

Crystal growth and the fast reaction paradox: Mathematical resolution and implications for habit and compositional zoning

P. ORTOLEVA*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405, U.S.A.

ABSTRACT

Fast reactions in the medium from which a crystal is growing (e.g., $H^+ + HCO_3^- \leftrightarrow H_2CO_3$) occurring near the crystal surface can conflict with the stoichiometry of crystal formula-unit creation (e.g., CO_3^{2-} is readily incorporated in calcite but H^+ is not). As a result, a thin fast-reaction boundary layer (FRBL) is created within which the fast reactions are out of equilibrium even though they are maintained at equilibrium far from the crystal surface. The FRBL corrects the fluxes of components to and from the surface of the crystal; not taking the FRBL into account leads to violation of mass conservation. This “paradox” is resolved by showing how the equations of crystal growth can be solved in the fast-reaction limit without violating mass conservation. As this paradox was not understood in the literature, models and geological conclusions drawn should be re-examined.

Keywords: Crystal growth, oscillatory crystal zoning, calcite, equilibrium, multiscale analysis

INTRODUCTION

The occurrence of widely separated time scales in a reaction-transport system can lead to a narrow fast reaction boundary layer (FRBL) across which concentration gradients may be extremely large (see Ortoleva 1992, Chapters 2 and 3). In the case of the growth of a crystal from a liquid in which there are very fast reactions, thus there are narrow transition zones that may develop within which the fast reactions are out of equilibrium, even though they are very close to equilibrium everywhere else in the growth medium. Since gradients in the FRBL affect fluxes of chemical components to the crystal surface, the FRBL can modify the rate of crystal growth from its value as computed from gradients just beyond the FRBL. The objective of the present study was to present a mathematical resolution of the apparent paradox whereby equilibrium relations well maintained just beyond the FRBL lead to contradictions of mass balance when applied close to the surface of a growing crystal.

A rough estimate of the thickness of the FRBL can be obtained from dimensional analysis. If D is a typical diffusion coefficient and τ is a reaction time, then $(D\tau^{1/2})$ is a reaction-diffusion length. For H^+ , D is roughly 10^{-3} cm²/s, whereas protonation reactions can be extremely fast (e.g., $\tau \approx 10^{-9}$ s). Thus, the FRBL for this case can be 100 Å in width. The FRBL is non-conspicuous, but is shown here to be influential. When the width of the FRBL is on the nanoscale, this phenomenon must be analyzed using mesoscopic theory or molecular dynamics. From the above estimate, the FRBL can easily be similar to the Debye length providing another mechanism by which it can be influential.

A ubiquitous case is the growth of carbonate minerals from an aqueous solution in which fast reactions such as $H^+ + OH^- \leftrightarrow$ water and $H^+ + HCO_3^- \leftrightarrow H_2CO_3$ play key roles. As these reactions take place on short (even nanosecond) timescales, whereas diffusion and crystal growth occur on the minute-to-day scale, one expects FRBL effects may be important.

The fast-reaction limit in the behavior of the growth medium presents a paradox in that mass conservation at the surface of a growing crystal can be violated if the FRBL is ignored. Not addressing this phenomenon could lead to spurious estimates of crystal growth rate and total mass bookkeeping. If geological implications are drawn from such studies, this could be an issue for concern. Here, the FRBL paradox is illustrated and resolved using boundary layer theory. It is shown quantitatively that a thin FRBL in the growth medium near the surface of the crystal exists that allows mass conservation to be maintained. The treatment corrects misconceptions in the literature (e.g., Wang and Merino 1992).

