

GEM-Selektor v.3: Simulations of Mineral- Aqueous Reaction Kinetics

Dmitrii A. Kulik

Laboratory for Waste Management, NES

Paul Scherrer Institut

on behalf of the GEMS Development Team



Downloads, technical info, publications: on web site

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

The “complete equilibrium” limit

Complete equilibrium limit: ➡

- all reactions are infinitely fast
- slow reactions over infinite time



Almost never attained at Earth surface conditions!

Metastable components: ➡ N_2 gas in the Earth atmosphere ($4 \cdot 10^9$ years)

Metastable phases: ➡

- Any dissolving or growing solid
- Any solid with non-reactive surface
- Any solid phase with large surface

❖ How to account for the time-dependent **metastability** of mineral phases and minor element **uptake** in them in thermodynamic models and in coupled reactive transport simulations?

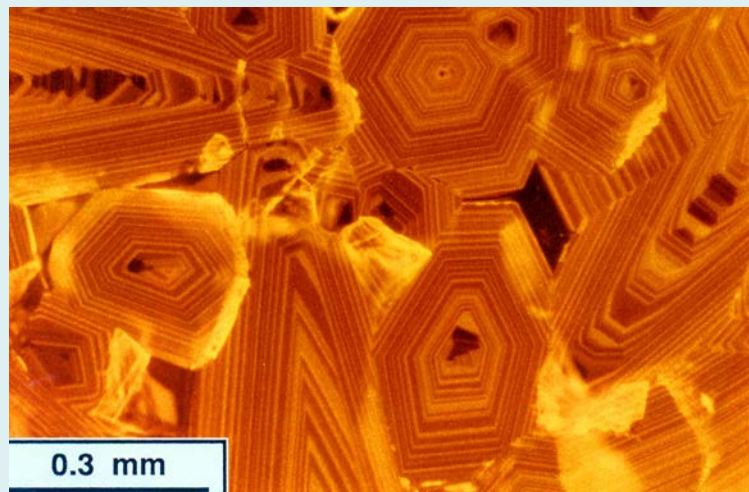


➡ Use principles of partial and local equilibria!

Phase metastability and kinetics

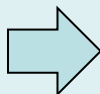
TYPICAL ASSUMPTIONS:

- There is a process-extent variable
- Aqueous and gaseous species are in chemical equilibrium with each other
- At least one phase (species) is inert or out of equilibrium with the rest of the system
- Dissolution of primary minerals is slow
- Precipitation of secondary minerals is fast



<http://serc.carleton.edu/NAGTWorkshops/complexsystems/workshop2010/participants/dutrow.html>

*Reaction-path and
process-extent
models*



Implementations using time-dependent:

- ❖ Amount constraints on metastable species or phases
- ❖ Mineral specific surface areas and sorption capacities
- ❖ Phase metastability linked to surface area of other phases

GEM: Solving for constrained equilibria

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



Gibbs Energy Minimization: Method and Software

- GEMS finds amounts of chemical components in phases with stability indexes Ω in an equilibrium state defined by T, P, bulk elemental composition, thermodynamic data
- Any computed chemical speciation is subject to the mass balance relative to bulk elemental composition of the system (+ trivial non-negative amounts of species)
- Amount of any component in any phase can be constrained from in mass balance by Additional Metastability Restriction (AMR) from below and/or from above
- Lower AMRs allow stepwise simulation of mineral **dissolution**
- Upper AMRs allow stepwise simulation of mineral **precipitation**

Any AMR can cause a partial equilibrium state!

TSolMod library of models of mixing in fluids / aqueous / solid / liquid solutions

A (new) TKinMet library of models for metastability and kinetics of mineral-aqueous reactions?

The simplest form of GEM IPM

The IPM algorithm finds simultaneously the *primal* $\hat{n}^{(x)}$ and the *dual* u solutions of the problem (F) using *Karush-Kuhn-Tucker* necessary and sufficient conditions:

$v - A^T u \geq 0;$	←	Stability (dual thermodynamics)
$A\hat{n}^{(x)} = n^{(b)}; \hat{n}^{(x)} \geq 0;$	←	Mole balance, non-negativity
$\hat{n}^{(x)}(v - A^T u) = 0$	←	Orthogonality (DC selection)

Metastability can be controlled here !

The first condition, re-written with indexes, is

$$\frac{g_j^o}{RT} + \ln C_j + \ln \gamma_j + \Xi - \sum_i a_{ij} u_i \geq 0, \quad j \in L, \quad i \in N \quad \text{implying that}$$

$$v_j \geq \eta_j, \quad j \in L, \quad i \in N \quad \text{where} \quad \eta_j = \sum_i a_{ij} u_i, \quad j \in L, \quad i \in N \quad \text{is the dual chemical potential}$$

Metastability restrictions in GEM IPM 3

At given T, p, b, g^o , and parameters of mixing in solution phases, **find**

such amounts of species (dependent components) $n^{(x)} = \{ n_j^{(x)}, j \in L \}$ that

$$G(n^{(x)}) \Rightarrow \min \quad \text{s. t.} \\ A \cdot n^{(x)} = n^{(b)}$$

← Mole balance

Total Gibbs energy function:

$$G(n^{(x)}) = \sum_j n_j^{(x)} \nu_j, \quad j \in L$$

ν_j is primal chemical potential of j -th species

$$\nu_j = g_j^o / RT + \ln C_j + \ln \gamma_j + \Xi, \quad j \in L$$

AND

Extended KKT conditions
for a partial equilibrium state



$$\left. \begin{array}{l} \nu_j - \hat{\eta}_j \geq 0, \\ (\nu_j - \hat{\eta}_j) \hat{n}_j^{(x)} = 0, \quad \hat{n}_j^{(x)} \geq 0 \end{array} \right\}, \quad j \in D_0 \quad \underline{n}_j$$

$$\left. \begin{array}{l} \nu_j - \hat{\eta}_j \geq 0, \\ (\nu_j - \hat{\eta}_j)(\underline{n}_j^{(x)} - \hat{n}_j^{(x)}) = 0 \end{array} \right\}, \quad j \in D_1 \quad \underline{n}_j \quad \text{Dissolution}$$

$$\left. \begin{array}{l} \nu_j - \hat{\eta}_j \geq 0, \\ (\nu_j - \hat{\eta}_j)(\hat{n}_j^{(x)} - \bar{n}_j^{(x)}) = 0 \end{array} \right\}, \quad j \in D_2 \quad \bar{n}_j \quad \text{Precipitation}$$

$$\left. \begin{array}{l} \nu_j - \hat{\eta}_j + \hat{p}_j \geq 0, \\ (\nu_j - \hat{\eta}_j + \hat{p}_j)(\underline{n}_j^{(x)} - \hat{n}_j^{(x)}) = 0, \\ \hat{p}_j \geq 0, \quad \hat{p}_j(\hat{n}_j^{(x)} - \bar{n}_j^{(x)}) = 0 \end{array} \right\}, \quad j \in D_3 \quad \underline{n}_j, \bar{n}_j \quad \text{Both}$$

$$\sum_j \mathbf{a}_{ij} \hat{n}_j^{(x)} = n_i^{(b)}, \quad i \in N, j \in L \quad \text{Common balance}$$

\hat{p}_j Lagrange multiplier conjugate to j -th non-trivial two-side constraints

(Karpov et al., 2001, Geochemistry International)

Kinetics as series of partial equilibria

AMR

Time step duration Δt , time t , net kinetic rate $R_{n,k,t}$
surface area $A_{k,t}$ of k -th solid (solution) phase

TKinMet

$$\bar{n}_{k,t+\Delta t} = n_{k,t} + A_{k,t} R_{n,k,t} \Delta t \quad \text{if} \quad \log_{10} \Omega_k > \varepsilon$$

$$\underline{n}_{k,t+\Delta t} = n_{k,t} - A_{k,t} R_{n,k,t} \Delta t \quad \text{if} \quad \log_{10} \Omega_k < -\varepsilon$$

$$A_{k,t} = A_{S,k} M_{M,k} n_{k,t}$$

$A_{S,k}$: specific surface area; $M_{M,k}$: molar mass; $n_{k,t}$: amount (mol) of k -th phase



Stability index of k -th phase

$$\Omega_k = \sum_j \hat{x}_j = \sum_j \exp \left(\hat{\eta}_j - \frac{g_j^o}{RT} - \ln \lambda_j - \Xi_k \right)$$

Standard-state Gibbs energy

Activity coefficient

Dual-solution chemical potential

$$\hat{\eta}_j = \sum_i a_{ij} \hat{u}_i^{(b)}$$

To-mole-fraction conversion term

$n_{k,t}$

Calculation of phase stability index: a proof

For a single-component (pure substance) phase, the saturation index SI:

$$\Omega_{S,p} = \frac{1}{\ln 10} \left(\sum_i a_{ip} u_i - g_p^o / RT \right), \quad p \in L_p, \quad i \in N$$



Proof: For an ionic solid BL,
compare with usual definition

$$10^{\Omega_{S,BL}} = Q_{S,BL} / K_{S,BL} = (a_{B+} a_{L-}) / K_{S,BL}$$

Activities of aqueous ions and their product $Q_{S,BL}$ can be found as:

$$\ln Q_{S,BL} = \left[u_B + u_{\text{Charge}} - g_{B+}^o / RT \right] + \left[u_L - u_{\text{Charge}} - g_{L-}^o / RT \right] = u_B + u_L - (g_{B+}^o + g_{L-}^o) / (RT)$$

solubility product $K_{S,BL}$ is defined as

$$\ln K_{S,BL} = -(g_{B+}^o + g_{L-}^o) / (RT) + g_{s,BL}^o / (RT)$$

Substitution
results in

$$\Omega_{S,BL} = \frac{1}{\ln 10} \ln \left(Q_{S,BL} / K_{S,BL} \right) = \frac{1}{\ln 10} \left(u_B + u_L - g_{s,BL}^o / RT \right)$$

which is
the proof

Phase stability indices in GEM IPM output

Chemical potential
of j -th compound from
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 l_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)**



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

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

SysEq Recipe 2: 'calclitesw' 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

Metastable vs 'excluded' mineral phase

MB = mass balance in system bulk composition;

TDB = chemical thermodynamic data base

Phase/species present:	(Over-)stable phase	Under-stable phase
Not in MB; not in TDB	Unknown (maybe large) metastability artifact	No effect on system state
Not in MB (by $\bar{n}_j = 0$) but in TDB	Known metastability ($\Omega > 1$); effect on MB	No effect on system state ($\Omega < 1$)
In TDB; amount \bar{n}_j constraint in MB	System 'oversaturated' ($\Omega > 1$, precipitation)	No effect on system state ($\Omega < 1$)
In TDB; amount \underline{n}_j constraint in MB	No effect on MB ($\Omega \geq 1$, stable)	System 'undersaturated' ($\Omega < 1$, dissolution)
In TDB; two-side amount constraint in MB \bar{n}_j	Effect on MB, metastability ($\Omega \geq 1$, 'oversaturation')	Effect on MB, metastability ($\Omega < 1$, 'undersaturation')

Assuming all species formulae to be consistent with the bulk system stoichiometry;
 Ω is phase stability index.

