Kinetics of Precipitation of Non-ideal Binary Solid-solutions in an Aqueous Medium

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Kinetics of precipitation of non-ideal binary solid-solutions in an aqueous medium

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Abstract

We have developed a formalism which accounts for the kinetics of precipitation of binary non-ideal solid-solutions, and includes nucleation, growth and/or re-dissolution processes. It allows prediction of the time evolution of the aqueous ion activities together with all characteristics of the solid phase: crystal size distribution function and composition profiles of particles. We show that different scenarios of precipitation are possible depending on the thermodynamic properties of the solid solution end-members, the degree of non-ideality of the solid solution and the initial conditions of precipitation. We illustrate the various scenarios by simulations performed under a few simplifying assumptions for some carbonate solid solutions of geochemical interest. To our knowledge, this is the first time in the field of geochemistry that these out-of-equilibrium precipitation processes of non-ideal solid solutions are fully described.

1. Introduction

The simulation of water-rock interaction (WRI) processes on the Earth Surface has long been a challenging field of research for geochemists. In natural systems, secondary phases are generally not defined compounds but often solid solutions. While the equilibrium behavior of a solid solution in contact with an aqueous solution is now well established, the inclusion of kinetic effects in the modeling of a solid solution formation still remains a difficult task. In the past, we introduced elements of the theory of nucleation and growth[1,2] into WRI codes, which led to the creation of the code NANOKIN. It first allowed predicting the formation of minerals with fixed composition[3-5], then

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of ideal binary solid solutions[6], including cation exchange[7] and finally of doubly substituted solid solutions[8]. These last steps assumed that the solid solutions were ideal. We present here a summary of the recently developed formalism for the precipitation of non-ideal solid solutions[9]. Using a few simplifying assumptions, we describe thecharacteristics of the precipitation of two carbonate solid solutions of geochemical interest and highlight the conditions of occurrence of the various generic scenarios of precipitation.

2. Method

We consider[9] a regular non-ideal solid solution of composition $A_{1-x}B_xC$ ($0<x<1$), with AC and BC its end-members, for which the enthalpy of mixing is represented by a single term in the Guggenheim expansion $\Delta H_M(x)= -RTx(1-x)A_0$ (with R the gas constant and T the temperature). The stoichiometric saturation state is given by:

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

In Eq. 1, $I_{AC}=[A][C]/K_{AC}$ and $I_{BC}=[B][C]/K_{BC}$ are the saturation states of the aqueous solution with respect to the pure end-members AC and BC, respectively and $\lambda_{AC}=\exp[A_0x^2]$ and $\lambda_{BC}=\exp[A_0(1-x)^2]$ are the end-member activity coefficients, functions of the solid solution composition x. K_{AC} and K_{BC} are the end-member solubility products and [A], [B] and [C] the relevant ion activities in the aqueous solution.

Nucleation is treated within the framework of the classical theory of nucleation in its continuum limit[9]. The change in Gibbs free energy in the formation of a nucleus containing n formula units of composition x is the sum of two competing terms $\Delta G(n,x) = -nk_BT \ln I(x)+ n^{2/3}v(x)^{2/3}(36\pi)^{1/3}\sigma$. The first one, with $I(x)$ the stoichiometric saturation state given by Eq.1 and k_B the Boltzman constant, represents the gain (if $I(x) >1$) of Gibbs free energy when ions from the aqueous solution condense into a solid phase. The second term $E_s= n^{2/3}v(x)^{2/3}(36\pi)^{1/3}\sigma$ is the total surface energy of the nucleus. In this expression, σ is the surface energy per unit area (assumed to be independent on composition) and $v(x)$ is the volume of a formula unit of composition x, that will be assumed to vary linearly between its end-member values: $v(x)=(1-x)v_{AC}+xv_{BC}$. When $I(x)>1$, $\Delta G(n, x)$ displays a maximum as a function of n, which defines the characteristics of the critical nucleus: its size $n_m(x)$ and the barrier $\Delta G_m(x)$ to be overcome for its formation. The composition x^* of the critical nuclei is determined by the condition that the nucleation barrier is minimum with respect to x. It is the solution of the implicit equation:

$$\left[\frac{I_{AC}}{(1-x^*)\lambda_{AC}(x^*)}\right]^{v_{BC}} = \left[\frac{I_{BC}}{x^*\lambda_{BC}(x^*)}\right]^{v_{AC}} \tag{2}$$