The self-organization of compositional zoning patterns in impurity doped calcite (Paquette and Reeder 1990) illustrates the FRBL phenomenon. Consider the system to consist of crystal formula units of types A and B, where A contains the impurity M^{2+} . For illustrative purposes, consider the unit-addition reaction scheme:



In the context of this mechanism, the FRBL problem is illustrated in Figure 1. Growth of calcite releases H^+ and therefore

* E-mail: ortoleva@indiana.edu

creates a gradient of H^+ as shown. If $H^+ + OH^- \leftrightarrow H_2O$ is fast everywhere, then the OH^- profile is the solid OH^- curve. However, OH^- is not created/consumed at the crystal surface and hence its gradient there is zero. But it cannot be zero and comply with the H^+ profile if water dissociation equilibrium is maintained (Fig. 1a). Thus, the assumption that water dissociation equilibrium is maintained near the crystal surface implies an incorrect value of the gradient there. Such gradients mediate the fluxes of components from which the crystal is growing and on which mechanisms of oscillatory zoning or other phenomena depend sensitively. The FRBL would therefore play an important role in both diffusion-limited and surface-reaction-limited situations. In the following sections, we formulate a reaction-transport-crystal growth model for this system, illustrate the FRBL phenomenon and the fast-reaction paradox, and resolve the latter using boundary layer mathematical techniques.

CRYSTAL GROWTH, DIFFUSION, BULK REACTION EQUATIONS

To identify the origins of the FRBL paradox of mass non-conservation, it is necessary to start with a model that conserves mass and subsequently examine it in the limit of fast reaction. To this end, we first write the conservation of mass laws for the calcite/impurity system introduced above. In that system, reac-

tions take place at the crystal-growth medium interface and in the growth medium itself.

From the stoichiometry of the reactions constructing crystal formula units, one may write the boundary conditions expressing conservation of mass at the crystal-growth medium interface:

$$-\vec{n} \cdot \vec{J}_{M^{2+}} + uc_{M^{2+}} = G_A \quad (5)$$

$$-\vec{n} \cdot J_{Ca^{2+}} + uc_{Ca^{2+}} = G_B \quad (6)$$

$$-\vec{n} \cdot \vec{J}_{HCO_3^-} + uc_{HCO_3^-} = G_A + G_B \quad (7)$$

$$-\vec{n} \cdot \vec{J}_{H^+} + uc_{H^+} = -G_A - G_B \quad (8)$$

$$-\vec{n} \cdot J_i + uc_i = 0, \quad i = OH^-, H_2CO_3, \quad (9)$$

where \vec{n} is a unit vector normal to the crystal surface pointing into the growth medium. The \vec{J} values are diffusional fluxes (moles/area-time), u is the crystal growth velocity (length/time), $\rho u = G_A + G_B$, the G values are rates of formation of the A or B formula units (moles/area-time), ρ is the total number of moles of formula units per crystal volume, and the c values are molar concentrations.

Conservation of mass in the growth medium implies:

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i, \quad i = Ca^{2+}, M^{2+}. \quad (10)$$

Contributions from the fast reactions appear in the conservation equations for H^+ , OH^- , HCO_3^- , and H_2CO_3 .

Let W_1/ϵ and W_2/ϵ be the rates (moles/volume-time) of reactions 3 and 4, respectively. Inclusion of the factor ϵ (≈ 1) in these rate laws is a way to indicate that the corresponding reactions are fast. That the reactions are fast is thereby reflected in the fact that the corresponding rate coefficient (proportional to ϵ^{-1}) is large, i.e., that ϵ is small. The parameter ϵ is the ratio of the characteristic time for the fast reactions (e.g., 10^{-9} s for water dissociation) to that for slower processes (e.g., growth of a crystal with an inhibiting surface monolayer). Thus the W expressions would in the absence of ϵ , make all processes occur on the same (slow) timestep. Reformulating the problem via ϵ allows one to extract the limiting (small ϵ) behavior in an efficient and self-consistent manner. With this, conservation of mass for the concentration of OH^- in the growth medium implies:

$$\frac{\partial c_{OH^-}}{\partial t} = -\vec{\nabla} \cdot \vec{J}_{OH^-} - \frac{W_2}{\epsilon}. \quad (11)$$

The model is completed by writing equation analogous to reaction 11 for the remaining species in the growth medium. c_{OH^-} has singular behavior for $\epsilon \ll 1$, suggesting that either c_{OH^-} changes rapidly in time or space, or that W_2 is small. This behavior is addressed in the next section in the formal $\epsilon \rightarrow 0$ limit. Techniques for carrying out such computations are reviewed in Ortoleva (1992, 1994).