Setting additional metastability restrictions

System: Portlandite + 1 kg water + N₂-O₂ air
(data from PSI/Nagra TDB)

Saturation

Recipe 0: 'PortlKin' at 1 bar 25 C, var. 0

Property	Name	Quantity	Units
xa_	Aqua	1	kg
xd_	Portlandite	0.05	mol
bi_	Nit	0.0016	mol
bi_	O	0.0004	mol



Complete equilibrium:

pH = 12.47; IS= 0.05 m

[Ca]_{aq} = 0.0203 m

n(Portlandite) = 0.02971 mol

Ω (Portlandite) = 1.0

Oversaturation

Recipe 0: 'PortlKin' at 1 bar 25 C, var. 1

Property	Name	Quantity	Units
xa_	Aqua	1	kg
xd_	Portlandite	0.05	mol
bi_	Nit	0.0016	mol
bi_	O	0.0004	mol
dul_	Portlandite	0.01	mol



Partial equilibrium:

pH = 12.73; IS= 0.096 m

[Ca]_{aq} = 0.04 m

n(Portlandite) = 0.01 mol

Ω (Portlandite) = 4.75

+ upper amount constraint in MB

Additional metastability restrictions: Dissolution

System: Portlandite + 1 kg water + N₂-O₂ air

Undersaturation

Recipe 1: 'PortlKin' at 1 bar 25 C, var. 0

Property	Name	Quantity	Units
xa_	Aqua	1	kg
xd_	Portlandite	0.02	mol
bi_	Nit	0.0016	mol
bi_	O	0.0004	mol



Complete equilibrium:

pH = 12.47; IS= 0.05 m

[Ca]_{aq} = 0.02 m

n(Portlandite) = 0 mol

Ω (Portlandite) = 0.967

Recipe 1: 'PortlKin' at 1 bar 25 C, var. 1

Property	Name	Quantity	Units
xa_	Aqua	1	kg
xd_	Portlandite	0.02	mol
bi_	Nit	0.0016	mol
bi_	O	0.0004	mol



Undersaturation

Partial equilibrium:

pH = 12.20; IS= 0.027 m

[Ca]_{aq} = 0.01 m

n(Portlandite) = 0.01 mol

Ω (Portlandite) = 0.183

d11_ Portlandite 0.01 mol

+ lower amount constraint in MB

Kinetic rate expression and its terms

$N(r)_k \geq 1$ "parallel reactions"

Reactive fraction of surface

$$R_{n,k,t} = - \sum_r^{N(r)_k} \left\{ \theta_{k,r,t} f(\kappa, E)_{k,r} f(\Pi a)_{k,r,t} f(\Omega)_{k,r,t} \right\}$$

mol/m²/s

Activation energy

Reaction rate constant at T_r

$$f(\kappa, E) = \kappa_{k,r}^o \Lambda_{k,r} e^{\frac{-E_{k,r}}{RT}}$$

Arrhenius term

$$f(\Pi a)_{k,r} = I^{b_{I,k,r}} \text{pH}^{b_{\text{pH},k,r}} \text{pe}^{b_{\text{pe},k,r}} \text{Eh}^{b_{\text{Eh},k,r}} \left(\prod_j^{n(j)_{k,r}} a_{j,k,r}^{b_{j,k,r}} \right)^{p_{k,r}}$$

Reaction activity product term

TKinMet Input kinetic parameters for r-th parallel reaction

$$f(\Omega)_{k,r} = (1 + u_{k,r} - \Omega_k^{q_{k,r}})^{m_{k,r}}$$

Reaction affinity term (choices)

Length rate of surface propagation (m/s)

$$R_{L,k,t} = V_{M,k} R_{n,k,t} = \frac{M_{M,k}}{\rho_k} R_{n,k,t}$$

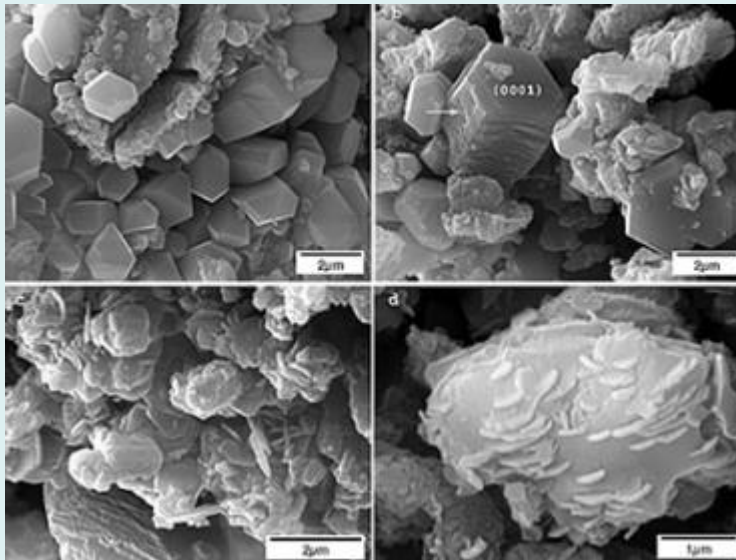
Molar volume

Molar mass

Density

Index	Comment	Symbol	Default value
0	Net rate constant (mol/m ² /s) at T_o	$\kappa_{k,r}^+ \kappa_{k,r}^-$	0
1	Gross rate constant (mol/m ² /s) at T_o	$\bar{\kappa}_{k,r}^+ \bar{\kappa}_{k,r}^-$	0
2	Arrhenius factor	$\Lambda_{k,r}$	1
3	Activation energy (J mol ⁻¹)	$E_{k,r}$	0
4	Empirical parameter for IS	$b_{I,k,r}$	0
5	Empirical parameter for pH	$b_{\text{pH},k,r}$	0
6	Empirical parameter for pe	$b_{\text{pe},k,r}$	0
7	Empirical parameter for Eh	$b_{\text{Eh},k,r}$	0
8	Parameter for the activity product	$p_{k,r}$	1
9	Reaction order parameter in affinity term	$q_{k,r}$	1
10	Parameter in the affinity term	$m_{k,r}$	0
11	Optional constant in the affinity term	$u_{k,r}$	0
12	«Effective» saturation index for nucleation	$\Omega_{k,\text{eff}}$	1
13	Parameter for nucleation (reserved)		0

Simple simulations for portlandite



Kinetics of Portlandite $\text{Ca}(\text{OH})_2$
(1 bar, 25 °C):

$$A_S = 1.482 \text{ m}^2/\text{mol} = 0.02 \text{ m}^2/\text{g}$$

Rate constants (mol/m²/s):

$$k_{dis} = 0.0000323$$

[Bullard, JACS **91**, 2091 (2008)]

$$k_{gro} = 0.000036$$

[fit, data Tadros_ea, JCIS, 1976)

Rate
equation
(M is the
mass of
phase)

$$\bar{n}_{Portl}^{(x,r+1)} = n_{Portl}^{(x,r)} - A_{S,Portl}^{(r)} M_{Portl}^{(r)} \cdot k_{Portl} (1 - \Omega_{Portl}^{(r)}) \cdot \Delta\tau$$

$$A_{S,Portl}^{(r)} = A_{S,Portl}^{(0)} \left(\frac{M_{Portl}^{(0)}}{M_{Portl}^{(r)}} \right)^{1/3}$$

Change in A_S upon growth
(no nucleation), B.Thien 2011.

Creating a simulator for a dissolution process

CarbSulf:G:PortlKin:0:0:1:25:0:dissolution:S:

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

	iTm	iV	iP	iTC	iNv	iTau	ipXi
From	1000	0	1	25	0	0	0
Until	1300	0	1	25	0	300	0
Step	1	0	0	0	0	3	0

☒ Titration cNu (linear)
 ☐ Diagram logD vs linear x
 ☐ Titration cpXi logarithmic

Skip assembling a script at Step 2

Dimensions of sampled and experimental data

101 nPS - Number of steps (1 to 9999) t
 1 Number of 'modC' array columns (1
 3 Number of columns in the 'yp' table (rows will be nPS.

Enter Control script

```

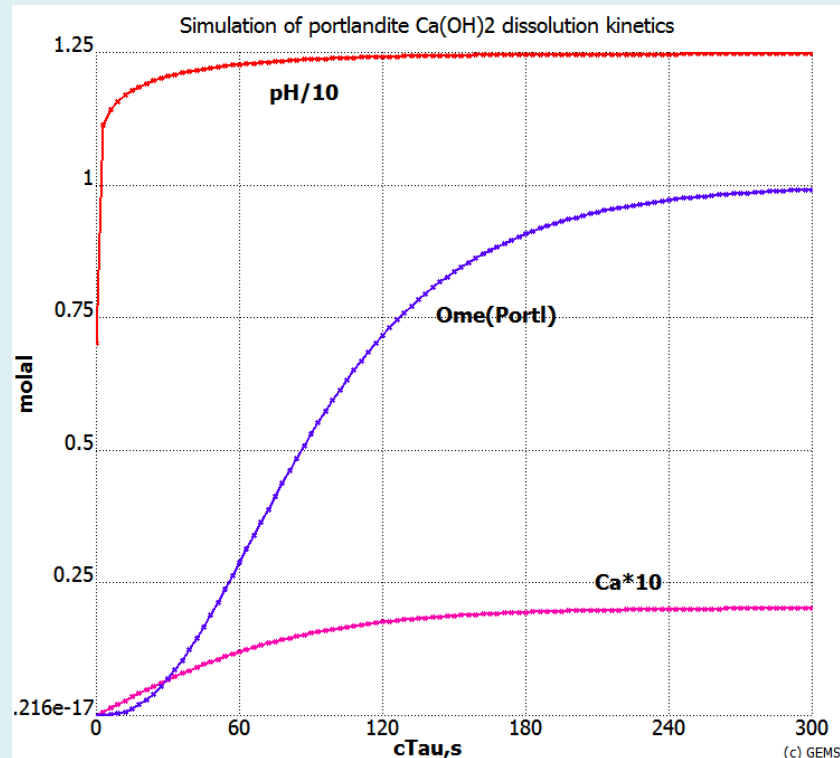
$ Rate equation for portlandite as
$ f(time) = surface area * kp * (1-IAP/KSO) * dTau
$ As0 = 2 m2/g = 148.2 m2/mol; k = 3.23e-5 mol/m2/s
$ (k+ from Bullard, JACS 2008)
Aalp_[{Portlandite}] =: 2 * ( J=0? 1:
    (xd_[{Portlandite}]/x[{Portlandite}])^(1/3) );
modC[J] =: ( J=0? xd_[{Portlandite}]*1e-7 : 3.23e-5
    * pHM[{Portlandite}]*Aalp_[{Portlandite}]
    * ( 1 - 10^lgA[{Portlandite}] ) * iTau[2] );
$ Dissolution from almost initial amount of Ca(OH)2
dll_[{Portlandite}] =: ( J = 0? xd_[{Portlandite}] :
    x[{Portlandite}] ) - modC[J];
dul_[{Portlandite}] =: dll_[{Portlandite}];
    
```

Sampling script



```

xp[J] =: cTau;
yp[J][0] =: pH/10;
yp[J][1] =: m_t[{Ca}]*10;
yp[J][2] =: 10^(lgA[{Portlandite}]);
    
```



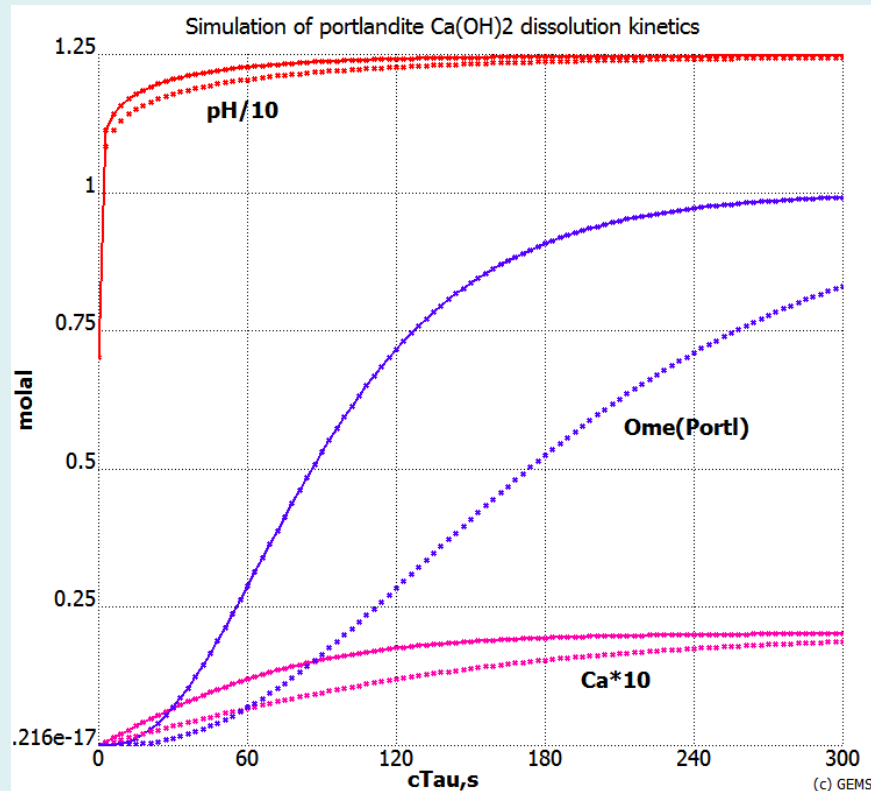
Exploring the parameter sensitivity (A_s , k , $d\tau$)