For ideal solid solutions, Eq.2 has a single root. For non-ideal solid solutions, it may have one or three roots depending upon the composition of the aqueous solution and whether A_0 is smaller or larger than 2, respectively. The roots are functions of A_0, $z=v_{BC}/v_{AC}$ and the ratio $W=I_{BC}/I_{AC}^z$ which contains information on the aqueous solution composition at each time. When Eq.2 has a single root, x^* varies smoothly as a function of W. When there are three roots, two correspond to maxima of the nucleation barrier and one to a minimum, and x^* is equal to the latter. In that case, x^* displays a discontinuity between two values x_1 and x_2 at a value W_c of W which is equal to 1 if $z=1$ and close to 1 otherwise. In between x_1 and x_2, which only depend on z and A_0, the phase diagram of the solid solution presents a miscibility gap.

Growth involves the condensation of ions from the aqueous solution on the surface of the particles. We restrict ourselves to a continuous growth mechanism, limited by the incorporation of growth units at the surface of a rough nucleus. It can be shown that the composition x of the layer which is deposited is equal to $x^*(t)$. Actually, the particle size may increase or decrease according to whether it is larger or smaller than the instantaneous size of the critical nuclei. This is the Ostwald ripening process. For example, for increasing particle sizes, the growth equation used for particles of fixed composition[1,2] can be straightforwardly generalized to solid solutions[6,9].

Assuming a closed system, from the number of moles of end-members withdrawn from the aqueous solution and an ionic speciation model, all activities in the aqueous solution and the saturation indices $I_{AC}(t)$, $I_{BC}(t)$ and $I(t,x)$ may be calculated. Including feed-back effects on the aqueous solution allows an evolution of its composition towards thermodynamic equilibrium. The equations of nucleation, growth and feed-back form a complete set which, together

with the speciation equations, allow the full determination of the precipitate and aqueous solution characteristics at all times. They are solved by a time discretization method. While the formalism is presented here in its simplest version (homogeneous nucleation, spherical particles, composition independent surface energy), a more general treatment may be found in Ref. 9. The development of a new version of the NANOKIN code to include solid solution non-ideality properties is presently under progress.

3. Results

In the following discussion we use simplifying assumptions to present some characteristics of the precipitation of two carbonate solid solutions. The aim is to highlight the various precipitation scenarios which may take place. We restrict our simulations, to strongly non-ideal solid solutions characterized by a Guggenheim parameter $A_0 > 2$. Actually, when $A_0 < 2$, the only difference compared to truly ideal solid solutions[6] lies in the corrections due to the activity coefficients λ_{AC} and λ_{BC}. In the following, we will refer to this case as Scenario #1

