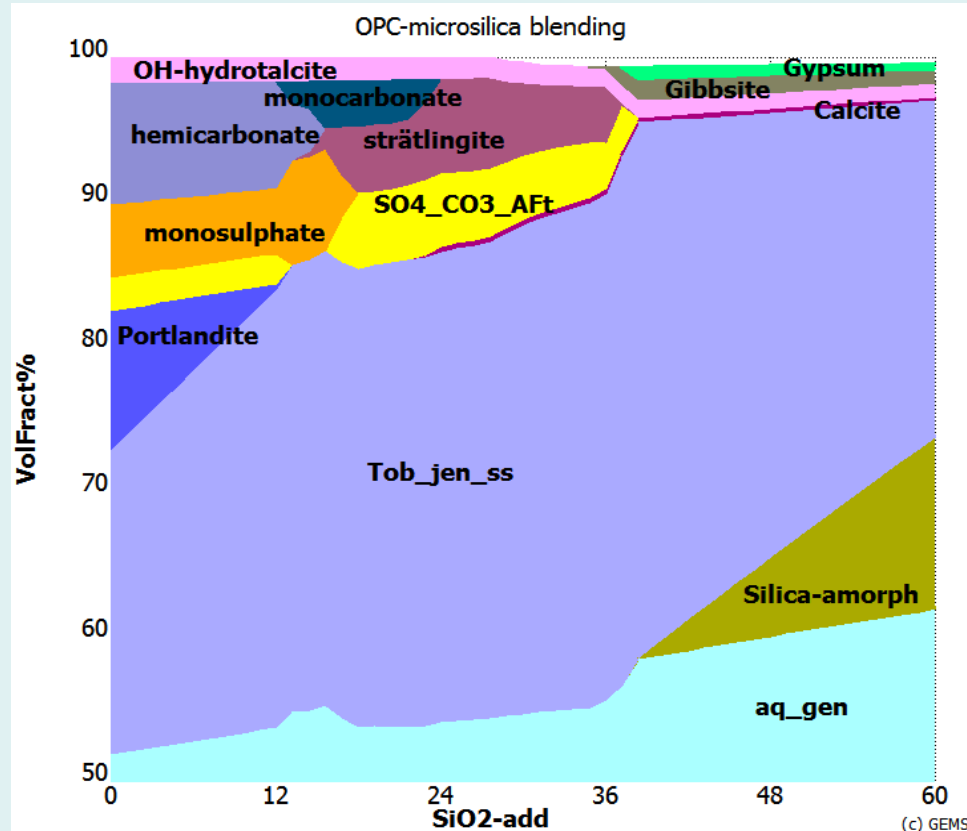
Switch to Results page and run GtDemo without graphics, then plot the graphics and customize it



Process simulation “MS-blending”

Open graphics dialog, adjust colors, output mode, customize scales:

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Exercises: Clone, change OPC/water ratio, re-run, observe the effect; modify to show phase masses instead of volumes

Home work:

Try different temperature

Try different assumptions about stable/metastable phases;

Activate the Tob_SiO₂_ss phase;