Clone a Proces record

CarbSulf:G:PortlKin:0:0:1:25:0:dissol-sens:S:

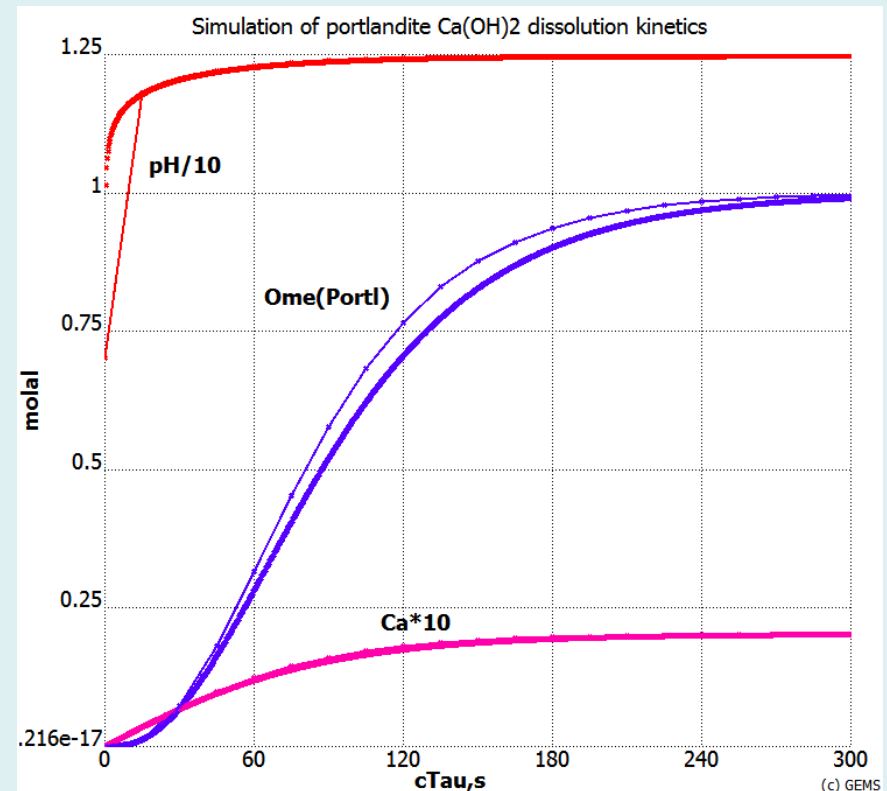
Skip all Process Wizard steps

In Control script, change A_s to $1.0 \text{ m}^2/\text{g}$



Re-run with
graphic output

Change time stepping:
remake to set 1001 steps;
set iTau[2] to 0.3 s, then to 15 s



A process simulator for precipitation

Open the 'dissolution' Proces record and clone it to

CarbSulf:G:PortlKin:0:0:1:25:0:precipitation:S:

Skip all Process Wizard steps, change $iTm[1] = 1000$,
 $iTm[2] = 10$ s.

No nucleation assumed; Precipitation starts by adding 0.001 mol seed crystals with $A_s = 0.7$ m²/g

To simulate this: in the Control script, modify the lines:

```
modC[J] =: ( J=0? xd_[{Portlandite}]*1e-7 : 0.01  
to
```

```
modC[J] =: ( J=0? xd_[{Portlandite}]*(-2e-2) : 0.01
```

and

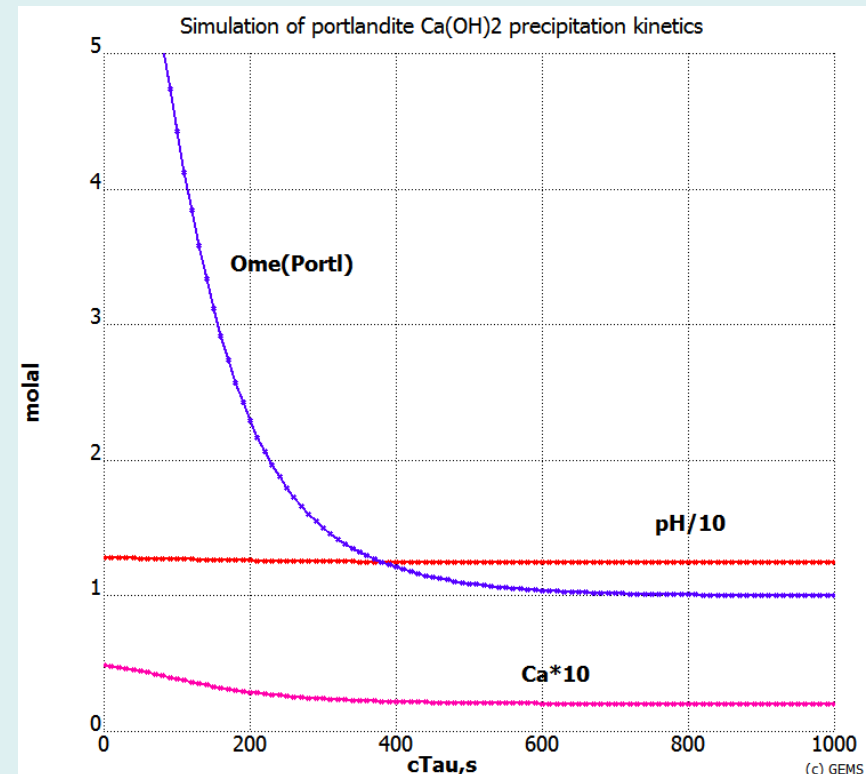
```
$ Dissolution from almost initial amount of Ca(OH)2  
dll_[{Portlandite}] =: ( J = 0? xd_[{Portlandite}] :  
to
```

```
$ Precipitation from 0.001 mol seed Ca(OH)2 crystals  
dll_[{Portlandite}] =: ( J = 0? 0.001 :
```

Run the process simulator with graphic output



Modify the Control script
and re-run to explore sensitivity to:
rate constant; seed amount and
specific surface area;
initial addition of Ca(OH)_2



A simulator for fitting the precipitation data

1. Create SysEq record CarbSulf:G:PortlKinExp:0:0:1:25:0:

xa_	Aqua	299.26	g
xa_	CaCl2	0.0105	M
Xa_	NaOH	0.021	M
xd_	Portlandite	0.01	g
bi_	Nit	0.0016	M
bi_	O	0.0004	M
dul_	Portlandite	0.00135	M

Run and check: pH = 12.54; IS = 0.062 m;
m_t(Ca) = 0.0244 m; Fa(Portlandite) = 0.186

Sampling script

```
xp[J] =: cTau;
yp[J][0] =: Aalp[{Portlandite}];
yp[J][1] =: m_t[{Ca}]*10;
yp[J][2] =:
10.^lga[{Portlandite}];
```

Experimental data (after
Tadros et al., JC/S 1976)

cTau	Ca*10
26.88	0.2457
125.32	0.2408
189.69	0.2390
254.47	0.2367
331.49	0.2347
383.47	0.2327
448.00	0.2307
499.62	0.2291
575.37	0.2285
639.43	0.2270
678.20	0.2257
749.10	0.2236
869.68	0.2220
920.83	0.2209
971.71	0.2201
1048.04	0.2189
1123.95	0.2181
1187.38	0.2173
1225.57	0.2167
1288.94	0.2159
1358.48	0.2153
1409.21	0.2147
1472.58	0.2139
1807.31	0.2112
2002.65	0.2101
2656.90	0.2077
3248.29	0.2054
3838.17	0.2049
4434.47	0.2041
5670.34	0.2033

Clone a Process (order 30 experimental points)

CarbSulf:G:PortlKinExp:0:0:1:25:0:precipTadros_ea:S:

Control script

```
$ f(time) = surface area * kp * (1-IAP/KSO) * dTau
$ As0 = 2.1 m2/g = 155.6 m2/mol; k = 0.000036 mol/m2/s
Aalp[{Portlandite}] =: 2.1 * ( J=0? 1:
(0.000135/x[{Portlandite}])^(1/3) );
modC[J] =: ( J=0? 0.000135*(-0.2) : 0.000036
* pHM[{Portlandite}]*Aalp[{Portlandite}]
* ( 1 - 10^lga[{Portlandite}] ) * iTau[2] );
$ Growth from 10 mg (=0.000135 mol) seed crystals
dll[{Portlandite}] =: ( J = 0? 0.000135 :
x[{Portlandite}] ) - modC[J];
dul[{Portlandite}] =: dll[{Portlandite}];
```

*Assume no
nucleation;
Growth occurs in
300 ml solution
on 10 mg seed
crystals with $A_s =$
2.1 m²/g; Total
time < 100 min*



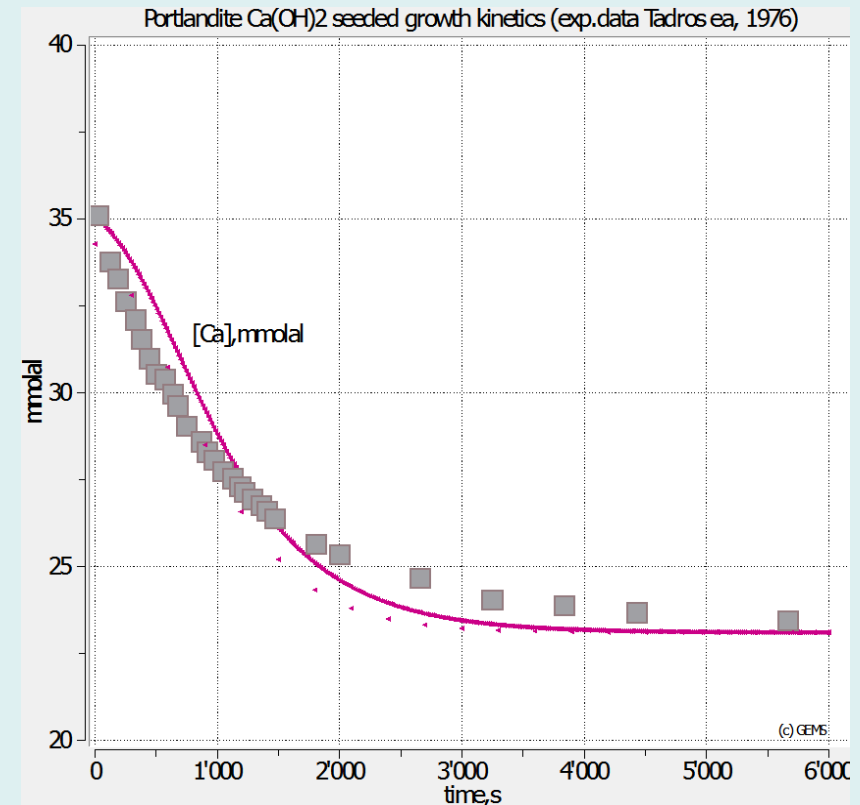
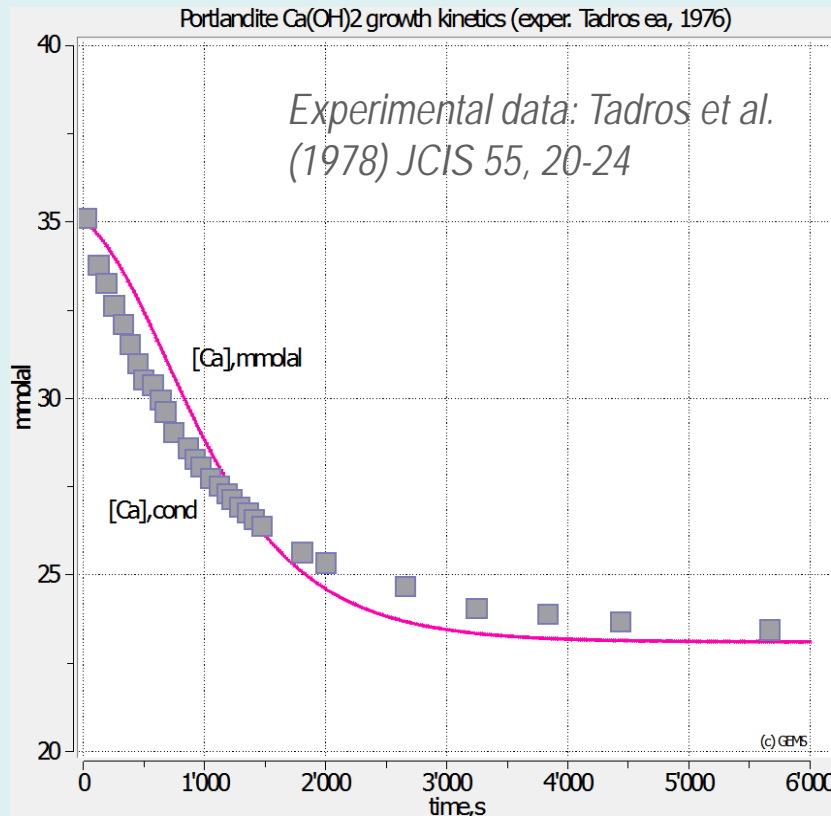
Portlandite growth: data fit and its sensitivity

