Daval et al. Deposit AM-09-053   Appendix A   Nov/Dec 2009 American Mineralogist

The goal of the present section is to show that the size of the critical nuclei is smaller in experiments conducted in alkaline solution compared to water. First, one can express the quantity of carbonate ion for the two experiments (carbonation in water, alkaline solution) as follows:

$$[CO_3^{2-}]^{wat}_{eq} < [CO_3^{2-}]^{alk}_{eq} \qquad (A1)$$

where $[CO_3^{2-}]^{wat}_{eq}$ and $[CO_3^{2-}]^{alk}_{eq}$ represent the concentration of CO_3^{2-} species in equilibrium with calcite under constant CO_2 fugacity, in water and in the alkaline solution, respectively. The time needed for achievement of calcite saturation is considered arbitrary, and is called t_0 in both cases. Because the initial pH values of both solutions were 3.1 and 5.6 (water and alkaline solution, respectively), and assuming that wollastonite dissolution rates are independent of pH in the range 2–6 (Weissbart and Rimstidt 2000), then over an infinitesimal interval of time Δt, the same amount of calcium (Δn_{Ca}^{wat} and Δn_{Ca}^{alk}, respectively) is released to the fluid by wollastonite dissolution at each condition:

$$\Delta n_{Ca}^{wat} = \Delta n_{Ca}^{alk} \qquad (A2)$$

Multiplying the left and right terms of Equation A1 by the respective number of incremental moles of Ca released (Eq. A2), and dividing by the volume, yields:

$$(\Delta n_{Ca}^{wat}/V_f) \times [CO_3^{2-}]^{wat}_{eq} < [CO_3^{2-}]^{alk}_{eq} \times (\Delta n_{Ca}^{alk}/V_f) \quad (A3)$$

If activities are equated with aqueous concentrations, and the activity of calcite is unity, one can write:

$$K_s = [Ca^{2+}]^{wat}_{eq} \times [CO_3^{2-}]^{wat}_{eq} = [Ca^{2+}]^{alk}_{eq} \times [CO_3^{2-}]^{alk}_{eq} \; (A4)$$

where $[Ca^{2+}]^{wat}_{eq}$ and $[Ca^{2+}]^{alk}_{eq}$ are the concentration of Ca^{2+} species in equilibrium with calcite under constant CO_2 fugacity, in water and in the alkaline solution, respectively, and K_s is the equilibrium constant for the reaction:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \qquad (A5)$$

Summing Equations A3 and A4, and rearranging the carbonate terms, results in:

$$[CO_3^{2-}]^{wat}_{eq} \times (\Delta n_{Ca}^{wat}/V_f + [Ca^{2+}]^{wat}_{eq}) < [CO_3^{2-}]^{alk}_{eq} \times (\Delta n_{Ca}^{alk}/V_f + [Ca^{2+}]^{alk}_{eq}) \, (A6)$$

At this stage, each side of Equation A6 nearly represents the ion activity product of Equation A5 at $t_0 + \Delta t$ in water and in alkaline solution, respectively, a point at which the fluid is supersaturated with respect to calcite, although it has not yet formed. This is, however, not exactly correct because the release of Δn_{Ca}^{wat} (or Δn_{Ca}^{alk}) to the respective solutions is necessarily accompanied by a pH increase and a concomitant modification of the fluid speciation. As revealed in Table 1, the carbonation reaction in both cases (water, alkaline solution) takes place at pH < pKa_1 << pKa_2

[where pKa_1 and pKa_2 stand for the pKa of the reactions $CO_2 + H_2O \rightarrow HCO_3^- + H^+$ and $HCO_3^- \rightarrow CO_3^{2-} + H^+$, respectively, equal to 6.39 and 10.08 at 100 °C (CHESS ref.)]. Thus, in this acidic to circum-neutral pH range, the main effect of the consumption of protons by the dissolution step will be the decomposition of carbonic acid and production of HCO_3^- species, while the concentration of CO_3^{2-} species will remain approximately the same. Therefore, the following approximations can be considered as reasonable:

$$[CO_3^{2-}]^{wat}_{eq} + (\Delta n_{CO3}^{wat}/V_f) \approx [CO_3^{2-}]^{wat}_{eq} \qquad (A7a)$$
$$[CO_3^{2-}]^{alk}_{eq} + (\Delta n_{CO3}^{alk}/V_f) \approx [CO_3^{2-}]^{alk}_{eq} \qquad (A7b)$$

where Δn_{CO3}^{wat} and Δn_{CO3}^{alk} are the amount of CO_3^{2-} species produced when Δn_{Ca}^{wat} and Δn_{Ca}^{alk} are released in water and in the alkaline solution respectively. Substituting $[CO_3^{2-}]^{wat}_{eq}$ and $[CO_3^{2-}]^{alk}_{eq}$ in Equation A6 by their values taken from Equations A7a and A7b, assuming that aqueous species concentrations are equivalent to activities and knowing that at $t_0 + \Delta t$, the fluid is supersaturated with respect to calcite, leads to:

$$0 < \Delta G_r(CaCO_3)_{t0+\Delta t}^{wat} < \Delta G_r(CaCO_3)_{t0+\Delta t}^{alk} \qquad (A8)$$

where $\Delta G_r(CaCO_3)_{t0+\Delta t}^{wat}$ and $\Delta G_r(CaCO_3)_{t0+\Delta t}^{alk}$ are the Gibbs free energy of calcite dissolution at $t_0 + \Delta t$ in water and in the alkaline solution, respectively. Thus, the incremental dissolution of wollastonite results in a higher degree of calcite supersaturation in the alkaline solution compared to water. Two important consequences follow from this result. First, as the critical radius (r_c) of a simple spherical nucleus is given by:

$$r_c = 2\gamma/\Delta G_r \qquad\qquad\qquad (A9)$$

where γ is its surface tension, then, the combination of Equations A8 and A9 yields:

$$r_c^{alk} < r_c^{wat} \qquad (A10)$$

The difference in the critical radii may explain why calcite is more prevalent in the silica layer (nano-crystallites in pores and cracks) when carbonation takes place in an alkaline solution compared to water. Such crystals could in turn fill up the pores and cracks in experiments with alkaline fluid. Secondly, larger initial supersaturations lead to faster nucleation rates, which translates into more numerous and smaller crystal sizes. Similar reasoning could be used for the precipitation of C-S-H phases, leading to the same consequences as the ones described above with respect to the silica layer.

