The Canadian Mineralogist
Vol. 38, pp. 1029-1031 (2000)

THE CASE AGAINST OSTWALD RIPENING OF PORPHYROBLASTS: REPLY

WILLIAM D. CARLSON[§]

Department of Geological Sciences, University of Texas at Austin, Austin , Texas 78712, U.S.A.

The discussion presented by Miyazaki does not dispute the contention of Carlson (1999) that the best available values for the factors that control the intergranular diffusion of Al will not allow Ostwald ripening to govern size distributions of crystals larger than a fraction of a micrometer. Instead, it raises objections to previous descriptions of the diffusion-controlled growth of porphyroblasts during metamorphism. Those objections are based upon a diffusional scenario and a corresponding set of equations that are, unfortunately, inapplicable to porphyroblast crystallization. The discussion relies upon a metallurgical model for the growth of precipitates from a single-phase matrix with continuously variable composition. Because that model fails to capture critical features of the crystallization of porphyroblasts from a polyphase matrix, the argument made in the discussion, and the conclusion it reaches, are invalid.

Miyazaki's analysis parallels exactly the derivation in Kretz (1994), but the original source (as Kretz acknowledges) is Burke's (1965) text on the kinetics of phase transformations in metals. Burke's equations, and those in the discussion, apply only to the nucleation and growth of a crystal of phase β within a crystal of a single precursor phase α (Fig. 1a). If the β phase is enriched in component i relative to the host crystal of phase α, precipitation of a crystal of the β phase reduces the concentration of component i in the host crystal of phase α in the vicinity of the precipitate, and generates a compositional gradient within the host crystal: the concentration of component i increases with distance from the precipitate. With continued growth, this gradient becomes progressively shallower, as the nutrient component i must continually be drawn from greater and greater distances from the growing precipitate crystal.

But the situation during the crystallization of garnet porphyroblasts is quite different, in a vitally important way. When garnet grows under diffusional control from a polyphase matrix (chlorite and quartz in Miyazaki's example), the modal proportions of the reactants in the region surrounding the porphyroblast decrease, but the concentration of Al in the intergranular medium remains fixed at the value imposed by local equilibrium with the reactants ($C_{\mathrm{Al,m}}$ in Miyazaki's terminology) as long as any finite amount of both reactants remains. This means that substantial growth can take place *without decreasing the concentration of Al in the intergranular medium except at short distances from the porphyroblast* (Fig. 1b), a situation very different from the one modeled in the discussion. During porphyroblast growth, the as-yet-unreacted precursor crystals closest to the growing porphyroblast function as local sources of Al; they continually supply Al to the intergranular medium as they react away, buffering the Al concentration to $C_{\mathrm{Al,m}}$ until they are wholly consumed. The persistence of these proximal sources of Al means that growth requires only local transport until local reaction is complete; thus the growing crystal does not draw Al from more distal sites until more proximal sources are exhausted. Much steeper compositional gradients than those modeled in the discussion are generated, and they persist to later stages of growth, because no decrease in the local intergranular concentration of Al occurs until one of the two reactants is totally consumed. This buffering effect produces something akin to a "reaction front" that advances outward from the growing porphyroblast, trailing in its wake a steep diffusional gradient that extends only across the region from which one reactant has been completely removed; this contrasts strongly with the wider, shallower, continuous gradient produced in the metallurgical situation modeled in the discussion.

Diffusional fluxes of Al are proportional to the concentration gradients in the intergranular medium, so the generation and persistence of gradients much steeper than those modeled in the discussion mean that Miyazaki's modeled fluxes are too low. In consequence, the modeled concentration values are too high, and the modeled crystallization times are too long. (These miscalculations are compounded by errors in Miyazaki's derivation, and by confusion of two dissimilar quantities, as noted in the Appendix to this reply.) Because

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[§] *E-mail address*: wcarlson@mail.utexas.edu