CarbSulf:G:PortlKinExp:0:0:1:25:0:precipTadros_ea:S:



Simple "cubic root" SSA correction

Effect of time step duration (*10)



Reasonable fit at $k_- = -0.000021 \text{ mol/m}^2/\text{s}$

Specific surface area A_S : initial 2.1 to $0.97 \text{ m}^2/\text{g}$

Wrong shape of the model curve. Correction for particle morphology change needed?

Corrections for particle surface area

SSA

$$A_{S,k} = A_k / m_k \quad \text{in } \text{m}^2 \cdot \text{kg}^{-1}$$

$$A_{V,k} = A_k / V_k \quad \text{in } \text{m}^{-1}$$

must be corrected for growth/
dissolution at time steps:

- ❖ **externally** by transport model;
- ❖ or **internally** in kinetic model

Simple “mass-cubic-root”
correction

$$A_{S,k,t} = A_{S,k,0} \sqrt[3]{\frac{n_{k,0}}{n_{k,t}}}$$

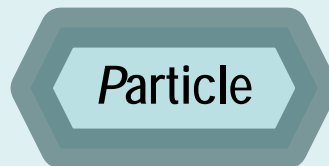
*Does not account for the
shape (morphology) change*

Internal SSA correction in TKinMet code library

$$A_{V,k,t} = A_{V,k,t-\Delta t} \frac{\psi_{k,t-\Delta t}}{\psi_{k,t}} \frac{d_{VS,k,t-\Delta t}}{d_{VS,k,t} + 2R_{L,k,t}\Delta t}$$

Growth:

↑ V_k, A_k, n_k, m_k



↓ $A_{S,k}, A_{V,k}$

$$\psi_k = \pi^{1/3} \frac{(6V_p)^{2/3}}{A_p} = \frac{6V_p}{d_p A_p}$$

Shape factor: Wadell sphericity

$$0 < \psi_k \leq 1$$

$$V_p = \frac{1}{6} \pi d_p^3$$

Volume

$$N_p = \frac{V_k}{V_p}$$

Number

$$A_p = \frac{A_k}{N_p}$$

Surface area

Mean particle diameter and sphericity

Internal SSA correction in TKinMet code library

$$A_{V,k,t} = A_{V,k,t-\Delta t} \frac{\psi_{k,t-\Delta t}}{\psi_{k,t}} \frac{d_{VS,k,t-\Delta t}}{d_{VS,k,t} + 2R_{L,k,t}\Delta t}$$

Diameter

$$d_p = d_{VS,k} = \frac{6}{\psi_k} A_{V,k} = \frac{d_{32}}{\psi_k}$$

PDF [3,2] moment (Sauter diameter)

Input **sphericity** (shape) factor

$$\psi_k = \pi^{1/3} \frac{(6V_p)^{2/3}}{A_p} = \frac{6V_p}{d_p A_p}$$

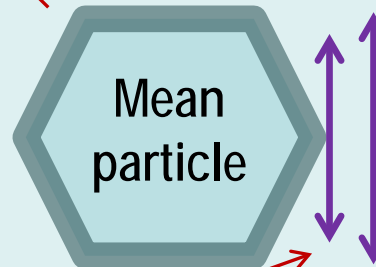
$$0 < \psi_k \leq 1$$

$$V_p = \frac{1}{6} \pi d_p^3$$

Volume

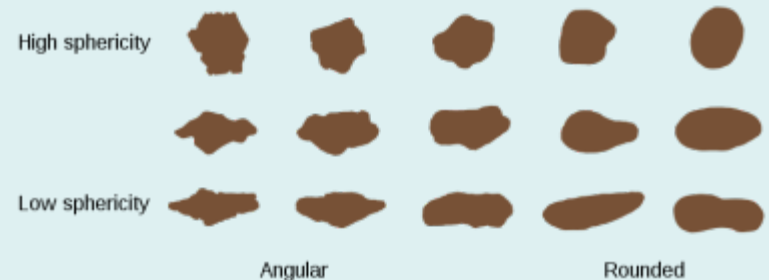
$$N_p = \frac{V_k}{V_p} \rightarrow A_p = \frac{A_k}{N_p}$$

Number Surface area



$$d_{VS,t}$$

$$d_{VS,t} + 2R_L\Delta t$$



<http://en.wikipedia.org/wiki/Sphericity>



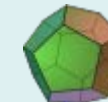
0.671



0.806



0.846



0.910

Shape factor functions:

$$\psi_k(t) = \psi_{0,k} + \psi_{1,k}u + \psi_{2,k}u^2 + \dots$$

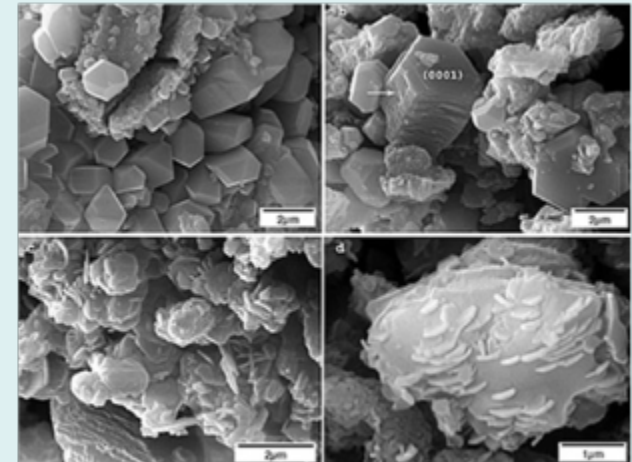
e.g. $u = \log_{10} \Omega_{k,t}$

Morphology change upon growth!

Seeded growth of $\text{Ca}(\text{OH})_2$ revisited

Initial recipe of chemical system "PortlKinExp" for Process simulation

Property	Name	Quantity	Units	Comment
xa_	Aqua (H_2O)	299.26	g	300 ml water H_2O at 1 bar, 25 C
xa_	CaCl_2	0.0105	mol	0.0105 moles of CaCl_2 (in 150 ml of 0.07 M CaCl_2 solution)
xa_	NaOH	0.021	mol	0.021 moles of NaOH (in 150 ml of 0.14 M NaOH solution)
xd_	Portlandite	0.01	g	10 mg $\text{Ca}(\text{OH})_2$ "seed" crystals
bi_	Nit	0.0016	mol	atmospheric nitrogen
bi_	O	0.0004	mol	oxygen (for CO_2 -free atmosphere)
dul_	Portlandite	0.000135	mol	Upper AMR for 10 mg of "seed"



<http://www.resintec.it>

$\text{Ca}(\text{OH})_2$ Portlandite

$$R_{\text{Port}} = \kappa_{\text{Port}}^- (1 - \Omega_{\text{Port}})$$

$$\psi_{\text{Portl}}(t) = \psi_0 + \psi_1 u \quad u = \log_{10} \Omega_{\text{Port},t}$$

$$\bar{n}_{\text{Portl}}^{(x,0)} = 0.135 \text{ mmol}; \quad A_S^{(0)} = 2.1 \text{ m}^2/\text{g}; \quad \Delta\tau = 60 \text{ s}$$

Experimental conductance data:

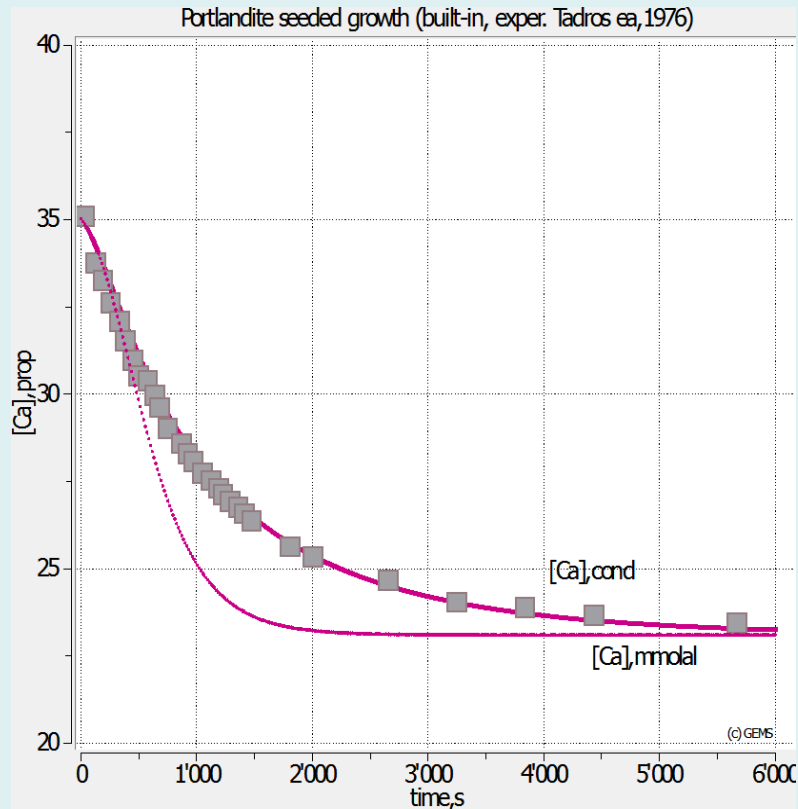
Tadros et al. (1976) *JCIS* v. 55, 20-24

Parameters of kinetic model for portlandite seeded growth

Parameter	Value	Comment
Net rate constant at 25 C ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) κ_{Port}^-	$-3.23\cdot 10^{-5}$	Fit to data
Arrhenius factor Λ_{Port}	1.0	Default
Activation energy E_{Port}	0	Default
Reactive surface area fraction θ_{Port}	1.0	Default
Sphericity factor dependence :	ψ_0	0.83
	ψ_1	-1.6
Initial specific surface area $A_{\text{S,Port},0}$ ($\text{m}^2\cdot\text{g}^{-1}$)	2.1	experiment
Initial portlandite "seed" mass m_{Port} (g)	0.01	experiment

