

Competitive diffusion-controlled growth of porphyroblasts

WILLIAM D. CARLSON

Department of Geological Sciences, University of Texas at Austin, Austin TX, 78713, U.S.A.

Abstract

In a diffusion-controlled process of nucleation and growth, adjacent porphyroblasts compete with one another for nutrients. When the effects of this competition are evaluated quantitatively for garnet porphyroblasts in pelitic rocks from the Picuris Range of New Mexico (U.S.A.), significant correlations arise between crystal sizes and the volumes of the domains from which the crystals drew their nutrients. These correlations strengthen the conclusion drawn from earlier work on spatial dispositions, zoning patterns, and crystal size distributions that the kinetics of intergranular diffusion governed the crystallisation of these porphyroblasts.

Computer simulations indicate that competition for nutrients during diffusion-controlled growth may have small but detectable effects on crystal size frequency distributions. Diffusional competition therefore introduces relatively minor inaccuracies into attempts to extract quantitative information on crystallisation processes from size distributions using models for the growth of isolated porphyroblasts. In contrast, the effects of diffusional competition on patterns of compositional zoning may be substantial, especially for porphyroblasts in rocks for which chemical inhomogeneity of the precursor leads to strongly clustered spatial dispositions. In such rocks, clustering may alter the patterns of compositional zoning in ways that obscure evidence for diffusion-controlled growth.

KEYWORDS: metamorphic crystallisation; intergranular diffusion; reaction kinetics.

Introduction

By combining inferences drawn from spatial dispositions, compositional zoning patterns, and crystal size distributions of garnets in pelitic rocks from the Picuris Range of north-central New Mexico, U.S.A., Carlson (1989) demonstrated that the kinetics of intergranular diffusion may dominate the textural development of some porphyroblastic metamorphic rocks. That treatment, however, ignored the effects upon growth rates of competition for nutrients between adjacent porphyroblasts. This article examines the role that such competition might play in the development of porphyroblastic textures.

The spatial disposition of porphyroblasts in metamorphic rocks should provide a critical discriminant between crystallisation processes governed by the rates of intergranular diffusion and processes governed by other possible kinetic controls, such as the rates of interface reaction or rates of heat flow. This is because during a diffusion-controlled process, each growing crystal becomes surrounded by a diffusionaly depleted

zone, within which the chemical affinity for the porphyroblast-producing reaction is reduced relative to the undepleted regions (cf. Carlson, 1989, p. 5 and Fig. 1). The lower chemical affinity for the reaction decreases the probability of nucleation inside these depleted zones. Consequently, in a diffusion-controlled nucleation-and-growth process, each early-formed porphyroblast suppresses further nucleation nearby. In rocks for which the potential nucleation sites are distributed nearly uniformly at scales larger than that of the grain size of the precursors, the development of these diffusionaly depleted zones leads to two distinctive textural characteristics.

First, porphyroblasts growing under diffusional kinetic control will exhibit a tendency toward ordering in their spatial arrangement, with the crystals' centres spaced further apart on average than they would be in a random arrangement of crystals of the same spatial density. By contrast, for an interface-controlled or a heat-flow-controlled process, in which the chemical affinity for the reaction remains spatially uniform throughout the rock, a uniformly distributed set

