Dynamique de précipitation de particules minérales en solution : approche théorique et modélisation

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Action soutenue par
ANR PNANO

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Soft Chemistry

Size tailoring of oxide nano-particles by precipitation in aqueous medium

J. P. Jolivet et al.

Hématite α-Fe$_2$O$_3$

TiO$_2$ rutile

Brookite TiO$_2$
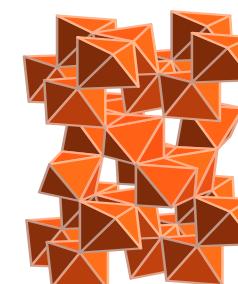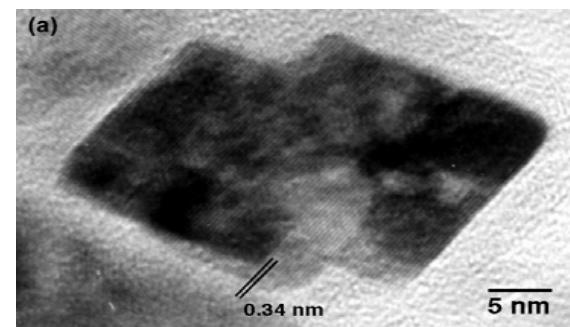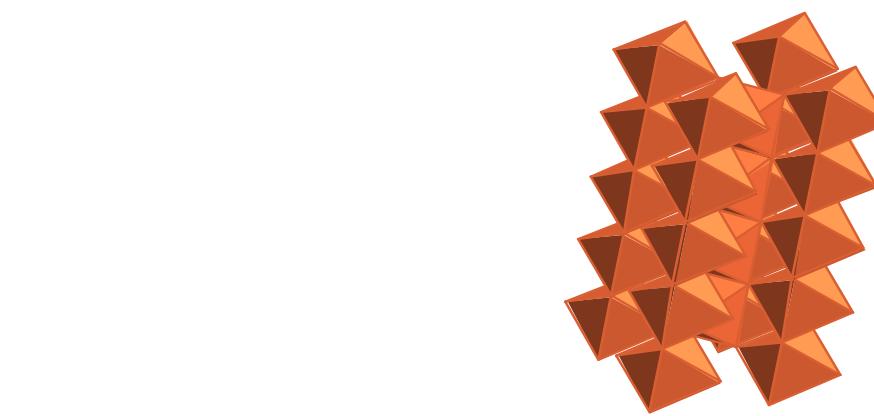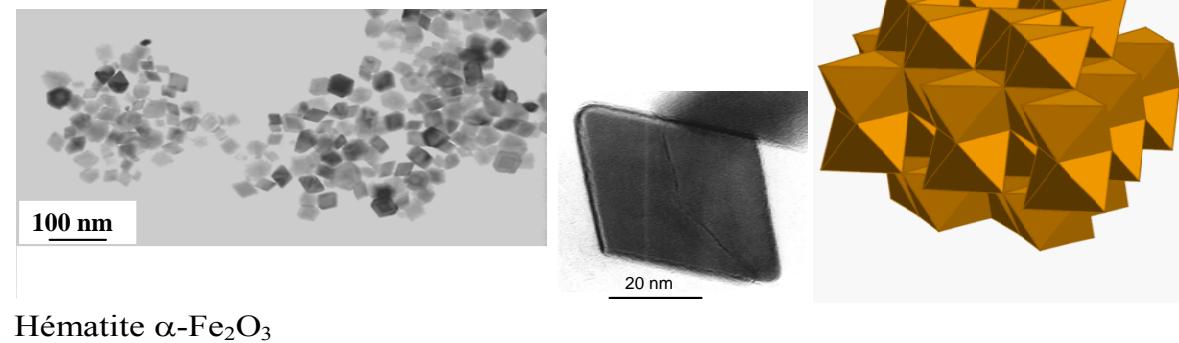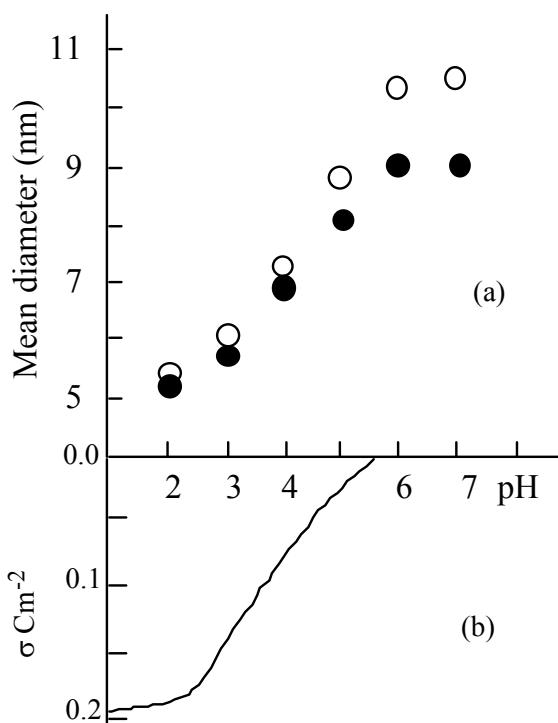
Geochimie:
Cycle de l'eau
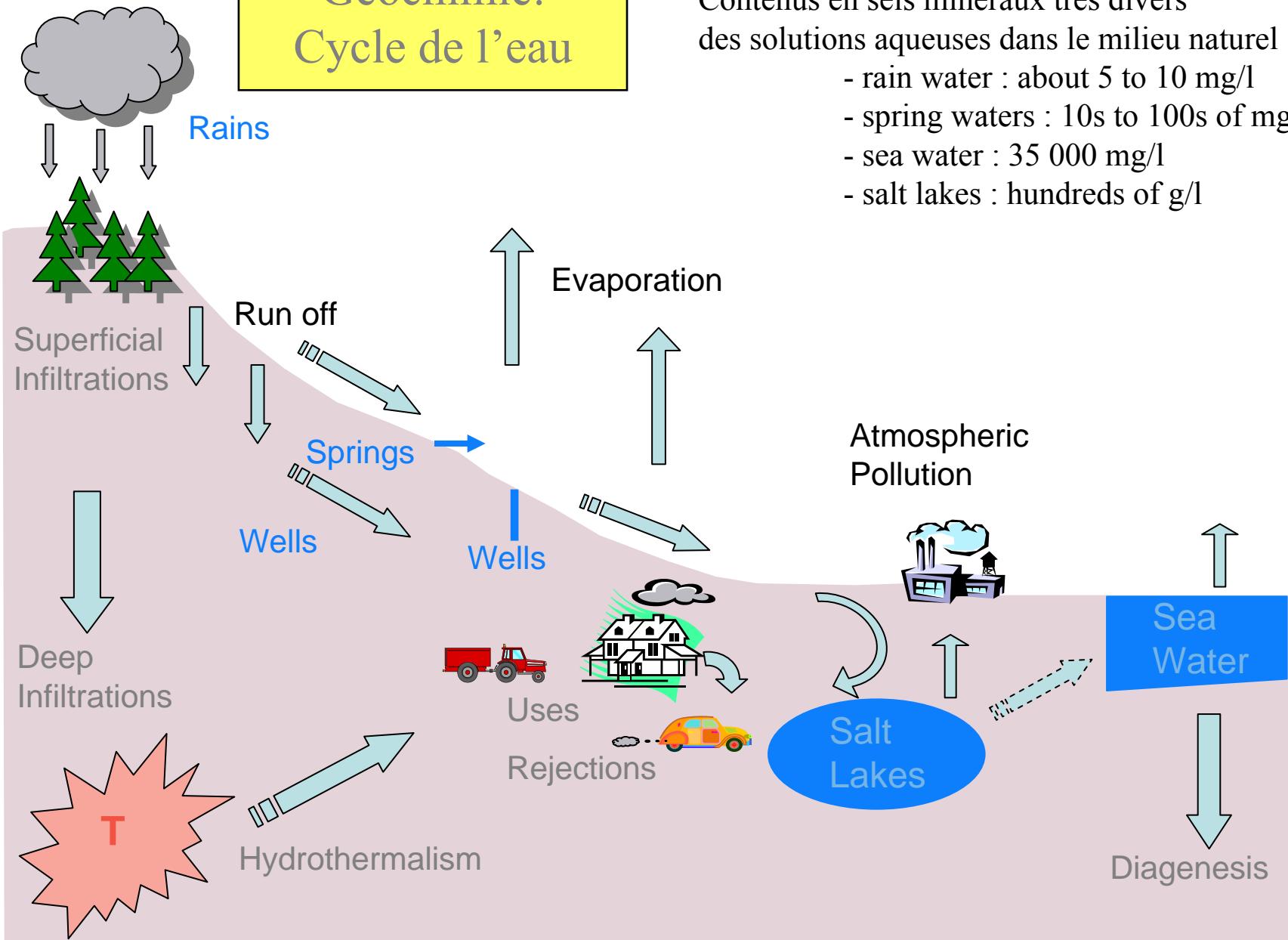
Contenus en sels minéraux très divers
des solutions aqueuses dans le milieu naturel
- rain water : about 5 to 10 mg/l
- spring waters : 10s to 100s of mg/l
- sea water : 35 000 mg/l
- salt lakes : hundreds of g/l