Impact of SSA and shape corrections

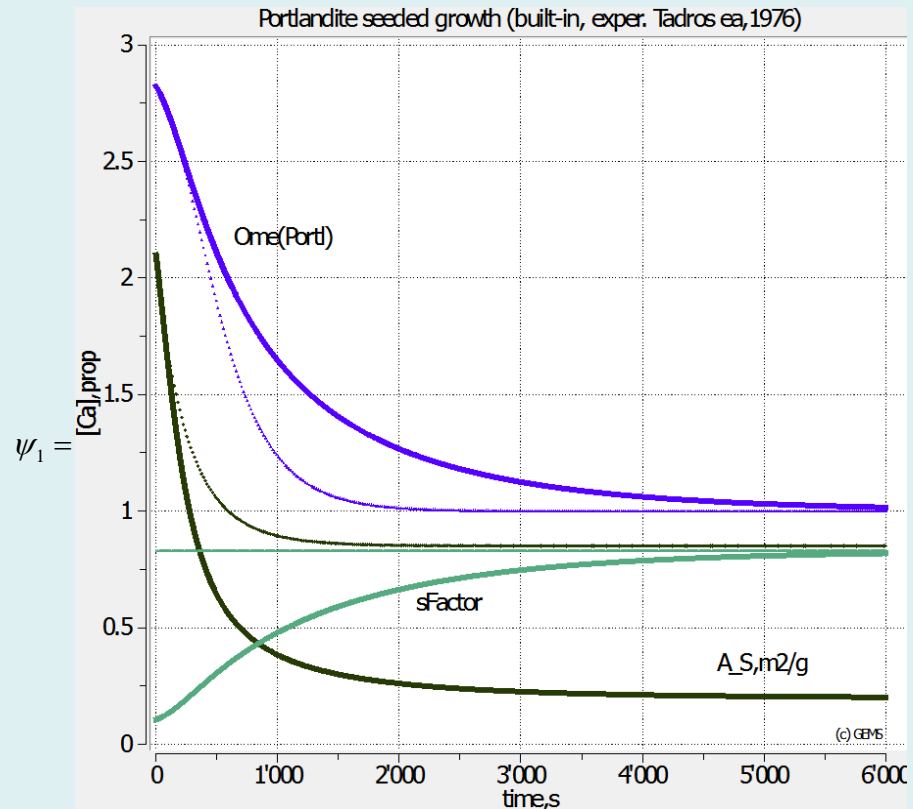
Internal SSA correction in TKinMet code library



Good fit at $k_- = -0.0000323 \text{ mol/m}^2/\text{s}$

Correct shape of the model curve!
Morphology change indeed?

Experimental data: Tadros et al. (1978) JCIS 55, 20-24



$$\psi_{Portl}(t) = \psi_0 + \psi_1 u \quad u = \log_{10} \Omega_{Port,t}$$

$$\psi_0 = 0.83 \quad \psi_1 = -1.6$$

disabled $\psi_1 = 0$ (thin dotted curves)

Rate laws for calcite precipitation

Initial recipe of chemical system "Calcite" for the GEM process simulation

Property	Name	Quantity	Units	Comment
xa_	Aqua	262	g	262 ml water H ₂ O at 1 bar, 10°C
xa_	CaCO ₃	0.00435	mol	0.00435 moles of CaCO ₃ .
xa_	CO ₂	0.0011	mol	0.011 mol CO ₂ to set pCO ₂ = 1·10 ⁻³ bar
xa_	O ₂	1·10 ⁻⁶	mol	O ₂ to stabilize redox state
dll_	Calcite	0.00316	mol	Lower AMR for 0.00316 mol of "seed"
dul_	Calcite	0.00316	mol	Upper AMR for 0.00316 mol of "seed"



<http://web.eps.utk.edu>

$$R_{L,Cal} = I^{-0.004} pH^{-10.71} \cdot \left(\frac{a_{Ca^{2+}}}{a_{CO_3^{2-}}} \right)^{-0.35} \cdot (\Omega^{0.5} - 1)^2 \quad \text{In NaCl}$$

$$R_{L,Cal,SW} = I^{0.36} pH^{-10.99} \cdot \left(\frac{a_{Ca^{2+}}}{a_{CO_3^{2-}}} \right)^{-0.71} \cdot (\Omega^{0.5} - 2)^2 \quad \text{In seawater}$$

(Wolthers et al., GCA, 2012)

Parameters of the kinetic rate model for calcite precipitation

$$R_{n,Cal} = 10^6 \frac{R_{L,Cal}}{V_{M,Cal}}$$

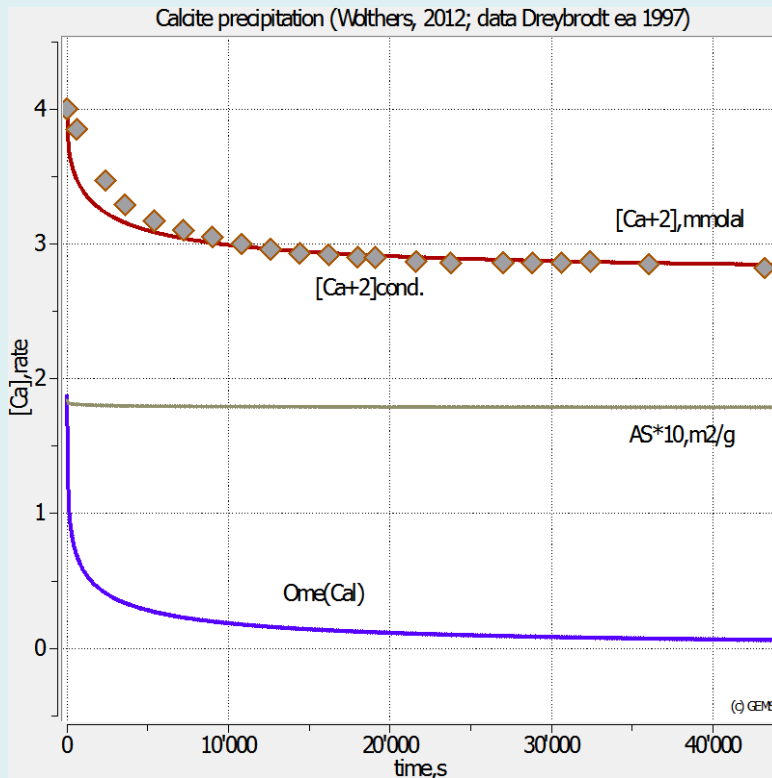
$$V_{M,cal} = 36.934 \text{ cm}^3 \cdot \text{mol}^{-1}$$



Comment	Value	Reference
Rate constant at 25°C (mol·m ⁻² ·s ⁻¹) K_{Cal}	-37800	From (Wolthers et al 2012)
Arrhenius factor Λ_{Cal}	2.671·10 ⁸	From activation energy
Activation energy E _{Cal} (kJ·mol ⁻¹)	48.1	(Inksee and Bloom 1985)
Reactive surface fraction θ_{Cal}	1.0	Default
Sphericity factor ψ_{Cal}	0.8	Geometry (as for cube)
Initial sp. surface area A _{S,Cal,0} (m ² ·g ⁻¹)	0.184	Experiment
Initial calcite "seed" mass (g)	0.316	Experiment

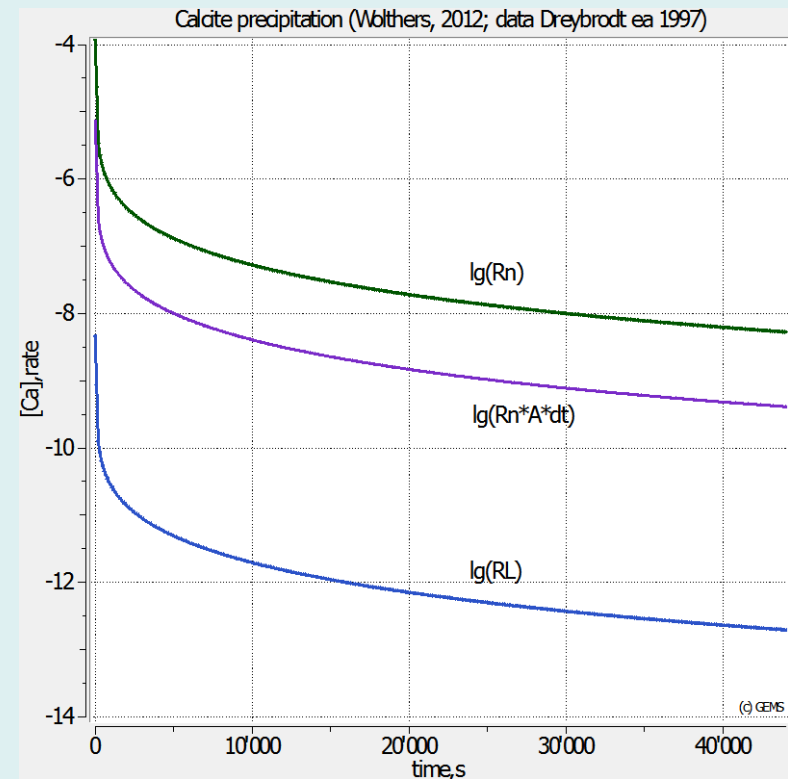
Simulation of seeded growth of calcite

Experimental data: Dreybrodt et al. (1997)



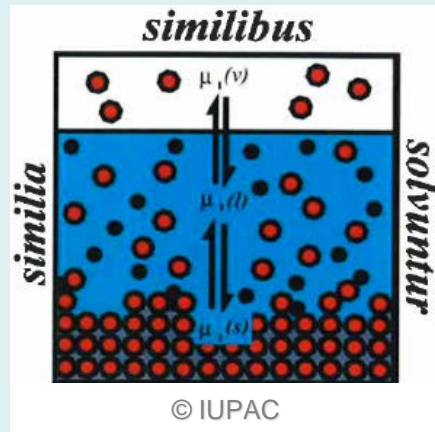
*Good fit at longer times without
adjustment of rate law parameters!
Morphology may change at short times*

SSA correction with constant $\psi = 0.8$



Wolthers (2012) rate equation is also
useful for modeling Tr uptake kinetics

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

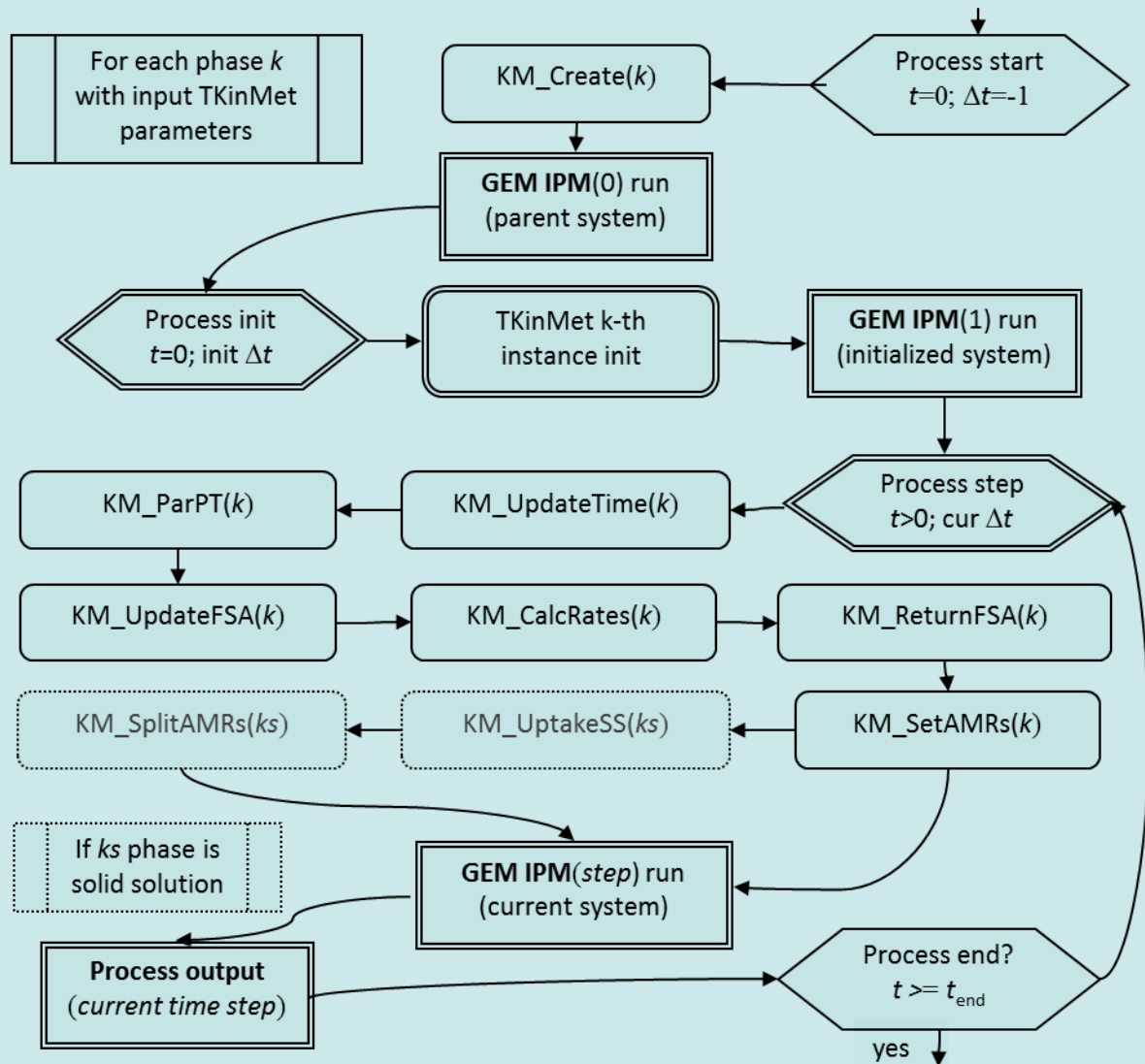
Define $x_{C,aq} = \frac{m_{C^{z+}}}{m_{B^{z+}} + m_{C^{z+}}}$