ILLUSTRATING AND RESOLVING THE FRBL PARADOX

Difficulties in the literature arise in the inappropriate treatment of terms like W_2/ϵ in reaction 11 for small ϵ , i.e., for fast reactions. Although it is true that W_1 and W_2 are small in the fast reaction limit (i.e., the corresponding reactions are near equilibrium), it is not true that W_1/ϵ and W_2/ϵ are negligible. In fact, W_1/ϵ and W_2/ϵ approach well-defined (finite, not zero) values as $\epsilon \rightarrow 0$ since W_1 and W_2 become small, i.e., $O(\epsilon)$, as

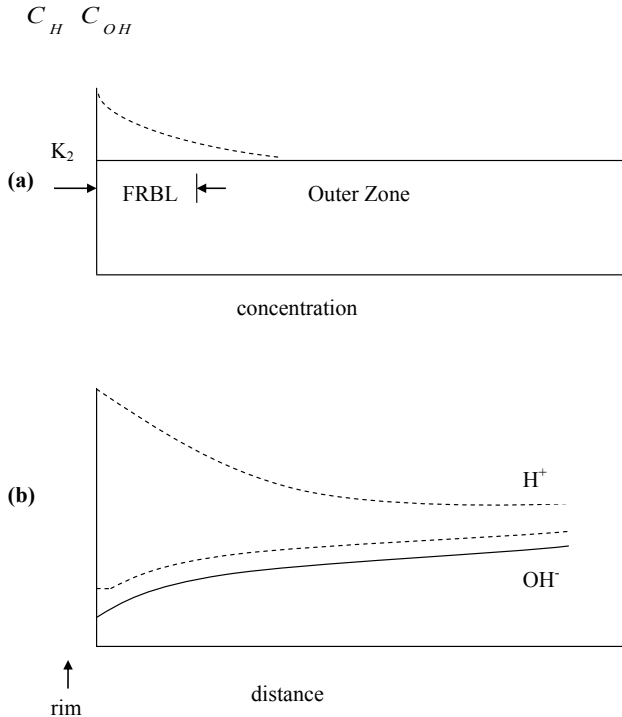


FIGURE 1. (a) The equilibrium relation $C_H + C_{OH^-} = K_2$ is maintained in the outer zone but in the FRBL, near the crystal rim, it is violated (dotted line). (b) If H^+ is relaxed due to calcite growth, and its profile is as sketched, then the OH^- profile must be the solid curve if $H^+ + OH^- = \text{water}$ is at equilibrium. Since OH^- is not part of the calcite growth reaction, then its concentration derivative at the crystal surface must be zero (the dotted curve). But this would be inconsistent with the H^+ profile shown. Thus, both H^+ and OH^- profiles are not predicted correctly by a theory neglecting the FRBL.

$\varepsilon \rightarrow 0$ where $O(\varepsilon)$ means vanishes proportional to ε . In what follows, the values of these ratios and their impact on crystal growth are determined.