Rains

Evaporation

Run off

Superficial
Infiltrations

Springs

Wells

Wells

Atmospheric
Pollution

Deep
Infiltrations

Sea
Water

Uses

Rejections

Salt
Lakes

T

Hydrothermalism

Diagenesis

Water-rock interaction:
 - out-of-equilibrium contact between rocks and natural waters
 - dissolution of primary minerals; precipitation of secondary minerals
 - evolution of the solution composition
 - transport of the fluid

Among secondary phases: clays:
 - large surface/volume ratio
 - variability of composition
 - specific properties: swelling,
   hydration, ion exchange

illite

SiO_4 tetrahedra
(Si^{4+} replaced by Al^{3+}, Fe^{3+}…)

10 Å

Interfoliar cations

$Al(OH)_2O_4$ octahedra
(Al^{3+} replaced by Mg^{2+}, Fe^{2+}.

TYPE 2/1
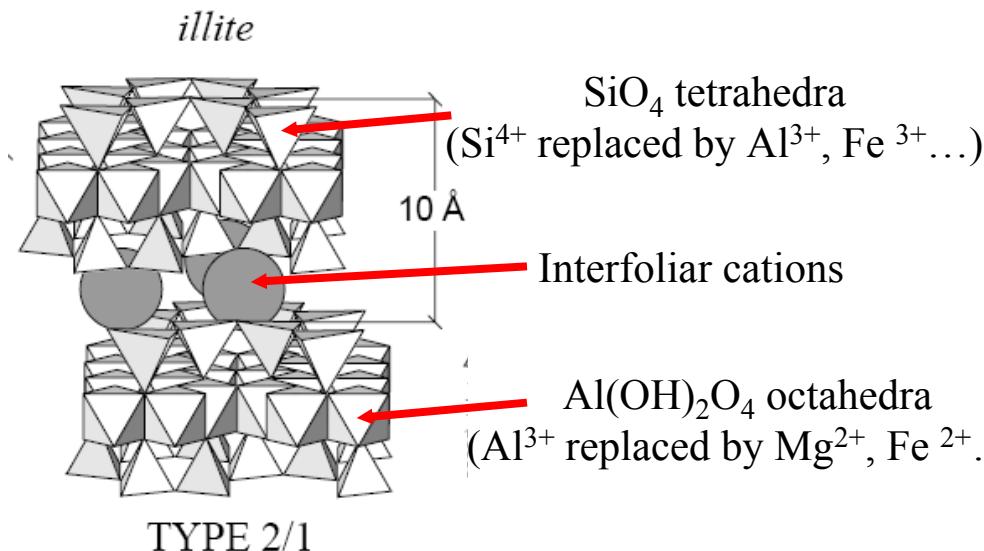
Geochemical codes
 - thermodynamic and kinetic codes for water-clay rock interactions
 - solid-solution models to account for the variability of composition
 - BUT no good account of finite size effects

Challenge: improve the description of the
first steps of nucleation and growth in solution

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I: Precipitation of minerals of fixed composition
- formalism
- similarity with other 1st order phase transitions
- some applications

II: Precipitation of minerals of variable composition
- formalism
- some applications

C. Noguera et al J. Cryst. Growth 297 (2006) 180
C. Noguera et al J. Cryst. Growth 297 (2006) 187
B. Fritz et al. GCA 73 (2009) 1340
B. Fritz and C. Noguera Rev. Mineralogy Geochemistry vol 70 (2009) 371

$$M \Leftrightarrow \sum_i \alpha_i E_i$$

Solubility product

$$K = \frac{\Pi_i [E_i]_{eq}^{\alpha_i}}{[M]_{eq}}$$

Ion activity product

$$Q = \frac{\Pi_i [E_i]^{\alpha_i}}{[M]}$$

Saturation state

$$I = \frac{Q}{K}$$

I <1
dissolution

Out-of equilibrium

I =1
Thermodynamic
equilibrium

I >1
precipitation

Out-of equilibrium

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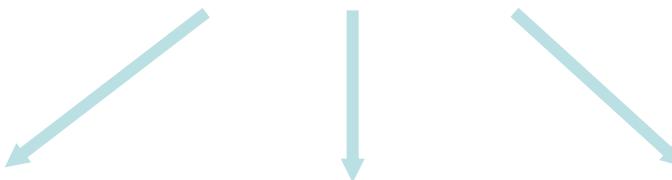
AS prepared in a closed system
or results from dissolution of
primary minerals
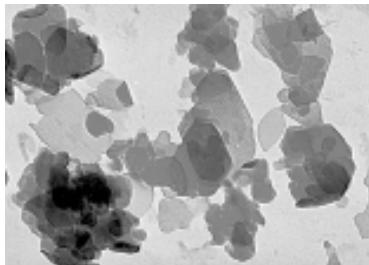
$I > 1$
Small nuclei
Large surface/volume ratio

$$\frac{4\pi\rho^2}{4\pi\rho^3/3} = \frac{3}{\rho}$$

Accretion of growth units:
Statistical approach
or classical nucleation theory

Classical nucleation theory

Gibb's energy variation to form a nucleus of radius ρ

$$\Delta G = -nk_B T \ln I + 4\pi\rho^2\sigma$$

Competition between
surface and volume terms

Bulk term
negative if I >1

Surface term
always positive

$$nv = \frac{4}{3}\pi\rho^3$$ n = number of growth units = « size » of the nucleus

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Equilibrium shapes: from the knowledge of surface energies and adhesion energies, one can reconstruct the crystal habit (Wulff and Wulff-Kaishev theorems)

$\dfrac{h_i}{\sigma_i}$ is constant

σ_i

h_i

σ_{bas}-W_{adh}

010

010

001

100

010

100

101

001
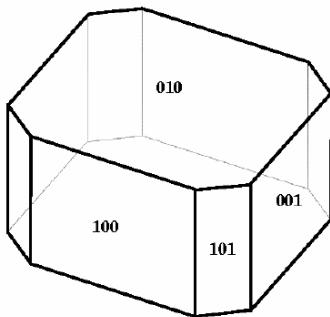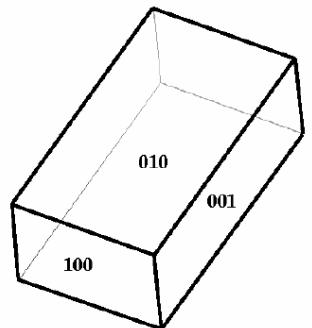
Boehmite in vacuum and in water

(H. Toulhoat et al.)