(Ca,Zn)CO$_3$ is a non-ideal solid solution with a Guggenheim coefficient A_0 equal to 2.2 and a ratio of its end-member solubility products K_{BC}/K_{AC} close to 0.03. For this value of A_0, $x_1 = 0.25$ and $x_2 = 0.75$. Fig.1 displays the time evolution of $I(t,x^*)$ and $x^*(t)$ for two initial aqueous solution concentrations. In the two left panels, $[B]/[A] = 0.025 < K_{BC}/K_{AC}$. $I(t,x^*)$ decreases as a function of time and tends towards 1 in the long term, signaling that thermodynamic equilibrium is reached. $x^*(t)$ also decreases as the aqueous solution gets more and more impoverished in Zn. Such precipitation dynamics in which the miscibility gap is not crossed, and in which the solid solution composition varies smoothly with time will be called in the following Scenario #2.
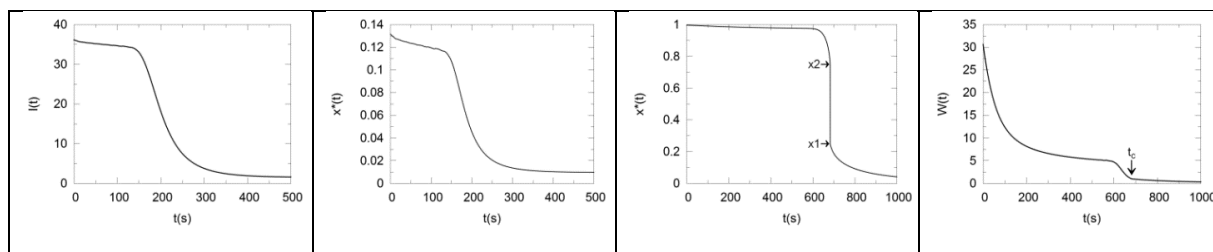

Fig. 1. From left to right: Time dependence of $I(t,x^*)$; $x^*(t)$ and $W(t)$. Parameters of the simulation: $A_0 = 2.2$, $K_{AC} = 4.6 \cdot 10^{-9}$, $K_{BC} = 1.5 \cdot 10^{-10}$, $F_0 = 10^{19}$ particles/s/kg H$_2$O, $\kappa = 10^{-12}$ m/s, $\sigma = 50$ mJ/m^2, $z = v_{BC}/v_{AC} = 1$; $[B]/[A] = 0.025$ for the two left panels and 1 for the two right panels

In the two right panels of Fig. 1 a completely different $x^*(t)$ behavior is found, when initially $[B]/[A]$ is larger than K_{BC}/K_{AC}. x^* starts at a value larger than x_2, then decreases with time. At a critical time t_c, it meets the miscibility gap and displays a discontinuity between x_2 and x_1, then goes on decreasing during the remaining time. Time t_c corresponds to the time at which $W = W_c = 1$. We note that, although $W(t)$ presents a slope discontinuity at $W_c = 1$, dW/dt has the same (negative) sign whether W is larger or smaller than 1. Such precipitation dynamics in which the miscibility gap is crossed, i.e. in which the solid solution composition varies discontinuously with time, but dW/dt keeps a constant sign, will be called in the following Scenario #3.

(Ca,Sr)CO$_3$ is a strongly non-ideal solid-solution with a large Guggenheim coefficients $A_0 = 5.5$, indicating poor solubility of Sr in aragonite and a miscibility gap occupying most of the phase diagram ($x_1 \sim 0.004$ and $x_2 \sim 0.996$). The ratio of end-member solubility products is equal to 0.116 at 25°C. Figure 2 (the two left panels) shows a typical time evolution of $x^*(t)$ and $W(t)$. Initially, W is larger than $W_c = 1$, so that x^* starts at a value larger than x_2. W and x^* both decrease in the first stage of precipitation, until W reaches W_c at a critical time $t_c \sim 565$s. However, dW/dt has opposite signs according to whether $W > 1$ or $W < 1$, which tends to bring it back towards $W_c = 1$ on both sides. There is thus a conflict between the variations of W forcing it to stay constant and equal to W_c. Phase separation between phases of compositions x_1 and x_2 takes place beyond t$_c$, with relative amounts α and $1-\alpha$ (here $\alpha \sim 0.90$). This scenario will be referred to as Scenario #4. The previous simulations show that depending upon the degree of non-ideality of the solid solution A0, the ratio of end-member solubility products KBC/KAC and the initial composition [B]/[A] of the aqueous solution which fixes the initial value of W, the precipitation scenarios may be quite different. Here, we specify their conditions of occurrence.