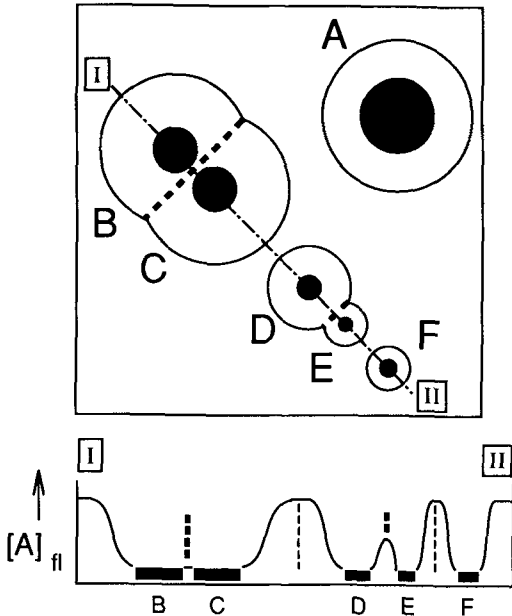


FIG. 1. (Top) Schematic representation of diffusionally depleted zones surrounding: an isolated crystal (A); two crystals (B and C) that both nucleated simultaneously with A but in close proximity to each other; two crystals (D and E) that nucleated after A, B, and C, in close proximity to each other but separated in time so that the later-forming crystal (E) nucleated near the edge of the depleted zone surrounding the earlier-formed crystal (D); and an isolated crystal (F) that nucleated simultaneously with crystal E. The instantaneous growth rate for each crystal is proportional to the instantaneous rate of enlargement of its surrounding depleted zone. Thus for crystal A, the radial growth rate at the time depicted is proportional to the square root of the time elapsed since the nucleation of A, but the radial growth rate for crystals B and C is roughly half as large as that for the isolated crystal A. As time progresses, the growth rate for crystal D will be little affected at first by the presence of crystal E, but the growth rate of crystal E will be roughly half that of crystal F, because of competition for nutrients with crystal D. (Bottom) Schematic representation of variation in chemical affinity for reaction in the intergranular fluid ($[A]_{fl}$) along the traverse I-II. Surfaces of impingement between adjacent depleted zones are boundaries of diffusional domains; their approximate locations are marked by dashed lines.

of potential sites for heterogeneous nucleation will lead to a random disposition of porphyroblasts throughout the rock. Departures from randomness in the spatial dispositions of crystals

are easily quantified, and the statistics compiled by Carlson (1989), following the approach of Kretz (1969), documented a significant tendency toward spatial ordering of garnet porphyroblasts in a suite of rocks from the Picuris Range. That evidence for diffusion-controlled garnet crystallisation was corroborated by patterns of compositional zoning and by crystal size frequency distributions.

Second, a diffusion-controlled nucleation-and-growth process should produce a correlation between the size of a porphyroblast and the size of the diffusional domain from which it extracted its nutrients, under the assumption that the nutrients are distributed nearly homogeneously throughout the rock at scales larger than the precursor grain size. In a diffusion-controlled process, the size of each diffusional domain and thus the size of each crystal will be determined not only by the relative times of nucleation of adjacent crystals but also by the degree of isolation of each crystal from its near neighbours, because the degree of isolation determines the intensity of competition for nutrients during growth. By contrast, in an interface-controlled or heat-flow-controlled process, the size of each crystal will be determined solely by the time at which it nucleated (without effects of competition with its near neighbours for nutrients), so that in such processes, no correlation is expected between the crystal size and any measure of the degree of isolation of the crystal. For the rocks of the Picuris Range suite, Carlson (1989) established statistically significant correlations between crystal size and crude measures of the degree of isolation of crystals from their neighbours, but no attempt was made to identify the actual diffusional domains.

During a diffusion-controlled reaction taking place in a homogeneous matrix, overall growth rates for crystals that nucleate in uncrowded environments should be more rapid than overall growth rates for crystals that nucleate in close proximity to other crystals, but instantaneous rates of porphyroblast growth may change abruptly when enlarging diffusional domains impinge upon one another as crystallization proceeds (Fig. 1). These variations in growth rate that result from competition for nutrients may then alter crystal size frequency distributions and patterns of compositional growth zoning. This article will first attempt to identify, on the basis of measurable textural features, diffusional domains in the rocks of the Picuris Range suite, and will then examine the more general question of the textural effects of diffusional competition for nutrients, using computer simulations of the crystallisation process.

Estimates of crystal isolation and sizes of diffusional domains

To confirm that diffusional competition affects textural development, one must seek meaningful correlations between crystal size and the size of diffusional domains. Several different methods for identifying diffusional domains have been suggested, but few tests of the methods on natural specimens have been published, and no comparisons between methods are available in the literature. Useful comparisons are easily made, however, because the relative value of each method is readily assessed: if a method identifies diffusional domains with complete accuracy, it should produce a perfect linear correlation between the volume of a crystal and the volume of the domain from which it extracted its nutrients, provided (i) that the porphyroblasts are growing from a homogeneous matrix, and (ii) that their sizes are unmodified by exchanges of material between porphyroblasts after nucleation and primary growth ceases (as might occur in Ostwald ripening or annealing). Less accurate methods of identifying domains will yield estimates for domain size that correlate less strongly with crystal size.

Simple measures of centre-to-centre distances. Carlson (1989) initially correlated crystal radius with the simplest measure of crystal isolation, namely the separation between the centre of a porphyroblast and the centre of its nearest neighbour. In an attempt to improve upon this measure of isolation, that work also defined a domain size D calculated by summing the squares of the centre-to-centre distances between each porphyroblast and its six nearest neighbours, then dividing the result by the factor $4\sqrt{3}$. This formulation was designed for analysis of essentially two-dimensional diffusional domains, a situation closely approached by the rocks studied from the Picuris Range in which garnet crystals with nearly coplanar centres grew within thin pelitic strata sandwiched between layers of quartzite. This measure of the size of the diffusional domain would be a completely accurate one only for the case of porphyroblasts that nucleated simultaneously on a planar, perfectly ordered hexagonal array of nucleation sites. Hereafter in this article, domain sizes estimated from this 'hexagonal' approximation will be denoted by the variable D_H . Obviously, a perfectly ordered simultaneous nucleation process corresponds poorly to a natural diffusion-controlled process; nevertheless, values of D_H for garnet porphyroblasts in rocks of the Picuris Range were found to correlate significantly with crystal radius, giving agreement with other more convincing lines of