Hypothesis that 3D growth shape is identical to 3D equilibrium shape

l

e

l

l

e

$$\frac{e}{l} = \frac{\sigma_{bas} - W_{adh}/2}{\sigma_{lat}}$$

2D limit:
e = cst (→0)
σ_{bas}=W_{adh}/2

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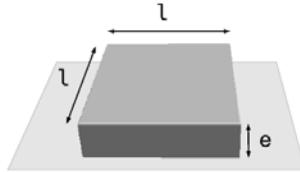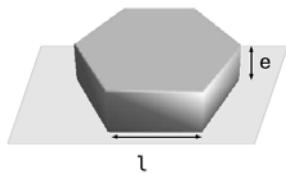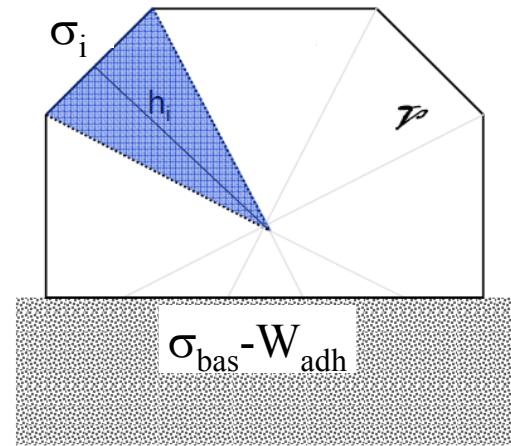
$$\Delta G = -n k_B T \ln I + 4\pi\rho^2\sigma$$
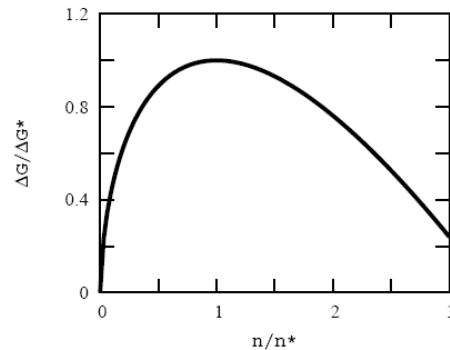
The maximum of ΔG defines
the size of critical nucleus n*
and the nucleation barrier ΔG*

$$\Delta G^* = \frac{1}{3} 4\pi\rho^{*2}\sigma \qquad\qquad n^* = \frac{32\pi\sigma^3 v^2}{3(k_B T \ln I)^3}$$

Stationary nucleation rate $\boxed{F = F_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right)}$

$$F_0 = \omega c Z$$
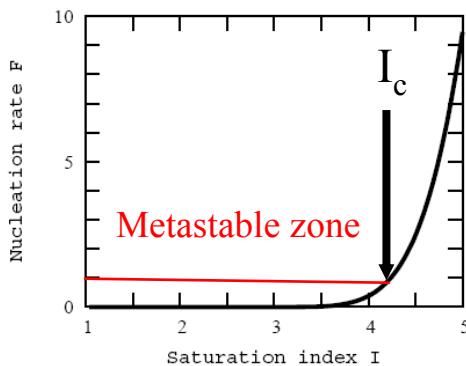
Z = Zeldovich factor
Related to the curvature of $\Delta G = f(\rho)$
(cf transition state theory)

$1 < I < I_c$: nucleation is thermodynamically allowed
but nucleation rate is exponentially small
At I_c, F=1
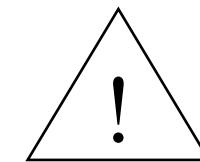
F_0 = highly unknown quantity
No data bank for σ for most minerals

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Growth mechanisms:

3D growth
on rough surface

2D nucleation
On flat face
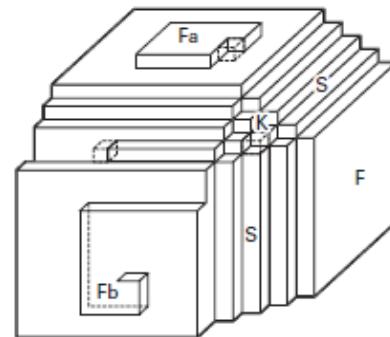
Spiral growth
On flat face
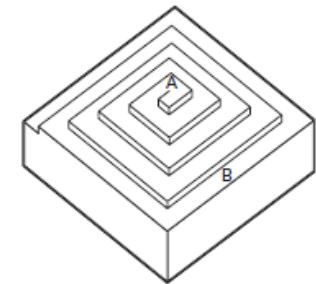
limited by diffusion in AS
or
limited by interface reaction

I

nucleation

3D
growth

2D
growth

Spiral growth

10 t
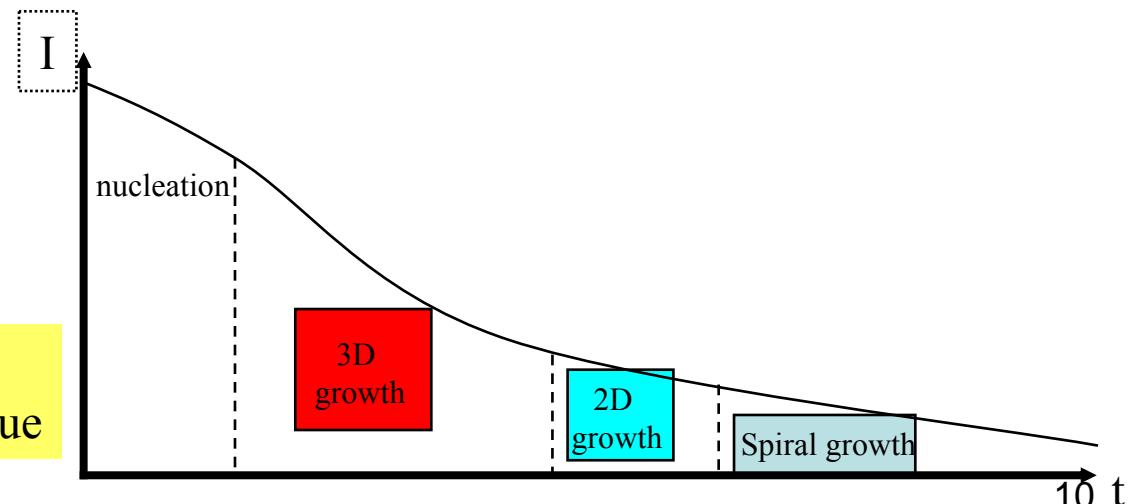
General scenario
as a function of saturation index value

3D growth on rough surfaces may be limited by:

 • Diffusion of ions in the AS

$$\frac{d\rho}{dt} = \frac{\kappa}{\rho}(I-1)$$ Results from the existence of a concentration gradient

 • Interface reactions

$$\frac{d\rho}{dt} = \kappa(I-1)$$

Size independent law is valid for large particles

$I > 1 \quad d\rho / dt > 0$
$I < 1 \quad d\rho / dt < 0$

For small particles, growth rate depends on size

ΔG Figure 1

ΔG^*

$$\frac{d\rho}{dt} = \kappa(I - \exp(\frac{2\sigma v}{k_B T\rho}))$$

$$I = \exp(\frac{2\sigma v}{k_B T\rho^*})$$

resorption

$$\frac{d\rho}{dt} < 0$$

ρ^*

ρ
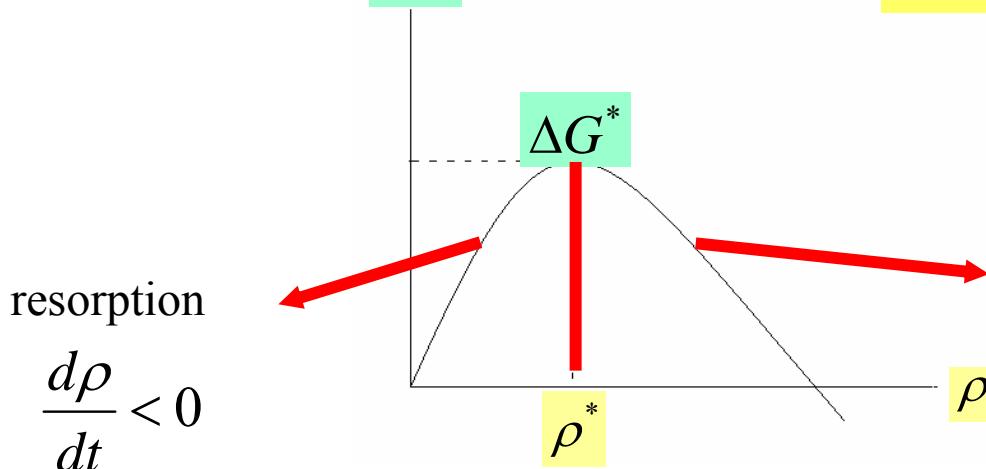
(positive) growth

$$\frac{d\rho}{dt} > 0$$

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Growth

Ostwald ripening
(Coarsening)