It is convenient to combine the conservation equations for H^+ , OH^- , HCO_3^- , and H_2CO_3 to yield two equations without the W terms:

$$\frac{\partial}{\partial t} \left\{ c_{HCO_3^-} + K_1 c_{H^+} c_{HCO_3^-} \right\} = -\bar{\nabla} \cdot \left(\bar{J}_{HCO_3^-} + \bar{J}_{H_2CO_3} \right) \quad (12)$$

$$\frac{\partial}{\partial t} \left\{ c_{H^+} + \frac{K_2}{c_{H^+}} - c_{HCO_3^-} \right\} = -\bar{\nabla} \cdot \left(\bar{J}_{H^+} - \bar{J}_{OH^-} - \bar{J}_{HCO_3^-} \right) \quad (13)$$

where K_1 and K_2 are equilibrium constants for reactions 3 and 4 (activity coefficient corrections have been neglected for simplicity). In this way, the problem is reduced to determining the four concentrations $c_{Ca^{2+}}$, $c_{M^{2+}}$, c_{H^+} , and $c_{HCO_3^-}$ in terms of which the others (c_{OH^-} , $c_{H_2CO_3}$) may be determined via equilibrium relations (i.e., $c_{OH^-} = K_2/c_{H^+}$, $c_{H_2CO_3} = K_1 c_{H^+} c_{HCO_3^-}$).

An apparent contradiction emerges from the boundary condition for OH^- , i.e., $-\bar{n} \cdot \bar{J}_{OH^-} + u c_{OH^-} = 0$ since OH^- is not involved in the formula unit-creation reactions. Using the equilibrium relations and Fick's diffusion law, this boundary condition implies that the quantity

$$\bar{n} \cdot D_{OH^-} \bar{\nabla} \left(\frac{K_2}{c_{H^+}} \right) + u \left(\frac{K_2}{c_{H^+}} \right) \neq 0$$

is not equal to 0 because of Equation 8 for H^+ . Thus, ignoring this fact leads to meaningless physical results (notably artificial accumulation or depletion of species near the crystal surface).

Resolution of this paradox is attained by a re-examination of a narrow layer in the growth medium near the crystal surface (the FRBL, Fig. 1). Introducing a short length-scale variable to capture the large gradients in the FRBL that emerge will compensate the aforementioned conflict between the equilibrium relations and the boundary conditions. It is now shown that there is an FRBL of width $O(\varepsilon^{1/2})$ in which reaction 4, and more generally, the fast growth-medium reactions, are out of equilibrium by a small amount of $O(\varepsilon^{1/2})$, just enough to preserve mass conservation. One might expect this scaling since the characteristic time for the fast reactions is $O(\varepsilon)$ and the square of the associated diffusion length should be proportional to this time. In order that transport and fast reactions balance in the FRBL as ε goes to zero, the fast reactions must be out of equilibrium by an amount $O(\varepsilon^{1/2})$. Whereas mass conservation is ensured in the original reaction-transport-crystal growth equations, it is lost by incorrect treatment of the fast reactions.

The above notions may be formalized as follows. Consider planar growth along the x -axis. While crystal growth is a moving boundary problem, (e.g., see Ortoleva 1992, 1994), if the growth medium is dilute one may measure x relative to the advancing crystal surface (henceforth $x = 0$) and neglect the u terms in the boundary conditions for the concentrations in the growth medium. The approach presented below and the conclusions drawn from it can readily be generalized to the case of growth from melts or concentrated solutions where the u term cannot be neglected. Introduce a scaled position variable $\zeta = x/\varepsilon^{1/2}$ to characterize variations in the FRBL starting at the crystal's surface,

$x = 0$. In the definition of ζ , it has been assumed the FRBL is $O(\varepsilon^{1/2})$ in thickness. That this is the case will be born out in the self-consistency it brings to the analysis as follows.

Multiscale expansions (Ortoleva 1992, Chapters 2 and 3) are used to solve reaction-transport equations when a system displays two or more characteristic length or time scales. For the present problem, the latter are due to the large scale profile of diffusion in the growth medium, while the FRBL [with thickness $O(\varepsilon^{1/2})$] involves the short scale. In the multiscale approach to the present problem, the concentration c_i of species i is taken to have two distinct dependencies, i.e., on x and ζ , so that c_i has the form $c_i(x, \zeta, t, \varepsilon^{1/2})$. Since $\varepsilon^{1/2}$ is small, it is assumed that c_i can be expanded in a Taylor series:

$$c_i = c_i^{(0)}(x, t) + c_i^{(1)}(\zeta, x, t) \varepsilon^{1/2} + \dots \quad (14)$$

The scaling of space in the FRBL is as $\varepsilon^{1/2}$, and that c_i can be expanded in powers of $\varepsilon^{1/2}$ (and not in another power of ε), is verified via the self-consistency of the analysis.