Appendix B

The purpose of the present section is to detail how the general diffusion equation (Eq. 4) can be solved, supposing that: (1) the rate of retreat of the fluid–solid interface is nul ($a = 0$, see section "Mechanism of silica layer formation" for details), and (2) the outward diffusion of cations Ca^{2+} and the inward diffusion of H^+ are coupled by an ion exchange reaction between H^+

and M^{n+} species.

The expression below can be used to describe binary cation diffusion behavior in silicate minerals (from Brady 1995; see original references therein):

$$\tilde{D} = D_{A_b B_{-a}} = \left[\frac{D_{AZ}^* D_{BZ}^* (aN_{AZ} + bN_{BZ})^2}{a^2 N_{AZ} D_{AZ}^* + b^2 N_{BZ} D_{BZ}^*} \right] \times \left[1 + \left(\frac{\partial \ln \gamma_{AZ}}{\partial \ln N_{AZ}} \right)_{P,T} \right] \quad \text{(A11)}$$

where the reaction is $A_z^{+a} Z_a^{-z} \rightarrow B_z^{+b} Z_b^{-z}$, D_{AZ}^* and D_{BZ}^* are the respective tracer diffusion coefficients for phases AZ and BZ, and N_{AZ} and N_{BZ} are the mole fractions for each phase. Neglecting the activity coefficient of Equation A11 ($\gamma_{AZ} \approx 1$, see details in Hellmann 1997), the diffusion coefficient describing interdiffusion of monovalent species (H^+) for divalent species (Ca^{2+}) is given by the following simplified expression:

$$\tilde{D} = \frac{D_{Ca} D_H (C+1)^2}{4 D_{Ca} C + D_H (1-C)} \quad \text{(A12)}$$

D_H is the diffusion coefficient of H^+. Due to the non-linearity of the $\tilde{D}$ expression in terms of concentration and consequently depth, solving Equation 4 analytically is difficult. However, this equation can be linearized and then solved numerically using a finite-volume approach and implicit-explicit discretization. Theoretical Ca gradients are numerically approximated by the general following equation:

$$C_i^{n+1} = C_i^n + \frac{\Delta t}{\Delta x^2} \left(d_{i+1}^n C_{i+1}^{n+1} - (d_{i+1}^n + d_i^n) C_i^{n+1} + d_i^n C_{i-1}^{n+1} \right) \quad \text{(A13)}$$

where Δx and Δt are infinitesimal space and time intervals respectively, C_i^n is the concentrations of Ca at time t and at depth x, C_i^{n+1}, C_{i+1}^{n+1}, and C_{i-1}^{n+1} are the concentrations of Ca at time $t + \Delta t$ and at depth x, $x + \Delta x$ and $x - \Delta x$, respectively. The parameter d_i^n represents the diffusion coefficient at the boundary between two adjacent meshes at depths $x - \Delta x$ and x, respectively, and for the time t. These boundary diffusion coefficients can then be calculated from the values of the interdiffusion coefficients in each mesh (see Cassou 2000 for further explanations):

$$\begin{cases} d_1^n = \tilde{D}_1^n \\ d_i^n = \dfrac{\tilde{D}_{i-1}^n \tilde{D}_i^n (\Delta x + \Delta x)}{\tilde{D}_{i-1}^n \Delta x + \tilde{D}_i^n \Delta x} = \dfrac{2 \times \tilde{D}_{i-1}^n \tilde{D}_i^n}{\tilde{D}_{i-1}^n + \tilde{D}_i^n} \quad \forall i \in [2, N] \\ d_{N+1}^n = 0 \end{cases} \quad \text{(A14)}$$

where $\tilde{D}_i^n$ is the interdiffusion within the ith mesh, and N is the total number of considered meshes during the course of the numerical simulation. This last expression takes into account the boundary conditions described earlier: there is a constant concentration at the "in-"boundary

flux of the first mesh and no flux at the "out-"boundary of the Nth mesh. Finally, the calculation of C_i^{n+1} consists in solving the following system of Equation A15a which also comprises the initial conditions of Equation A15b:

$$
\begin{cases}
C_1^{n+1} + \dfrac{\Delta t}{\Delta x^2}\left(-d_2^n C_2^{n+1} + (d_2^n + d_1^n)C_1^{n+1}\right) = C_1^n \\[2ex]
C_i^{n+1} + \dfrac{\Delta t}{\Delta x^2}\left(-d_{i+1}^n C_{i+1}^{n+1} + (d_{i+1}^n + d_i^n)C_i^{n+1} - d_i^n C_{i-1}^{n+1}\right) = C_i^n,\ \forall i \in \left[2,N\right[\\[2ex]
C_N^{n+1} + \dfrac{\Delta t}{\Delta x^2}\left(d_N^n C_N^{n+1} - d_N^n C_{N-1}^{n+1}\right) = C_N^n
\end{cases}
\qquad \text{(A15a)}
$$

$$
C_i^1 = 1 \quad \forall i \in [1,N] \qquad\qquad\qquad \text{(A15b)}
$$