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

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

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

Flow chart of TKinMet use in simulations



Solid phase

$$\bar{n}_{k,t+\Delta t} = n_{k,t} + A_{k,t} R_{n,k,t} \Delta t$$

$$\text{if } \log_{10} \Omega_k > \varepsilon$$

$$\underline{n}_{k,t+\Delta t} = n_{k,t} - A_{k,t} R_{n,k,t} \Delta t$$

$$\text{if } \log_{10} \Omega_k < -\varepsilon$$

Solid solution

$$\underline{n}_{k,t+\Delta t} = n_{k,t} - A_{k,t} R_{k,t} \Delta t$$

$$\text{if } \log_{10} \Omega_k < -\varepsilon$$

$$\underline{n}_{j,t+\Delta t}^{(x)} = n_{j,t}^{(x)} + x_{j,t} (\underline{n}_{k,t+\Delta t} - n_{k,t})$$

Uptake in solid solution

$$\bar{n}_{Hc,t+\Delta t}^{(x)} = n_{Hc,t}^{(x)} + A_{k,t} R_{k,t} \Delta t \cdot x_{Hc,t}$$

$$\bar{n}_{Tr,t+\Delta t}^{(x)} = n_{Tr,t}^{(x)} + A_{k,t} R_{k,t} \Delta t \cdot x_{Tr,t}$$

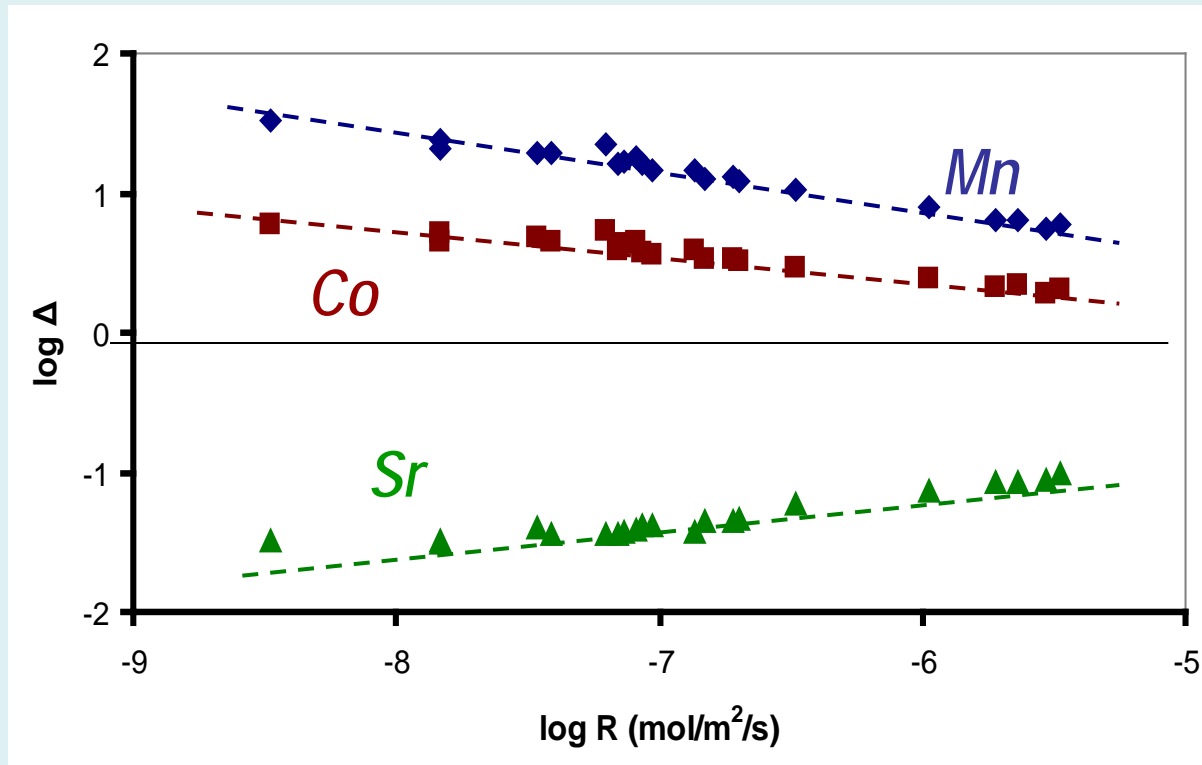
$$\text{where } x_{Tr,t} = \Delta_{TrHc,t} \frac{[Tr]_t}{[Hc]_t}$$

$$\text{and } x_{Hc,t} = 1 - x_{Tr,t}$$

Available in GEM-Selektor v.3.3 prototype (not yet fully documented)

Kinetics of Tr element uptake in calcite

Experimental facts



Data from Lorens, GCA 45, 1981

Equilibrium fractionation can be measured only at infinitely low R

Mn, Co, Cd: elements compatible with calcite structure

Sr, Ba, Ra: 'incompatible' elements

Opposite trends!

? Partial equilibrium concept for modeling uptake kinetics in Aq-SS systems needed

Unified Uptake Kinetics Model (UUKM)

Thien, Kulik and Curti (2013, *Appl. Geochem.* 2014), SKIN project

- Based on Growth Entrapment Model [Watson, GCA, 2004] and Surface Reaction Kinetic Model [DePaolo, GCA, 2011]
- Considers equilibria between aqueous phase, bulk solid solution, and surface adsorption, with the difference described by the enrichment factor F_{Tr}
- Increase of mineral growth rate R_L tends to produce a non-equilibrium sub-surface layer composition (by entrapment or burial of the surface adsorbed composition)
- Sub-surface diffusivity D_s (or gross backward dissolution rate) tends to restore the Aq-SS equilibrium sub-surface layer composition
- Competition between R_L and D_s defines the Tr (trace) content in the Hc (host mineral)

$$\Delta_{Tr,Hc} = \Delta_{Tr,Hc,eq} \frac{D_s + R_{L,k} ml}{D_s + \frac{R_{L,k} ml}{F_{Tr}}}$$

F_{Tr} = surface enrichment factor
 D_s = apparent sub-surface diffusivity coefficient
 ml = length at which sub-surface diffusivity occurs
 R_L = linear propagation rate of mineral surface

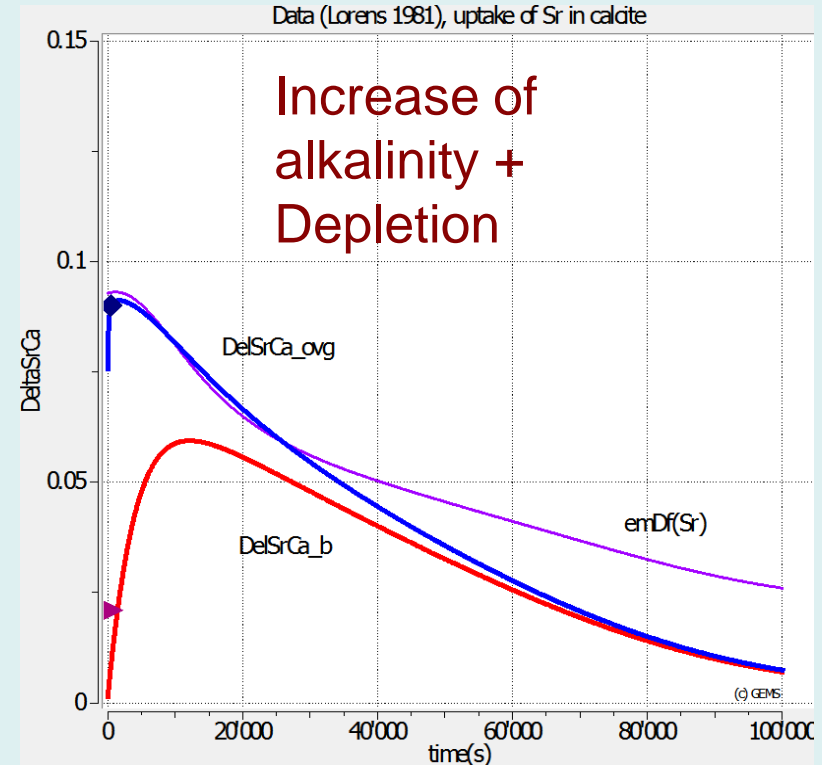
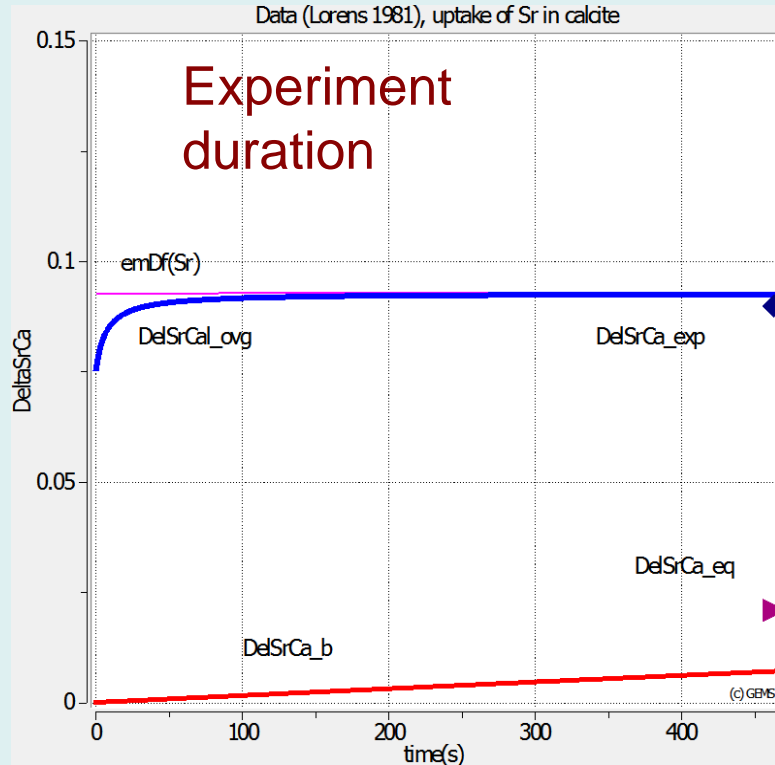
- $\Delta_{Tr,Hc}$ always varies between 2 limits: $\Delta_{Tr,Hc,eq}$ and $F_{Tr} \cdot \Delta_{Tr,Hc,eq}$