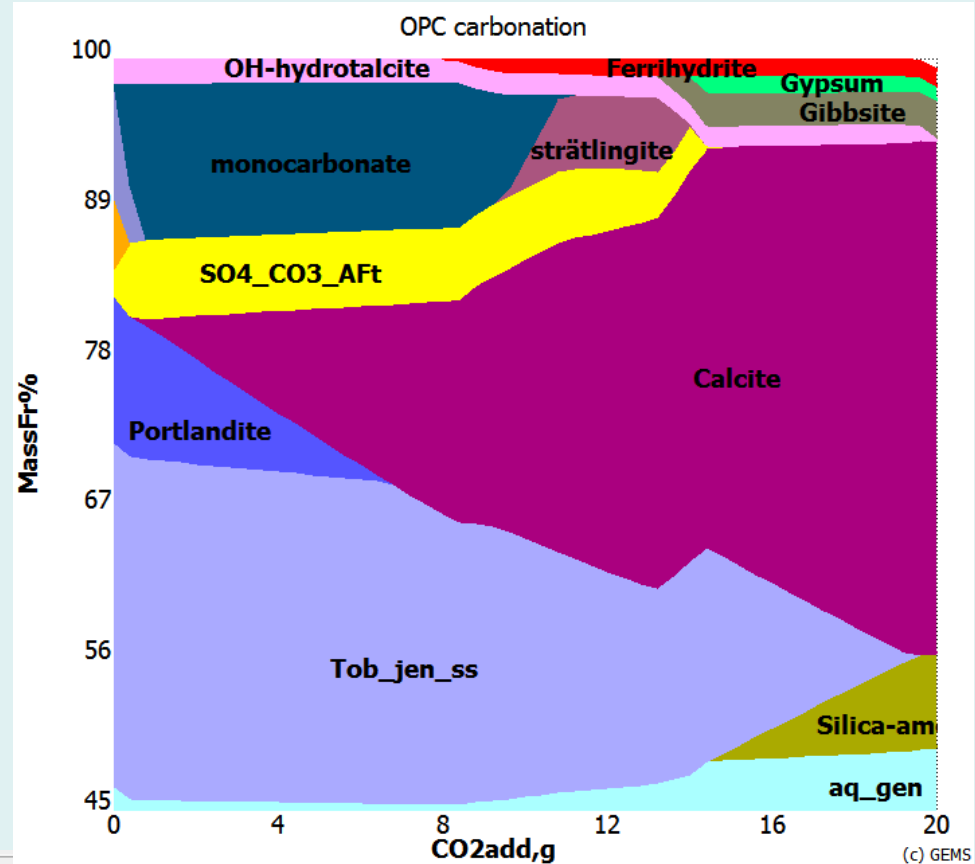
Clone, run and watch the effect

Process “Carbonation”: sample masses

In Sampling page (Mbx is system mass, kg):

```

xp[J] := cNu;
yp[J][0] := phM[{aq_gen}]/Mbx/10;
yp[J][1] := phM[{Silica-amorph}]/Mbx/10;
yp[J][2] := phM[{Tob_jen_ss}]/Mbx/10;
yp[J][3] := phM[{Portlandite}]/Mbx/10;
yp[J][4] := phM[{Calcite}]/Mbx/10;
yp[J][5] := (phM[{SO4_CO3_Aft}]]
            +phM[{CO3_SO4_Aft}]]/Mbx/10;
yp[J][6] := phM[{monosulphate}]/Mbx/10;
yp[J][7] := phM[{strätlingite}]/Mbx/10;
yp[J][8] := phM[{hem carbonate}]/Mbx/10;
yp[J][9] := phM[{monocarbonate}]/Mbx/10;
yp[J][10] := phM[{OH-hydrotalcite}]/Mbx/10;
yp[J][11] := phM[{Gibbsite}]/Mbx/10;
yp[J][12] := phM[{Anhydrite}]/Mbx/10;
yp[J][13] := phM[{Gypsum}]/Mbx/10;
yp[J][14] := phM[{C3AFH6}]/Mbx/10;
yp[J][15] := phM[{Ferrihydrite-mc}]/Mbx/10;
    
```



Controls						
Sampling						
Results						
Config						
28/02/2013, 10:49						
OPC carbonation				pY Nam	MassFr%	
pX Nam	CO2add,g	aq_gen	Silica-amorph	Tob_jen_ss	Portlandite	Calcite
0	0	46.805351	0	25.181454	10.674051	0
1	0.4	45.916298	0	25.081141	10.235681	0
2	0.8	45.793422	0	24.981612	9.7886062	0.47669338
3	1.2	45.774231	0	24.88287	9.084413	1.3736849

*Check legend
names, run, plot!*

Further implications for cement systems

- Presented techniques that allow realistic modeling of practically relevant aqueous- solid solution systems
- Element partitioning and uptake upon cement hydration, degradation, weathering, leaching, sulfate attack etc. can be simulated
- More work on mineral dissolution/precipitation kinetics is needed
- Several solid solution models yet to be elaborated (Cemdata update?)
- GEM chemical models can be embedded in reactive transport simulations

On-going research at EMPA (B.Lothenbach, F.Winnefeld), EPFL (K.Scrivener, P.Bowen), PSI (E.Wieland, J.Tits, D.Kulik, B.Thien), ETHZ, and other places!

Acknowledgments

- Partial financial support from Nagra (Wettingen) is gratefully acknowledged
- **Thanks to Barbara for Cemdata'07, tutorial materials, and enthusiasm**
- **Thanks to Natalia, Beatrice, Enzo, Bruno, and other PSI people**

Enjoy



and check for updates!