$$\rho < \frac{2\sigma v}{k_B T \ln I} = \rho^*(I)$$

$$\rho > \frac{2\sigma v}{k_B T \ln I} = \rho^*(I)$$

$$\frac{d\rho}{dt} < 0$$

$$\frac{d\rho}{dt} > 0$$

Small nuclei dissolve

Large nuclei grow
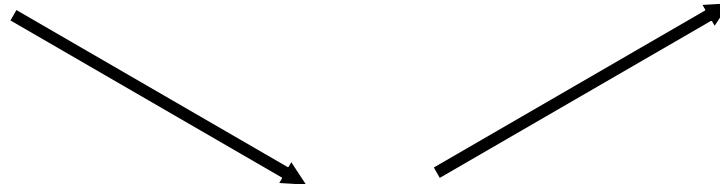
SOLUTION

Indirect transfer of matter from small to large nuclei through solution

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Especially important in CLOSED systems

Overall model   Analysis in terms of population of particles

t=0   t

Nucleation of new particles (if F≠0)

Size of particles: Size evolution of all particles nucleated at times $t_1 < t$

$$n(t_1, t) = \frac{32\, \pi\sigma^3 v^2}{3(k_B T\, \ln\, I(t_1))^3} + \int_{t_1}^{t} \frac{4\,\pi\kappa}{v}\, n(t_1, t')^{2/3}\, (I(t') - \exp\left(\frac{2\,\sigma v}{k_B T\, \rho(t_1, t')}\right))\, dt'$$

nucleation   (algebraic) growth

Nucleation rate:

$$\frac{dN_g(t_1)}{dt} = F_0 \exp(-\frac{16\pi\sigma^3 v^2}{3(k_B T)^3 \ln^2 I(t_1)})$$

Numerical resolution of these highly non-linear equations

Total amount of precipitate:

$$Q(t) = \frac{1}{N_{Avog}} \int_0^t \frac{dN_g(t_1)}{dt} (n(t_1, t) - 1) dt_1$$

Feed-back effect on the solution (closed system)

Reactant minerals   Aqueous solution   Secondary minerals

« infinite » size
Can only dissolve   Closed system
$d\rho/dt = \kappa f(I)$ Speciation model   Nucleation
                                              growth

I(t) or I(x,t)
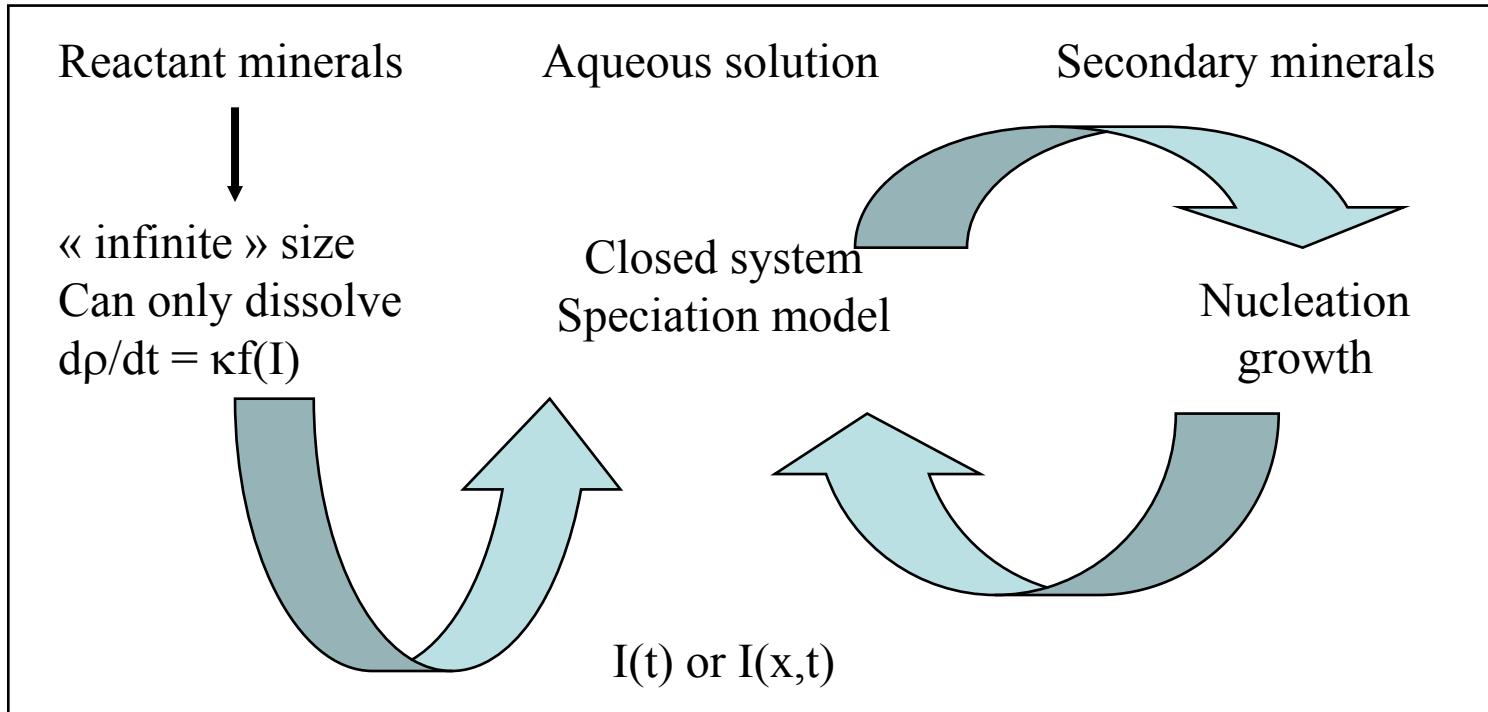
Potentialities:

       - homogeneous or heterogeneous nucleation

       - two growth modes

       - various particle shapes (growth shape assumed equivalent to equilibrium shapes)

At each time we know:

       - saturation of AS with respect to primary minerals

       - activity of all ions in solution

       - particle population for each secondary mineral (time of nucleation, size, composition)

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Precipitation in an aqueous solution

I=Q/K saturation state of the aqueous solution

$$\Delta G = -n k_B T \ln I + 4\pi\rho^2\sigma$$

Saturation state of a solution in equilibrium
with a particle of radius ρ

$$I_{\text{eff}} = \exp\left(\frac{2\sigma v}{k_B T \rho}\right) = \frac{K(\rho)}{K}$$

A small object is more
soluble than a big one

Condensation of droplets in the vapor phase

$\Pi = P/P_0$ excess of pressure wrt gaz-liquid transition pressure P_0

$$\Delta G = -N k_B T \ln \Pi + 4\pi N_g \sigma \rho^2$$

Pressure Π_{eff} with which a particle of radius ρ is in equilibrium

$$\Pi_{\text{eff}} = \exp\left(\frac{2\sigma v}{k_B T \rho}\right) = \frac{P(\rho)}{P_0}$$