Simulations of Sr uptake in growing calcite

System: $\text{H}_2\text{O} + \text{air} + \text{CaCO}_3 + \text{SrCO}_3$

$P = 1 \text{ bar}, T = 25 \text{ }^\circ\text{C}$

Experiment: Lorens, GCA (1981)



Sr-calcite solid solution:

- ❖ Host end-member Cal CaCO_3
- ❖ Trace end-member SrCal SrCO_3
- Regular mixing $W_G = 4.4 \text{ kJ/mol}$
- $\Delta^{\text{eq}}_{\text{Sr}} = 0.021$

$A_{\text{S},0} = 0.8 \text{ m}^2/\text{g};$
'seed' $n_0 = 0.0092 \text{ g}$

Initial rate: $3 \cdot 10^{-6} \text{ mol/m}^2/\text{s}$

$F_{\text{Sr}} = 6.2$

$D_{\text{S}} = 0.02 \text{ nm}^2/\text{s}$

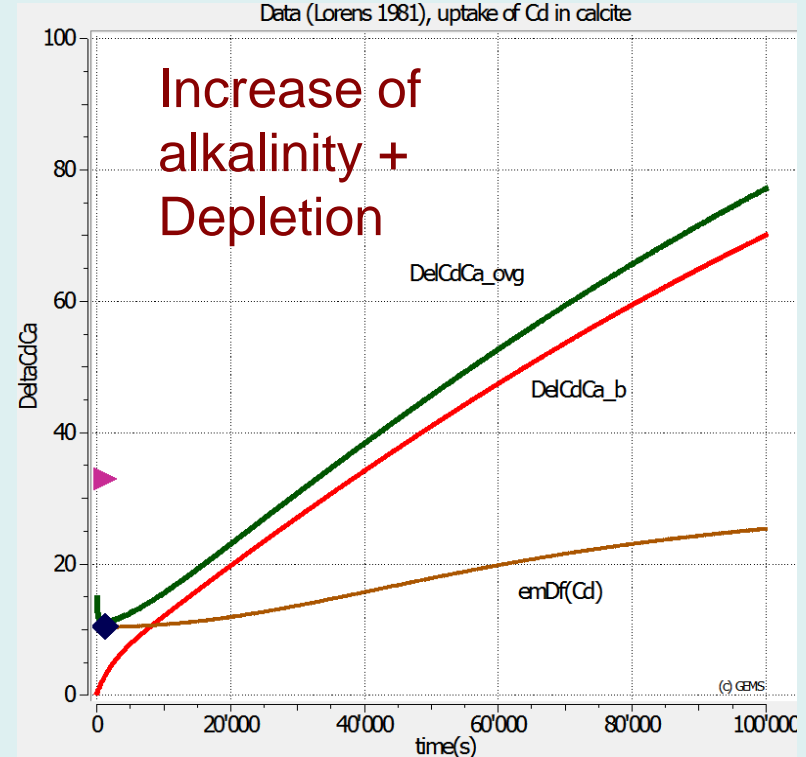
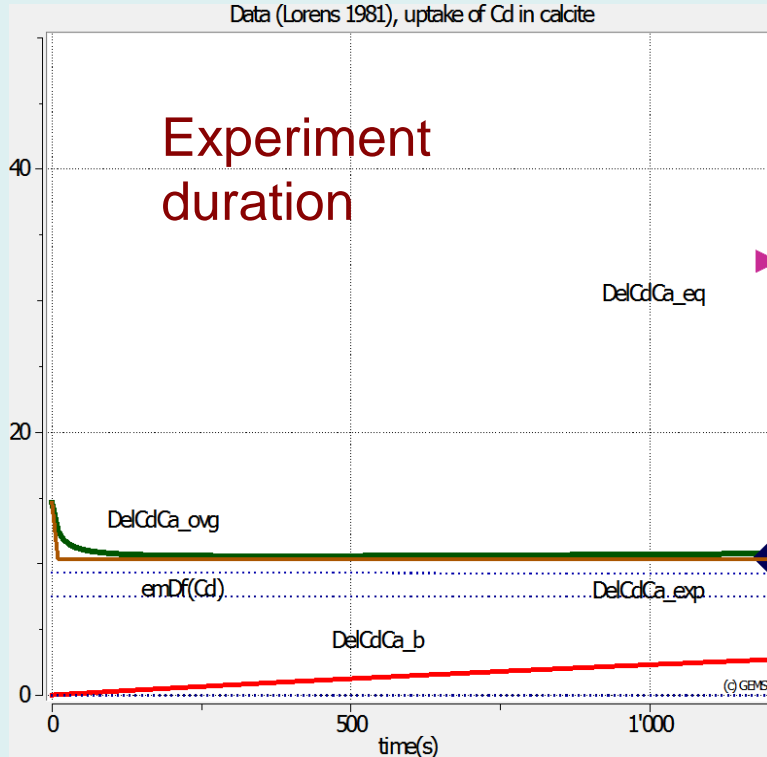
$m = 6; l = 0.5 \text{ nm}$

Seeded growth of $\text{Ca}(\text{OH})_2$ revisited

System: $\text{H}_2\text{O} + \text{air} + \text{CaCO}_3 + \text{CdCO}_3$

$P = 1 \text{ bar}, T = 25 \text{ C}$

Experiment: Lorens, GCA (1981)



Cd-calcite solid solution:

- ❖ Host end-member Cal CaCO_3
- ❖ Trace end-member Otavite CdCO_3
- Regular mixing $W_G = 2.98 \text{ kJ/mol}$
- $\Delta^{\text{eq}}_{\text{Cd}} = 33.0$

$A_{S,0} = 0.8 \text{ m}^2/\text{g};$

'seed' $n_0 = 0.0031 \text{ g}$

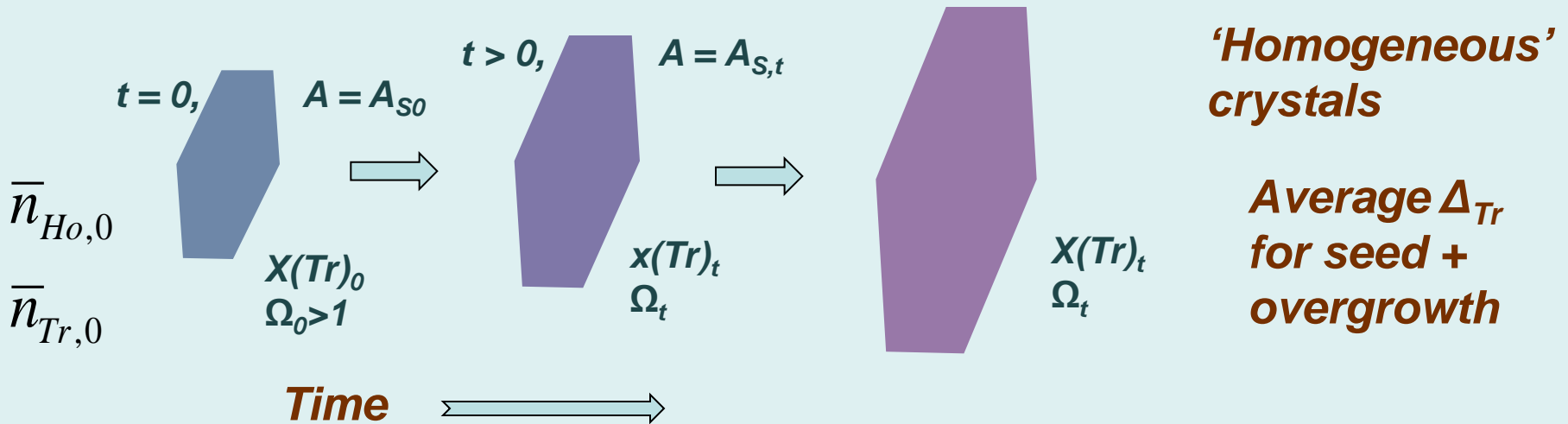
Initial rate: $4 \cdot 10^{-6} \text{ mol/m}^2/\text{s}$

$F_{\text{Sr}} = 0.3$

$D_S = 0.02 \text{ nm}^2/\text{s}$

$m = 6; l = 0.5 \text{ nm}$

Representation 1: One solid solution phase



SS phase 'Cal-Sr_cal':

Cal CaCO_3

SrCO₃-cal SrCO_3

$W_G \approx 4400 \text{ J/mol}$

Thermodynamic data:

Kulik et al., *Phys.Chem.Earth*, 2010

End-member amount constraints:

$$\bar{n}_{Ho,t+\Delta t} = n_{Ho,t} + f(A_t, r_H, t)$$

$$\bar{n}_{Tr,t+\Delta t} = n_{Tr,t} + f(r_H, r_U, t)$$

host rate

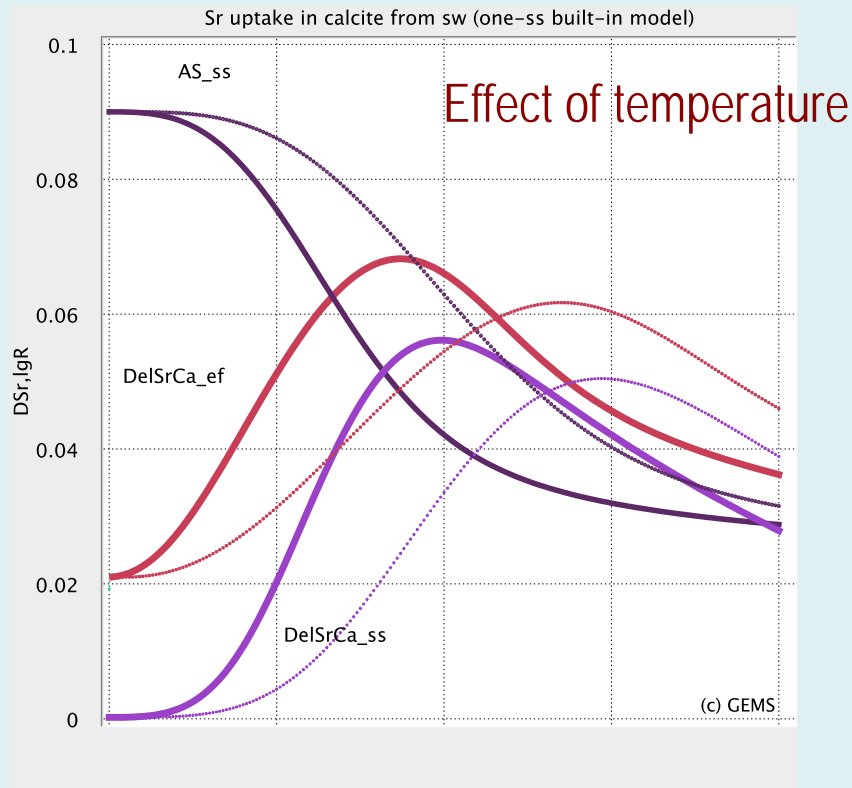
uptake rate

$A_{S,0} = 0.09 \text{ m}^2/\text{g};$

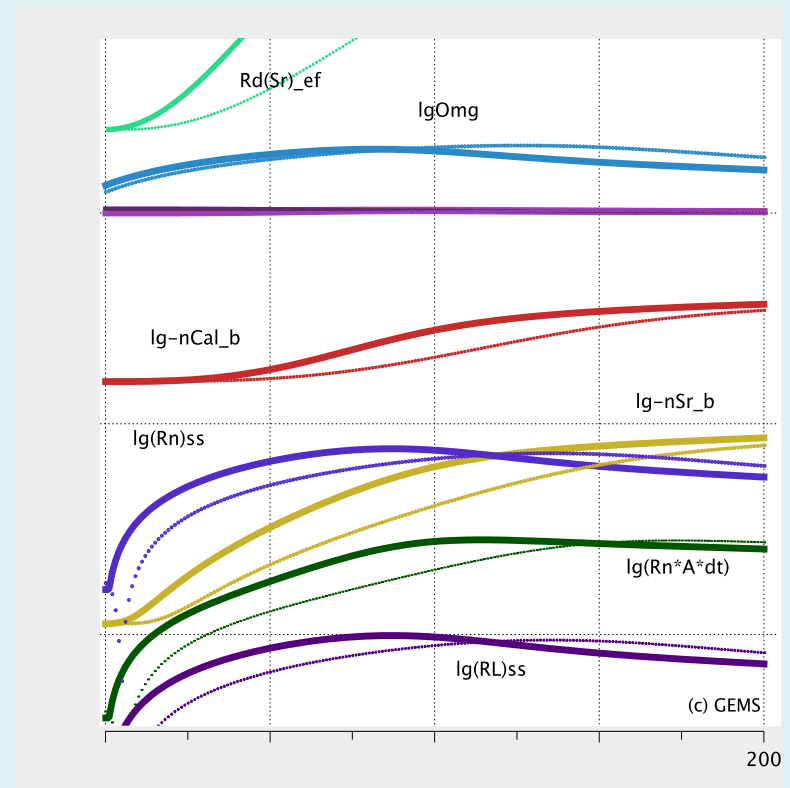
'seed' $n_0 = 0.0001 \text{ mol}$

Sr coprecipitation in calcite from seawater

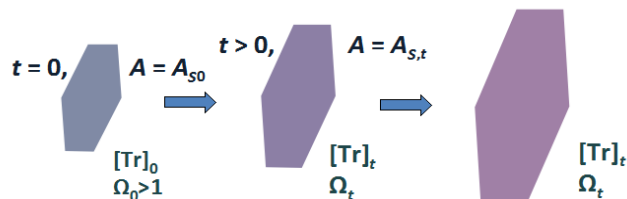
P=1 bar, T=25 C and 15 C (dotted curves)