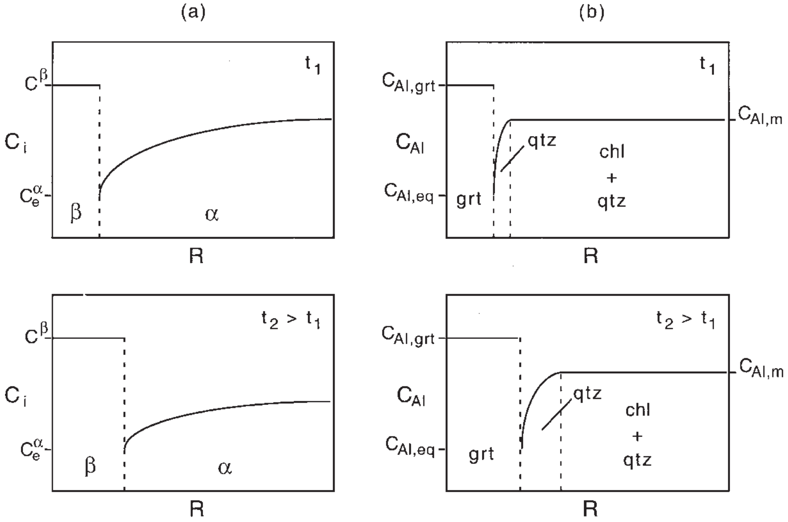

FIG. 1. Schematic illustrations of concentration profiles surrounding crystals growing in different kinds of diffusion-controlled processes. (a) Diagram modified from Burke (1965). In the case modeled in the discussion, a precipitate phase β grows at the expense of its host phase α. The gradient shown is the concentration C_i of component *i* within the α phase. From the earliest stages of growth (t_1, top), laterally extensive gradients are produced; these flatten and extend to greater distance over time ($t_2 > t_1$, bottom). Note that the diffusional medium is the α phase itself, and that the only source of nutrients for the growing crystal is the quantity of component *i* present in solid solution in the α phase. Consequently, any increment of growth causes the concentration to drop across the entire source region. (b) Crystallization of garnet from a polyphase matrix (*e.g.*, chlorite + quartz) is fundamentally different. The concentration gradient shown here is emphatically *not* the bulk concentration of Al in the polyphase matrix, but instead is the concentration of Al in the intergranular medium at various distances from the surface of the growing crystal. This concentration is buffered by the reactant assemblage to the value $C_{Al,m}$, so no gradient forms except in the region in which one of the reactants (here, chlorite) has been completely consumed by reaction. In this case, no diffusion takes place in more distal regions until all proximal sources are wholly exhausted. Also note that whereas material balance requires in case (a) that the increase in the area under the curve (horizontal line) in the β region for any increment of growth must be equal to the total decrease in the area under the curve in the α region, this is not true for case (b). The relative proportion of chlorite to quartz in the matrix determines, for any given increment of growth, the amount of outward migration of the interface between the monomineralic quartz zone and the undisturbed chlorite + quartz matrix, but the value of $C_{Al,m}$ will be the same regardless of the modal proportions of phases in the matrix.

the proper distribution in space and time of the Al sources during porphyroblast crystallization is not taken into account in the model used, the conclusions reached in the discussion have no quantitative validity.

That said, it should be acknowledged that accounting for these effects is by no means a simple task. The model of Carlson *et al.* (1995) employs a step function in the chemical affinity that advances outward from the growing crystal at a rate proportional to $t^{1/2}$, which approximates the “reaction front” in Figure 1b in that each increment of new growth consumes nutrients from a completely undepleted region. It does not, however, compute the effect of the compositional gradient behind this advancing front; the diffusional character of the process is instead inherent in the rate law that governs the advance of the front. To my knowledge, no model presented so far in the literature has attempted to link the crystallization process quantitatively to the actual values of the concentration of Al in the intergranular medium – with the laudable exception of Miyazaki’s (1996) original attempt. The model of Carlson *et al.* (1995) quantifies the magnitude of the effective diffusion coefficient for Al required for nucleation and growth processes; it demonstrates that millimeter-scale crystals grow over times of a few million years in a diffusion-controlled nucleation-and-growth process, with an effective diffusion-coefficient seven to eight orders of magnitude smaller than that called upon by Miyazaki (1996) for Ostwald ripening. It is still not known, however, whether the required diffusion coefficients are consistent with present estimates of the likely concentrations of Al in the intergranular medium. My colleagues and I are presently developing a new approach to such modeling that should allow us to compute this concentration more directly. All of our previous results, however, are based upon calculations that do not require knowledge of this quantity; as a result, they also do not constrain its value.