P(ρ) Laplace pressure
in a droplet

Cristallization of particles from a melt

Saturation Index

Particle size
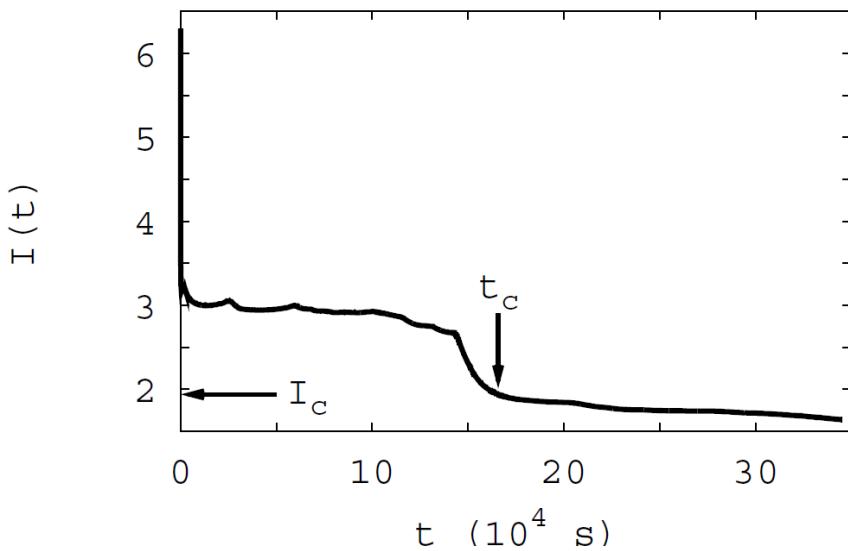
Precipitation of a single mineral
(eg SiO2 from an AS saturated with H_4SiO_4)
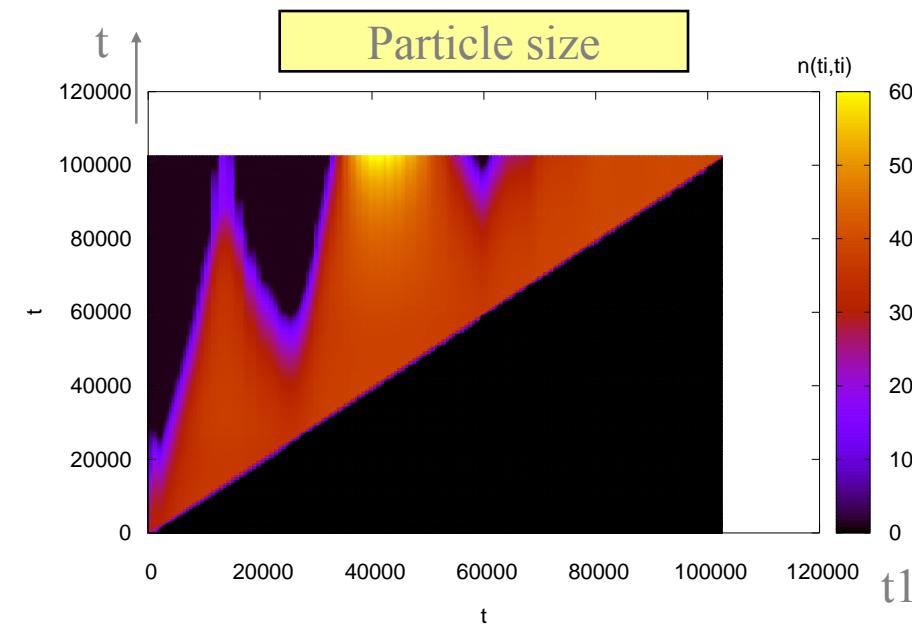
Full description of particle population
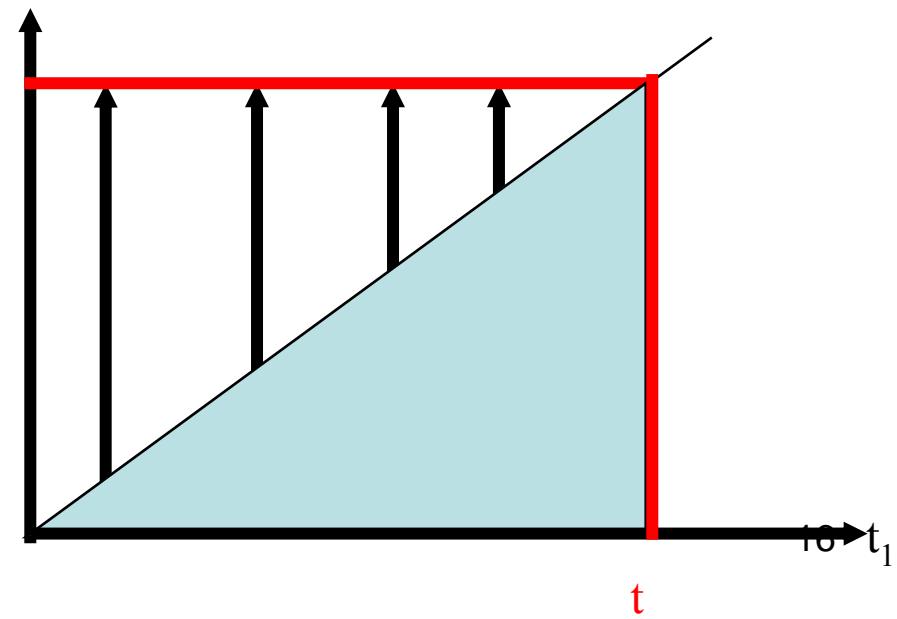
# Kaolinite precipitation as a function of initial conditions
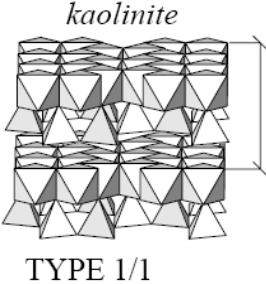
Two scenarios of precipitation

kaolinite

$Al_2Si_2O_5(OH)_4$

TYPE 1/1

From a supersaturated solution
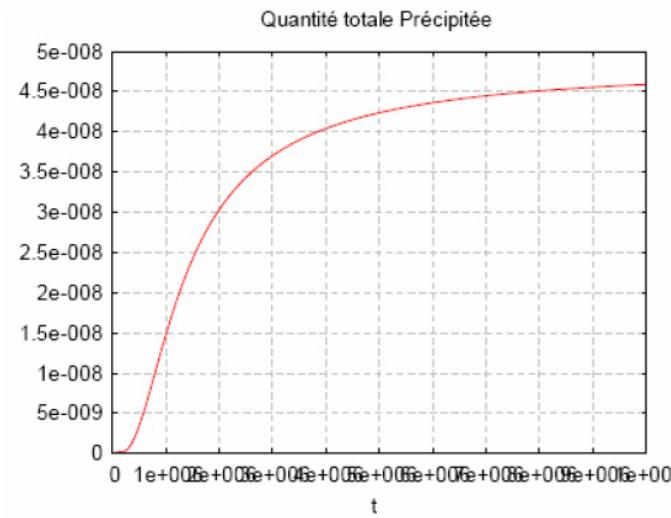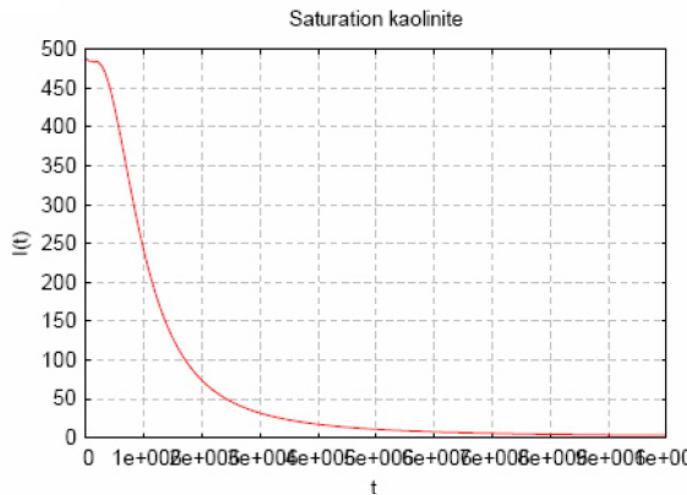
Via dissolution of granite