To $O(\varepsilon^{1/2})$, the conservation equations yield $W_k[c^{(0)}] = 0$ ($k = 1, 2$), i.e., the $c_i^{(0)}$ satisfy equilibrium conditions for the fast ($\varepsilon \ll 1$) reactions. To $O(\varepsilon^{1/2})$, the reaction-transport equations for H^+ , OH^- , and H_2CO_3 imply:

$$D_{H^+} \frac{\partial^2 c_{H^+}^{(1)}}{\partial \zeta^2} + W_1^{(1)} + W_2^{(1)} = 0 \quad (15)$$

$$D_{OH^-} \frac{\partial^2 c_{OH^-}^{(1)}}{\partial \zeta^2} + W_2^{(1)} = 0 \quad (16)$$

$$D_{HCO_3^-} \frac{\partial^2 c_{HCO_3^-}^{(1)}}{\partial \zeta^2} + W_1^{(1)} = 0 \quad (17)$$

where $W_1^{(1)}$ and $W_2^{(1)}$ are the coefficients of $\varepsilon^{1/2}$ for the rates W_1 and W_2 . These equations can be combined to yield:

$$\frac{\partial^2}{\partial \zeta^2} \left\{ D_{H^+} c_{H^+}^{(1)} - D_{OH^-} c_{OH^-}^{(1)} - D_{HCO_3^-} c_{HCO_3^-}^{(1)} \right\} = 0. \quad (18)$$

As concentrations must be finite, the $c_i^{(1)}$ must be bounded as $\zeta \rightarrow \infty$. This constraint implies:

$$D_{H^+} \frac{\partial c_{H^+}^{(1)}}{\partial \zeta} - D_{OH^-} \frac{\partial c_{OH^-}^{(1)}}{\partial \zeta} - D_{HCO_3^-} \frac{\partial c_{HCO_3^-}^{(1)}}{\partial \zeta} = 0. \quad (19)$$

This equation states that within the FRBL the flux corrections are related due to the stoichiometry of the fast reactions.

To $O(\varepsilon^0)$, the boundary conditions for H^+ , OH^- , and HCO_3^- yield:

$$D_{H^+} \left\{ \frac{\partial c_{H^+}^{(0)}}{\partial x} + \frac{\partial c_{H^+}^{(1)}}{\partial \zeta} \right\} = -G_A^{(0)} - G_B^{(0)} \quad (20)$$

$$D_{OH^-} \left\{ \frac{\partial c_{OH^-}^{(0)}}{\partial x} + \frac{\partial c_{OH^-}^{(1)}}{\partial \zeta} \right\} = 0 \quad (21)$$

$$D_{HCO_3^-} \left\{ \frac{\partial c_{HCO_3^-}^{(0)}}{\partial x} + \frac{\partial c_{HCO_3^-}^{(1)}}{\partial \zeta} \right\} = G_A^{(0)} - G_B^{(0)}. \quad (22)$$

Linear combinations of these equations yield the boundary

conditions in the fast reaction ($\epsilon \rightarrow 0$) limit:

$$\sum_{i=1}^N a_i D_i \partial c_i^{(0)} / \partial x = 0 \quad (23)$$

for $(a_{\text{H}^+}, a_{\text{OH}^-}, a_{\text{HCO}_3^-}, a_{\text{Ca}^{2+}}, a_{\text{M}^{2+}}, a_{\text{H}_2\text{CO}_3}) = (1, -1, -1, 0, 0, 0)$, and three other similar conditions involving the $c_i^{(0)}$ only, i.e., without the $c_i^{(1)}$.