Since $d[A]/dt$ and $d[B]/dt$ are proportional to $1-x^*$ and x^*, respectively, the time derivative of W is:

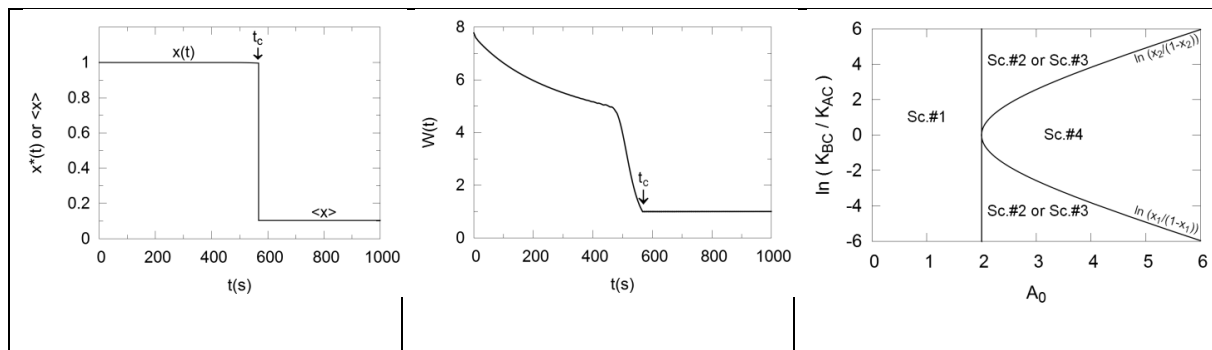$$\frac{1}{W}\frac{dW}{dt} \propto -\left[x^*(t) - (1 - x^*(t))\frac{K_{BC}}{K_{AC}}\right] \tag{3}$$

Fig. 2. Two left panels: Time dependence of $x^*(t)$ and $W(t)$ of $(Ca,Sr)CO_3$; Parameters of the simulation: A_0=5.5, K_{AC} =4.2 10^{-9}, K_{BC}=5.4 10^{-10}, F_0=10^{19} particles/s/kg H_2O, κ=10^{-12} m/s, σ=50 mJ/m^2, z=v_{BC}/v_{AC}=1, $[B]/[A]$ =1; Right panel: Diagram ln K_{BC}/K_{AC} as a function of A_0, representing the zones of existence of the scenarios #1, #2, #3, and #4.

Close to the discontinuity, $x^*(t)$ is equal to x_1 or x_2 when W is smaller or larger than 1, respectively, so that $W(t)$ displays a slope discontinuity and, in some cases, depending on the relative values of $x_1/(1-x_1)$, $x_2/(1-x_2)$ and K_{BC}/K_{AC}, dW/dt may change sign at the discontinuity. Scenario #2 for a strongly non-ideal solid solution with A_0>2 takes place when the discontinuity is not met, which means that, at t=0, W<1 and dW/dt<0 or W>1 and dW/dt>0. Scenario #3 for a strongly non-ideal solid solution with A_0>2 takes place when the discontinuity is met and dW/dt has the same sign on both sides of the discontinuity. Scenario #4 takes place for a strongly non-ideal solid solution with A_0>2 when dW/dt changes sign at the discontinuity. In that case phase separation between two solid solutions of composition x_1 and x_2, respectively, starts occurring at time t_c when W=1, with relative amounts α and $1-\alpha$ determined by the condition that dW/dt=0. Finally, weakly non-ideal solid solution, for which A_0<2 display Scenario #1. This discussion is summarized in Figure 2 (right panel), which allows predicting the characteristics of precipitation of any regular solid solution once its Guggenheim coefficient A_0 and the ratio of its end-member solubility products K_{BC}/K_{AC} are known. To our knowledge, this is the first time in the field of geochemistry that these out-of-equilibrium precipitation processes of non-ideal solid solutions are fully described. The application of this theoretical approach in water-rock interaction models will be very useful in order to predict the kinetic formation of complex mineral phases like various carbonates which behave as non-ideal solid solutions.

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