Saturation kaolinite

Saturation kaolinite

Quantité totale Précipitée

Quantité totale Précipitée
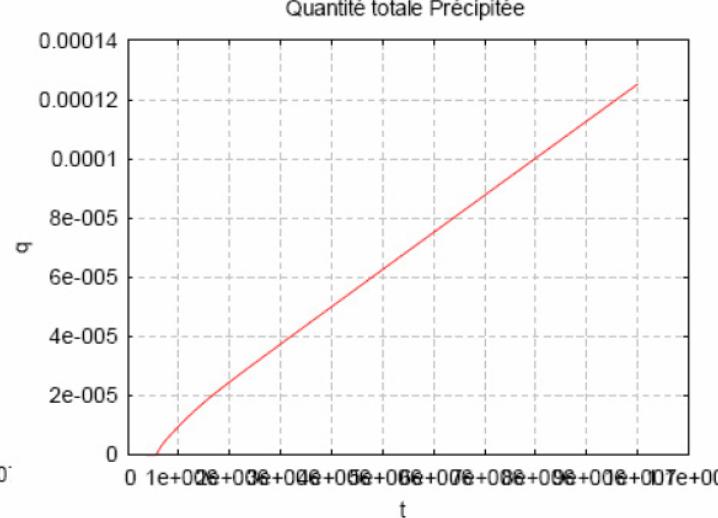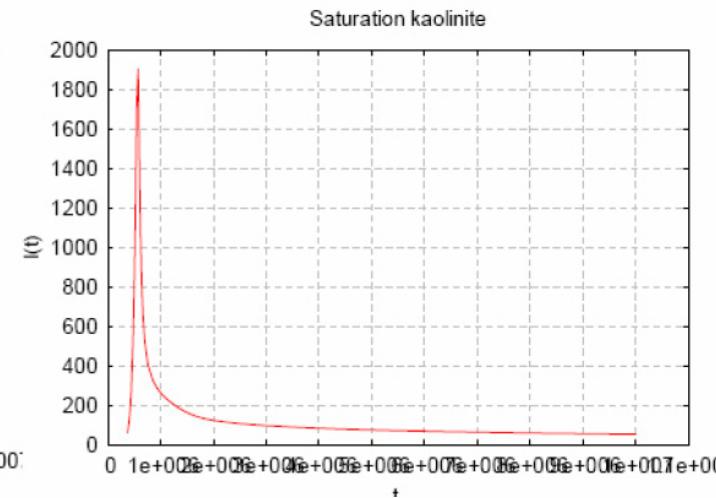
Mineral	Reaction			mol/kg of H_2O
Quartz	$SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$		Al	1×10^{-7}
Microcline	$KAlSi_3O_8 + 8H_2O \rightleftharpoons 3H_4SiO_4 + Al(OH)_4^- + K^+$		K	
Low albite	$NaAlSi_3O_8 + 8H_2O \rightleftharpoons 3H_4SiO_4 + Al(OH)_4^- + Na^+$		Na	1×10^{-6}
Muscovite	$Si_3Al_3O_{10}(OH)_2K + 12H_2O \rightleftharpoons 3H_4SiO_4 + 3Al(OH)_4^- + K^+ + 2H^+$		Ca	
Anorthite	$CaAl_2Si_2O_8 + 8H_2O \rightleftharpoons 2H_4SiO_4 + 2Al(OH)_4^- + Ca^{2+}$		Mg	
			Si	1.5×10^{-4}
			Cl	1×10^{-6}
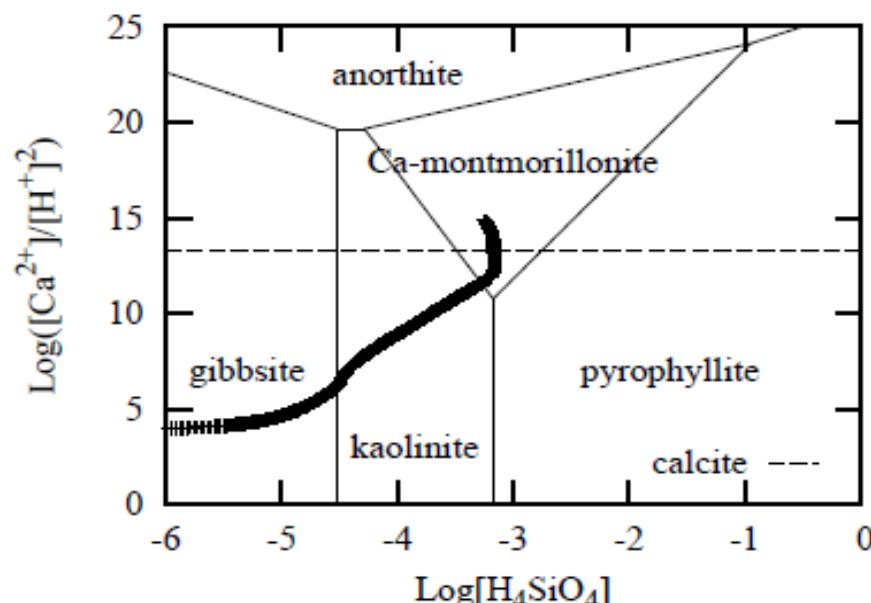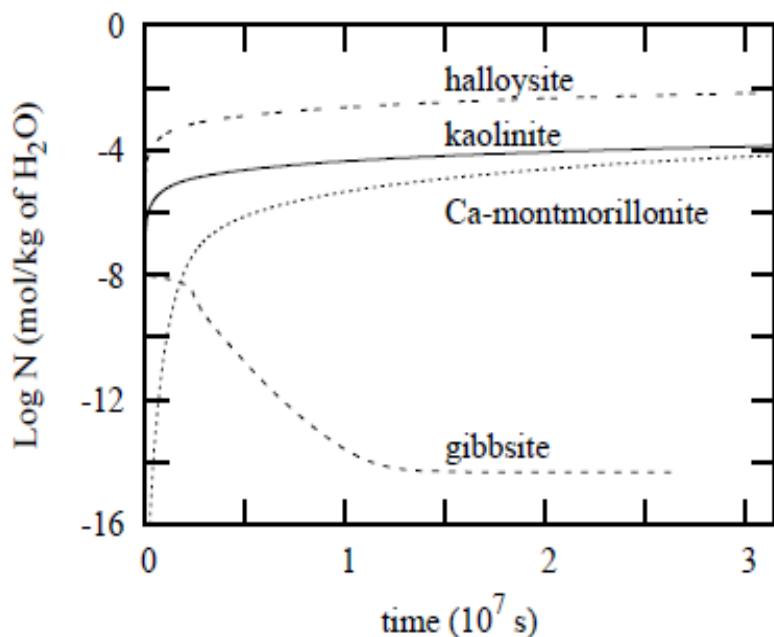
$(3 \times 10^7 \text{ s} \sim 1 \text{ year})$

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I: Precipitation of minerals of fixed composition
   - formalism
   - similarity with other 1st order phase transitions
   - some applications

II: Precipitation of minerals of variable composition
   - formalism
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C. Noguera et al Chem Geol. 269 (2010) 89
B. Fritz and C. Noguera Rev. Mineralogy Geochemistry vol 70 (2009) 371

Solid solution approach
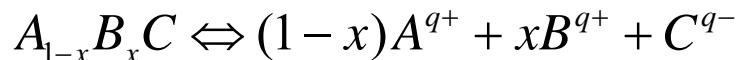
$$A_{1-x}B_x C \Leftrightarrow (1-x)A^{q+} + xB^{q+} + C^{q-}$$

AC end-member (x=0)

$$AC \Leftrightarrow A^{q+} + C^{q-}$$

$$K_{AC} = \exp\left(-\frac{\Delta G_{AC}}{k_B T}\right)$$

BC end-member (x=1)

$$BC \Leftrightarrow B^{q+} + C^{q-}$$

$$K_{BC} = \exp\left(-\frac{\Delta G_{BC}}{k_B T}\right)$$

Change in Gibbs free energy for
the formation of the compound

$$\Delta G(x) = (1-x)\Delta G_{AC} + x\Delta G_{BC}$$ Mechanical mixture

$$+ \boxed{Ax(1-x)} + ...$$ Mixing enthalpy (zero if ideal SS)

$$\boxed{-k_B T\big(x \ln x + (1-x)\ln(1-x)\big)}$$ Mixing entropy

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Ideal solid solution

Change in Gibbs free energy for
the formation of the compound

$$\Delta G(x) = (1-x)\Delta G_{AC} + x\Delta G_{BC} \quad - k_B T\left(x\ln x + (1-x)\ln(1-x)\right)$$