To conclude, it is appropriate to re-focus this exchange on the central issue raised in the original article: are crystal-size distributions of aluminous porphyroblasts like garnet more likely to be governed by primary nucleation-and-growth processes, or by subsequent Ostwald ripening? Both processes rely upon diffusional transport, and no matter what the values of the intergranular Al concentrations may turn out to be, marked differences exist between these two processes in the magnitudes of the diffusional fluxes. The driving forces (the chemical potential differences and the corresponding differences in concentration) are many orders of magnitude larger for primary nucleation and growth than for Ostwald ripening (*cf.* Fig. 2 of Carlson 1999). Given that the average distances of transport are comparable in both instances (in fact they are shorter for nucleation and growth by a small factor), the concentration gradients and the diffusional fluxes that are proportional to those gradients, and therefore the overall rates of reaction, will likewise be many orders of magnitude larger for primary nucleation-and-growth processes than for Ostwald ripening. Thus nothing in the discussion alters the fundamental conclusion that primary nucleation-and-growth processes are far more likely to govern the size distribution of porphyroblasts than is Ostwald ripening.

Acknowledgement

I am indebted to Richard Ketcham and David Hirsch for discussions that have extended over several years, in which the above concepts of crystallization processes have been developed and refined.

Appendix

Because the derivation presented in the discussion does not apply to porphyroblast crystallization, its correctness was not addressed in the above reply. However, in order to prevent propagation of error into later articles that might seek to use the derivation in circumstances to which it might be properly applied, I feel obliged to note a small mistake: integration of Eq. 6 should lead to

$$R = \left[2 \, \frac{\beta}{\beta - 1} \, \frac{C_{Al,eq}}{\left(\frac{2}{v}\right) - C_{Al,eq}} \, SDt \right]^{\frac{1}{2}}$$

so that Eq. 9 eventually becomes

$$C_{Al,eq} = \frac{2}{v} \, \frac{\beta - 1}{2S\beta^3 + \beta - 1} \, .$$

More importantly, in the next-to-last paragraph, $C_{\mathrm{Al,eq}}$ is equated to $C_{\mathrm{eff}\infty}$, which is incorrect. Because $C_{\mathrm{Al,eq}}$ denotes the concentration of Al in the intergranular medium at the surface of the growing crystal, it is properly equated to $C_{\mathrm{eq}\infty\mathrm{f}}$, a quantity that is some four orders of magnitude greater. This should be apparent from Eq. 13: $C_{\mathrm{Al,eq}}$ depends only on the relevant chemical potentials, and is independent of the value of the interconnected porosity. ($C_{\mathrm{eff}\infty}$ is the mathematical product of $C_{\mathrm{Al,eq}}$ and the interconnected porosity.) The comparison made in the next-to-last paragraph of the discussion is therefore in error by four orders of magnitude; a correspondingly large error enters into the crystallization times computed from Eq. 7 in the discussion's last paragraph.

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The following note was added by Dr. Miyazaki at the proof stage:

1) Small mistakes in Eqs. 7 and 9 were pointed out by Dr. Carlson. I thank him. The correct version is to be found in Dr. Carlson's appendix. With the corrected version of Eq. 9, $C_{Al,eq}$ becomes 5.5×10^{-6} and 5.9×10^{-7} mole/mm^3. These values are six or seven orders of magnitude greater than the appropriate value of concentration of Al in the medium, rather than seven or eight (*cf.* page 1028, right-hand column, middle of the page). With the corrected version of Eq. 7, the time of growth for a grain of garnet 1 mm in radius becomes 1.80×10^{14} years (for $S = 1.095$) and 2.41×10^{15} years (for $S = 0.082$), rather than 7.22×10^{14} and 9.64×10^{15} years, respectively (ninth line from the end of the Discussion).

2) $C_{Al,m}$ is the concentration at $r = R^{\mathrm{dpl}}$. Within the depleted region, a concentration gradient exists, and it can be described with Eq. 3.

3) $C_{eff\infty}$ in Miyazaki (1996) and Carlson (1999) is the mathematical product of $C_{Al,eq}$ and ϕ (porosity), but this is incorrect. If we use the effective diffusion coefficient, the factor ϕ is unnecessary. Here I use Carlson's $C_{eff\infty}$ to show how strange results will be obtained with a set of very low values.