The paradox is now removed upon recognizing that there is a narrow layer in the growth medium near the crystal surface across which the $c_i^{(1)}$ change rapidly, enabling c_i to transition to a smoothly varying profile with distance from the crystal surface. This result can be demonstrated by a more complete analysis of the equations for the $c_i^{(1)}$. In particular, one solves Equations 15 to 17 for the $c_i^{(1)}$ subject to conditions 20 to 22 [and similarly for $c_i^{(1)}$, $i = \text{H}_2\text{CO}_3, \text{Ca}^{2+}, \text{M}^{2+}$].

Interestingly, the change in the flux of the species in the growth medium near the crystal surface is caused by the small correction $c_i^{(1)}\epsilon^{1/2}$ to c_i that is just sufficient to account for the paradoxical variations in flux calculated in terms of the $c_i^{(0)}$ that would otherwise violate the boundary conditions [i.e., $D_{\text{OH}^-} \partial c_{\text{OH}^-}^{(0)} / \partial x \neq 0$]. Although the $c_i^{(1)}\epsilon^{1/2}$ corrections to c_i are small ($\epsilon \ll 1$), they vary rapidly in space, and hence near the crystal surface $\partial c_i^{(1)} / \partial \zeta$ corrects the partial fluxes computed in terms of the $\partial c_{\text{OH}^-}^{(0)} / \partial x$ only.

IMPLICATIONS OF THE FRBL

Fast reactions in the growth medium change the rate of influx (20 to 22) of components to the surface of a growing crystal in an unexpected manner. The cause is the conflict between the stoichiometry of the creation of crystal formula units and the fast reactions. This conflict leads to a narrow layer of rapid transition of composition gradients within the growth medium adjacent to the crystal surface. This gradient transition zone resolves the conflict between the stoichiometry of crystal growth and the relative gradients of species outside this near-crystal transition layer. This mismatch modifies the overall growth rate and relative rates of creation for the various formula unit types in a solid solution. These factors are key to crystal habit and intracrystalline compositional zoning (see Ortoleva 1994 for a review). Models that do not take these effects into account will likely yield results and conclusions for the geosciences that are spurious.

The effect of the FRBL can be even more significant if the lowest order concentration $c_i^{(0)}$ is very small for a key species affecting the kinetics (e.g., impurity incorporation in a growing crystal). In that case, the correction $c_i^{(1)}\epsilon^{1/2}$ can significantly change the crystal growth rate, although the modifications of the rate of influx to the growing crystal surface are significant in themselves. When the width of the FRBL is on the order of magnitude of the Debye length, the pH and other factors affecting

the charge on the crystal surface can have an additional influence on crystal growth.

Several other phenomena involve near-surface effects and therefore might be modified by the FRBL. Nucleation (Ozkan and Ortoleva 2000a) and the interaction of nanoparticles with the surroundings and each other (notably flocculation or attachment to surfaces) are strongly affected by surface phenomena, and therefore in principle by the FRBL. Similar remarks hold for the evolution of gouge (Ozkan and Ortoleva 2000b) and processes involving growing or dissolving nanoparticles. The “mushy layer” considered to be important for growth from a melt could modify the diffusion coefficients in the FRBL and, in turn, the latter could affect the flux of components to the mushy layer that could modify it. Crystal habit can be dramatically affected by near-surface composition (Tuncay et al. 2002) and, in turn, by the FRBL. Feedback mediated by the dependence of the rate of incorporation of end-member units of a solid solution on the state of the growth medium-crystal interface can lead to oscillatory and other patterns of intracrystalline compositional zoning (Haase et al. 1980; Ortoleva 1994). Modeling these phenomena requires careful attention to conditions near the crystal surface, and notably the relative rate of influx of key formula-unit-building components. In summary, crystal growth is a surface phenomenon and the FRBL can dramatically affect the rate of influx of components toward and away from the crystal surface.

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