Solubility product of the SS

$$K_{AC} = \exp\left(-\frac{\Delta G_{AC}}{k_B T}\right)$$

$$K_{BC} = \exp\left(-\frac{\Delta G_{BC}}{k_B T}\right)$$

$$K(x) = \exp\left(-\frac{\Delta G(x)}{k_B T}\right) = K_{AC}^{1-x} K_{BC}^{x} x^{x}(1-x)^{1-x}$$

Saturation state of the AS wrt SS

$$I(x) = \left(\frac{I_{AC}}{1-x}\right)^{1-x}\left(\frac{I_{BC}}{x}\right)^{x}$$

Roozeboom plot: $x_0 = f(X_{aq})$
$X_{aq} = [B]/\,[A]+[B] = I_{BC}K_{BC}/I_{AC}K_{AC}$

Thermodynamic equilibrium:
(dI/dx=0 and I(x)=1)
$I_{BC} = x_0$ and $I_{AC} = 1 - x_0$
$I(x_0) = I_{AC} + I_{BC} = 1$

(Ba,Sr)CO3 Roosenbloom diagram

$x_0 = 0.85$

$X_{aq} = 0.5$

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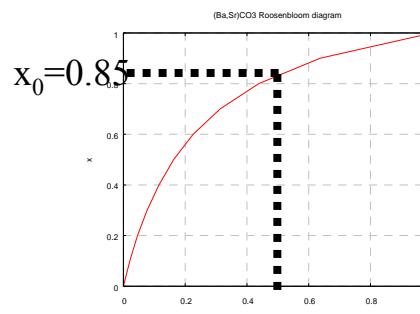
Gibb's energy to form a nucleus of radius ρ and composition x

$$\Delta G(\rho, x) = -nk_BT \ln I(x) + 4\pi\rho^2\sigma(x)$$

$$n \ln I(x) = n_{AC} \ln\left(\frac{I_{AC}}{1-x}\right) + n_{BC} \ln\left(\frac{I_{BC}}{x}\right)$$

$\downarrow$ $\qquad$ $\downarrow$

(1-x) n $\qquad$ x n

$!$

NB: if s function of x,
excess quantities at the surface
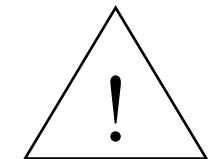
The critical nucleus is at a
saddle point of $\Delta G(\rho,x)$:
maximum wrt ρ
minimum wrt x

$v(x) = (1-x) \; v_{AC} + x \; v_{BC}$

$$nv(x) = \frac{4}{3}\pi\rho^3$$

Composition of the critical nucleus:

$$\left(\frac{I_{BC}}{x^*}\right)^{v_{AC}} = \left(\frac{I_{AC}}{1-x^*}\right)^{v_{BC}}$$

Usually $x^* \neq x_0$

Size of critical nucleus:

$$\rho^*(x) = \frac{2\sigma(x)v(x)}{k_BT \ln I(x)}$$

Nucleation barrier and rate

$$\frac{\Delta G(x)^*}{k_BT} = \frac{u(x)}{\ln^2 I(x)}$$

$$F = F_0 \exp\left(\frac{-\Delta G^*}{k_BT}\right)$$

Composition x of the deposited layers
Flux conservation of ions at the particle surface
Local equilibrium at the particle-solution interface

$$\ln\left(\frac{[C^{-q}]_i}{[C^{-q}]}\right) = \frac{2\sigma(x)v(x)}{k_BT}\left(\frac{1}{\rho} - \frac{1}{\rho^*}\right)$$

$$[A^{+q}]_i = [A^{+q}] \quad ; \quad [B^{+q}]_i = [B^{+q}]$$

$$v_{AC}\ln\frac{x^*}{x} - v_{BC}\ln\frac{1-x^*}{1-x} = (v_{BC} - v_{AC})\left(\frac{2\sigma(x)v(x)}{k_BT\rho} - \ln I(x,t)\right)$$

x depends on time
and on the particle radius
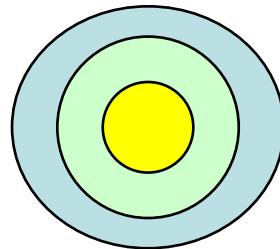
this generates composition profiles
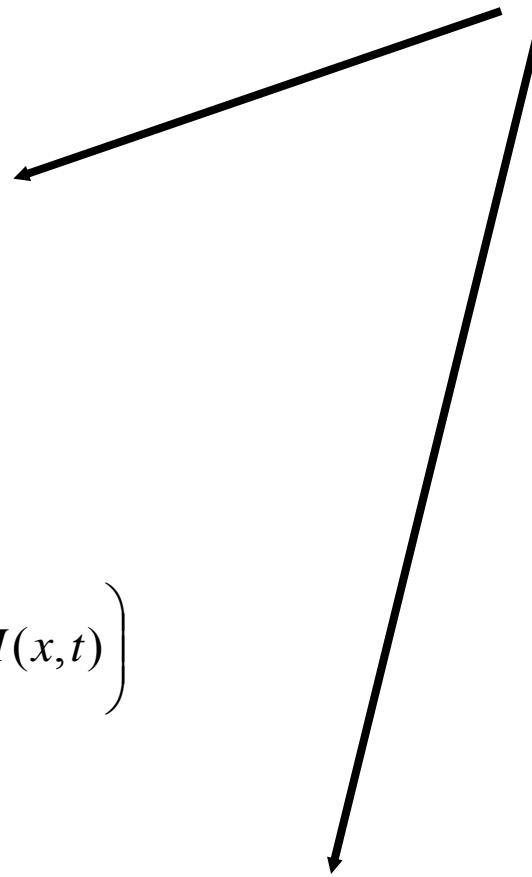
Size variation of the particles

$$\frac{d\rho(t_1,t)}{dt} = \kappa\left(I(t,x(\tau)) - \exp\frac{2\sigma(x(\tau))v(x(\tau))}{k_BT\rho(t_1,t)}\right)$$

accounts for Ostwald ripening

Feed-back effect on the aqueous solution (closed system)

Initial conditions:
composition of AS
(speciation model)

