



15th Water-Rock Interaction International Symposium, WRI-15

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.

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Peer-review under responsibility of the organizing committee of WRI-15

Keywords: Nucleation and growth; kinetic simulations; non-ideal solid-solutions; miscibility gap; core-shell nanoparticles; Nanokin code.

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 composition³⁻⁵, then

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of ideal binary solid solutions⁶, including cation exchange⁷ and finally of doubly substituted solid solutions⁸. 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 solutions⁹. Using a few simplifying assumptions, we describe the characteristics 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 consider⁹ 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:

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

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 limit⁹. 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 $\Delta G(n, x) = -nk_B T \ln I(x) + n^{2/3}v(x)^{2/3}(36\pi)^{1/3}\sigma$. 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:

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

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

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