Rate law: Wolthers ea (2012) for seawater



1: Aq + one solid solution phase



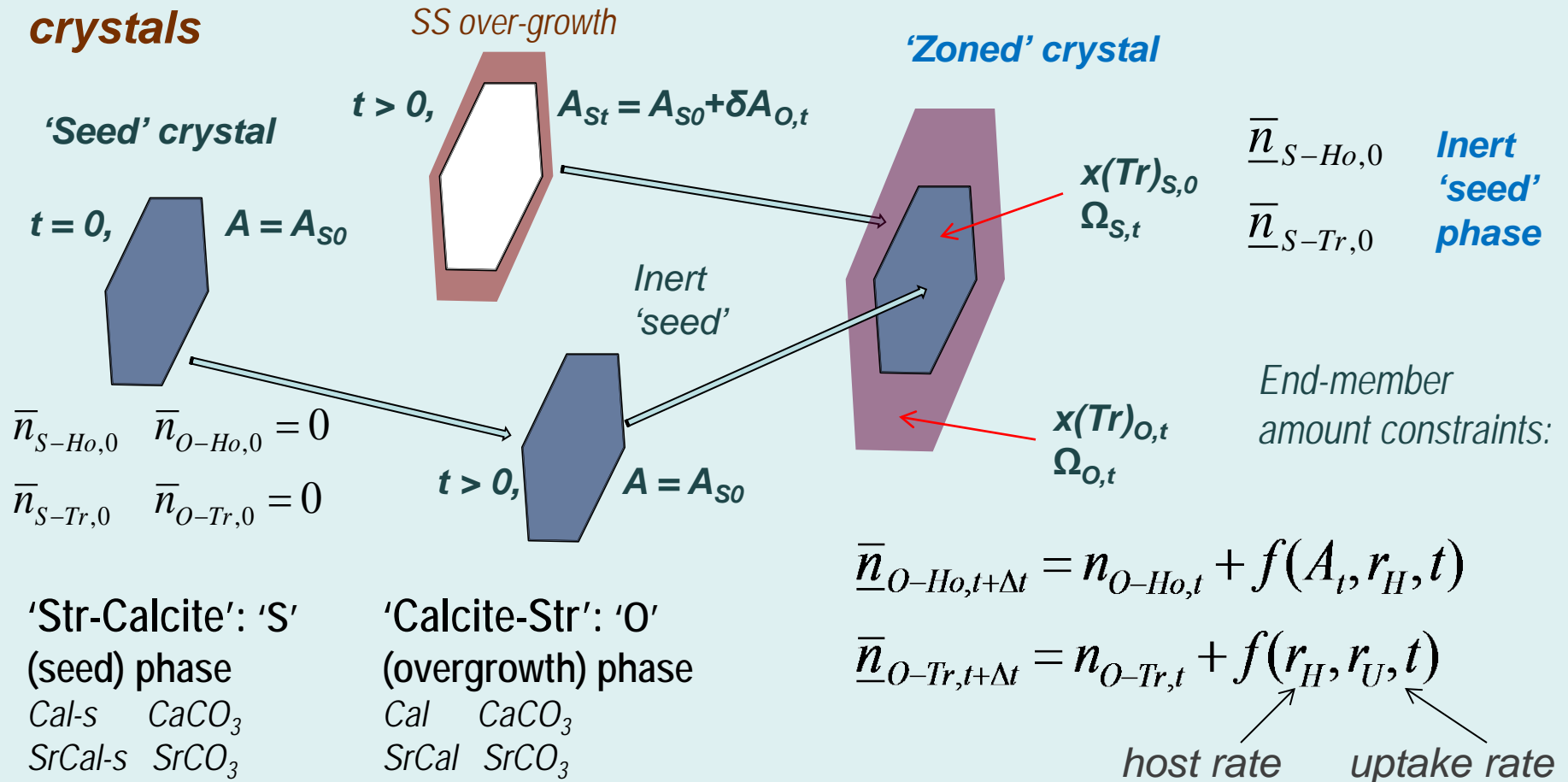
$A_{S,0} = 0.09 \text{ m}^2/\text{g}$; 'seed' AMRs at $n_0 = 0.0001 \text{ mol}$ (at trace Sr conc.)

Rate control: addition of 0.05 mmol/h Na_2CO_3 to 1 kg nsw

Representation 2 of the solid: two phases

'Heterogeneous' crystals

$x_{Tr} = \text{const}$ for 'seed'; Δ_{Tr} only for the overgrowth phase



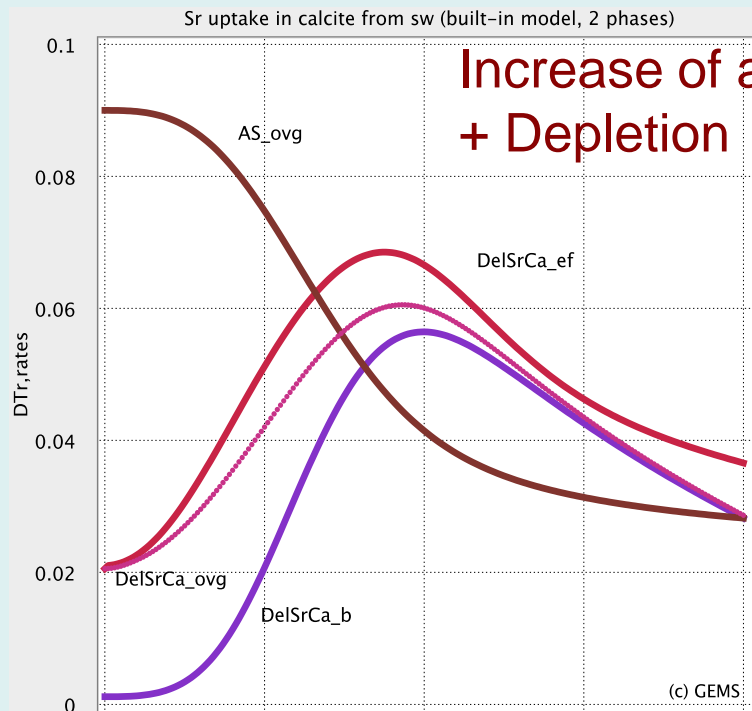
$A_{S,0} = 0.09 \text{ m}^2/\text{g};$
 $n_{S,0} = 0.0001 \text{ mol}$

$W_G = 4400 \text{ J/mol}$

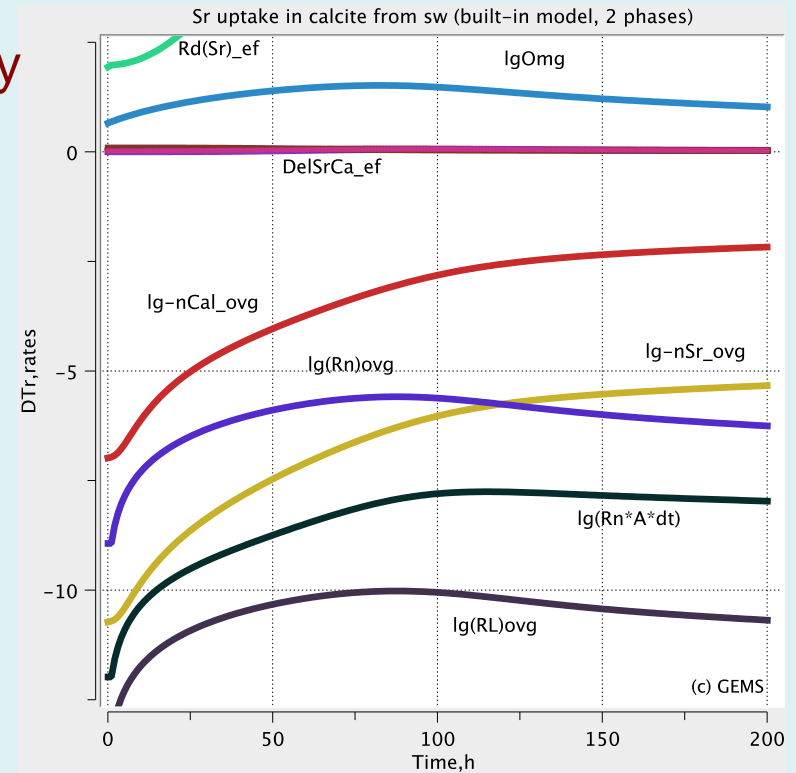
A_S linkage between phases; 'Metastability chain'

Sr in growing calcite: Two-ss-phase case

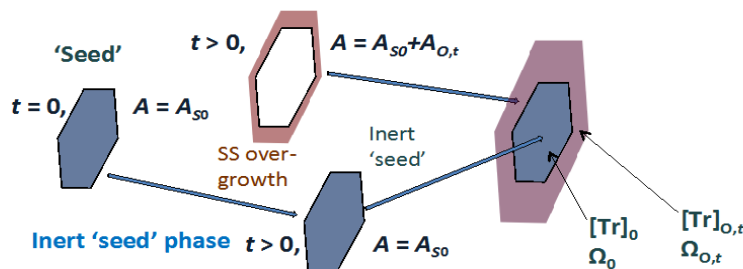
P=1 bar, T=25 C



"Ovg": the same Cal – Sr-cal SS phase



2: Aq + two solid solution phases



$A_{S,0} = 0.09 \text{ m}^2/\text{g}$; 'seed' :
Arg-Str SS (trace Sr) fixed by
AMR at $n_0 = 0.0001 \text{ mol}$

Rate control: addition of 0.05
mmol/h Na_2CO_3 to 1 kg nsw

Can now follow the
changes of the "ovg"
phase composition
separately from "seed"

Conclusions and outlook

- Mineral dissolution and precipitation with concurrent trace element adsorption and incorporation are chemical processes that deviate from “true” aqueous-mineral equilibrium
- We can model this beyond the “complete equilibrium” concept, invoking the principles of local and partial equilibrium
- Changes in amount and composition of an “overgrowth” phase (solid solution, “surface solution”, adsorbed layer solution) can be linked to the surface area or to volume of another, “substrate” phase, which can itself be stable or metastable
- Mineral reaction kinetic rate laws and uptake models for separate- or metastability-linked (layered) solution phases are implemented in the GEM-Selektor TKinMet code library, structured similar to the TSolMod library for models of mixing
- TKinMet and TSolMod libraries in the GEMS3K code will make the application of advanced reactive transport models of complex aqueous – solid solution systems possible in various repository safety scenarios
- Further development of TKinMet code library is foreseen in on-going and future projects

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!