At time t:
$I(t,x)$

Nucleation of new particles:
their size $\rho^*(t)$
their composition $x^*(t)$

Growth of supercritical particles
nucleated at $t_1 < t$
composition of deposited layer $x(t_1,t)$
function of I and size
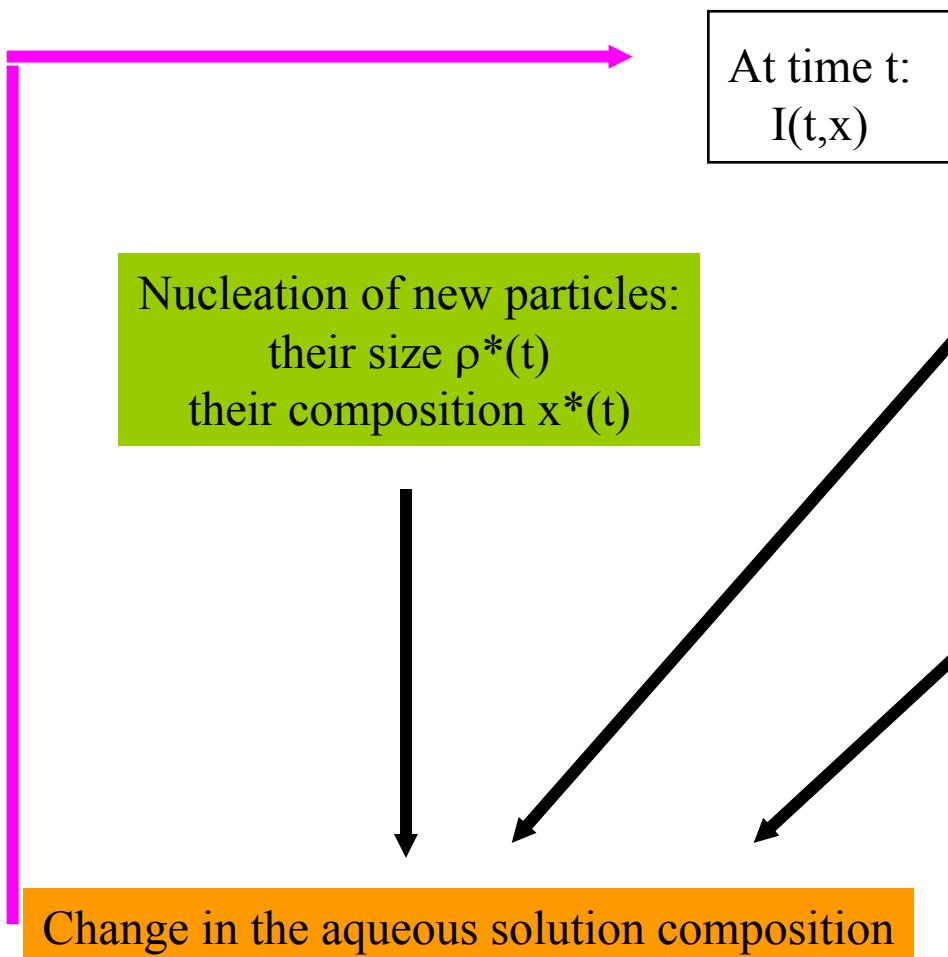
or

Resorption of older subcritical particles:
nucleated at $t1 < t$
Composition of removed layer $x(t_1,\tau)$

Change in the aqueous solution composition

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| x=0 witherite | Ba$_{1-x}$Sr$_x$CO$_3$ | x=1 strontiannite | | x=0 barite | Ba$_{1-x}$Sr$_x$SO$_4$ | x=1 celestite |

$K_{BaCO3} \sim K_{SrCO3}$

$\sigma_{BaCO3} \sim \sigma_{SrCO3}$

Variations of x* on a Roozeboom plot

$K_{BaSO4} \ll K_{SrSO4}$

$\sigma_{BaSO4} \gg \sigma_{SrSO4}$
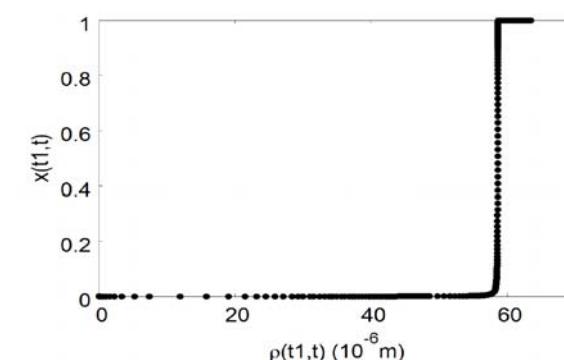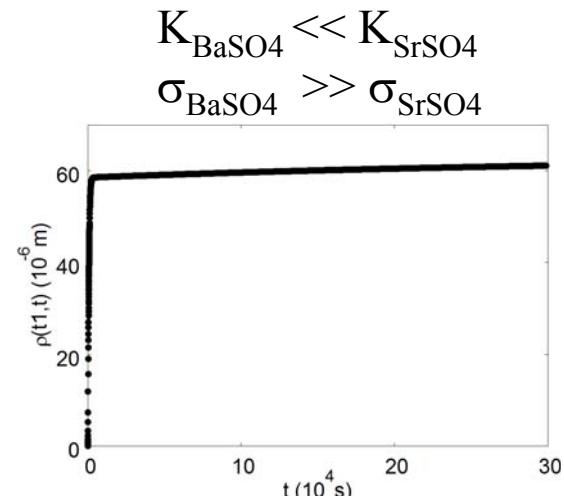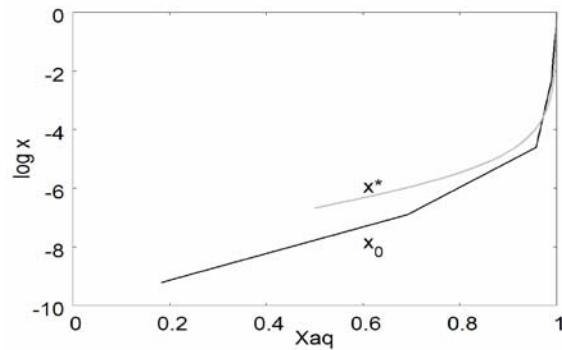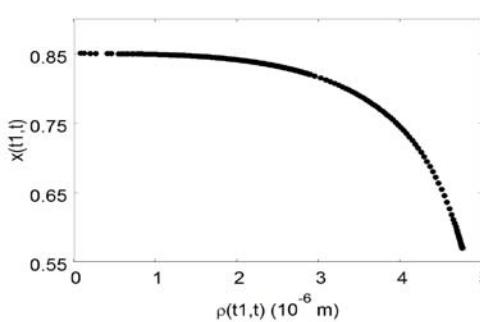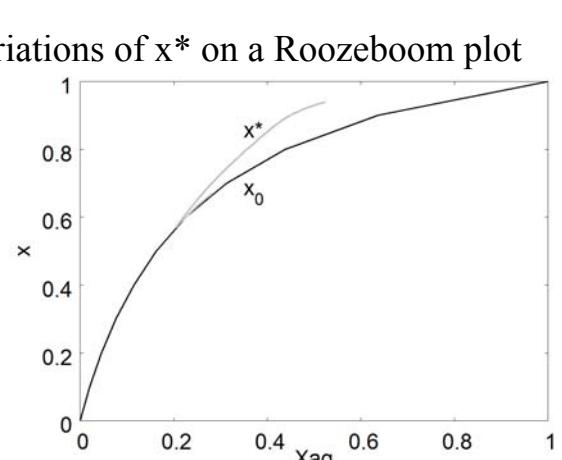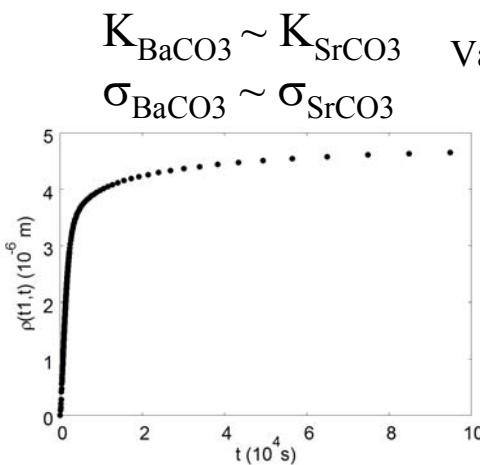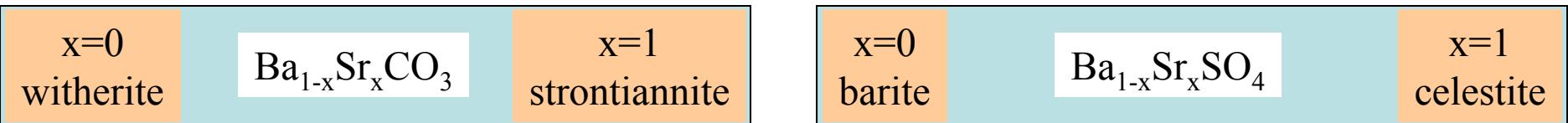
Center of particles rich in Sr

Core-shell particle

25

Summary

      - formalism for treating precipitation of multiple minerals in aqueous solutions
             (closed system)
      - based on sets of coupled integro-differential equations solved by discrete steps
             (applied mathematics thesis of Y. Amal)
      - extension to precipitation of minerals with variable composition
             (1 substitution; ideal solid solution)
      - already some applications of increasing difficulty

Future: - non-ideality
          - multiple substitutions (clays)
          - reactive transport