evidence for the operation of a diffusion-controlled process in these rocks.*

Voronoi polyhedra. Better estimates of the actual sizes of diffusional domains can be obtained by addressing explicitly the effects of competition for nutrients. The most common method for evaluating these effects is the calculation of Voronoi polyhedra (Gilbert, 1962; Boots and Murdoch, 1983; Hayes and Koch, 1984; Evans and Jones, 1987). Voronoi polygons were used, for example, in the analysis of natural textures in thin sections of metamorphic eclogites by Trevis and Kovnuro (1985); see also Kretz (1969, Fig. 7). In the Voronoi method, the diffusional domain is bounded in three dimensions by planes (or in two dimensions by lines) that orthogonally bisect the line segments connecting the centres of neighbouring porphyroblasts. Thus each polyhedron bounded by such planes or lines surrounds a single crystal, and each such polyhedron contains all points that are closer to the central crystal than to any of the other crystals. This measure of the size of the diffusional domain would be a completely accurate one only for the case of porphyroblasts that nucleated simultaneously on sites coincident with the present crystal centres. Hereafter in this paper, domain sizes estimated from this standard Voronoi method will be denoted by the variable D_V . Although D_V should estimate domain sizes more accurately than D_H , for this purpose the standard Voronoi method is still vitally flawed, because it fails to account for the fact that nucleation events are dispersed over time.

Modified Voronoi regions. It is possible in principle to modify the Voronoi method to generate still more accurate estimates of domains and their sizes, if one can incorporate information on the relative times of nucleation of porphyroblasts. Following Gilbert (1962), we recognize that a given point in a rock belongs to the diffusional domain of a given porphyroblast only if the depleted zone surrounding that porphyroblast is the first such zone to reach that point as the depleted zones enlarge during the course of the diffusional nucleation-and-growth episode. Rigorously, we state that a particular point, located at distance d_i from the centre of porphyroblast i , and located at distance d_j from the centre of porphyroblast j , belongs to the diffusio-

* The attempt in Carlson (1989) to establish for rocks of the Picuris Range suite a linear correlation between crystal radius and domain area is erroneous in part. That correlation should be positive but non-linear; a linear correlation should be expected between crystal volume (not radius) and the area of the diffusional domain.

nal domain of porphyroblast i if and only if, for all porphyroblasts j in the rock,

$$\tau_i + \left(\frac{d_i}{2\beta K}\right)^2 < \tau_j + \left(\frac{d_j}{2\beta K}\right)^2 \quad [1]$$

in which the symbols τ_i , τ_j , β and K are used as in Carlson (1989): τ_i and τ_j are dimensionless measures of time, numbers between 0 and 1 that represent the fraction of the nucleation interval that has elapsed prior to the nucleation of the i -th and the j -th crystals respectively; β refers to the ratio between the radius of a depleted zone and the radius of the crystal within it; and K is the growth-rate constant for a diffusion-controlled radial growth-rate law of the form

$$\left(\frac{dR_i}{d\tau}\right) = \frac{K}{\tau - \tau_i} \quad [2]$$

in which R_i is the radius of the porphyroblast. As detailed in Carlson (1989, p. 16), values of β can be estimated from model fits to crystal size distributions, whereas values of K can be estimated from measurements of the volumes of the largest and smallest porphyroblasts in a specimen (V_{\max} and V_{\min}), according to

$$K = \frac{1}{2} \sqrt[3]{\frac{3}{4\pi} (V_{\max} - V_{\min})}. \quad [3]$$

Hereafter in this paper, domain sizes estimated from this modified Voronoi method will be denoted by the variable D_M .

Using this modified Voronoi method, every point in a rock can be assigned uniquely to the diffusional domain of a single porphyroblast if relative nucleation times and the radial growth rates of depleted zones are known. In practice, however, relative times of nucleation cannot be assigned to individual crystals with absolute accuracy. Because crystals that nucleate simultaneously may grow to different sizes as a result of differences in the proximity of their near neighbours, one cannot rigorously compute relative times of nucleation from crystal radii; and unless one knows relative times of nucleation, one cannot rigorously compute domain sizes. Although Equations A15 and A16 of Carlson (1989, p. 23) allow calculation of fractional nucleation times from crystal radii and the simplified diffusion-controlled growth-rate law in Equation [2], such calculations require the assumption that all porphyroblasts in the rock obey an identical, time-invariant growth-rate law. Under that assumption, competition for nutrients

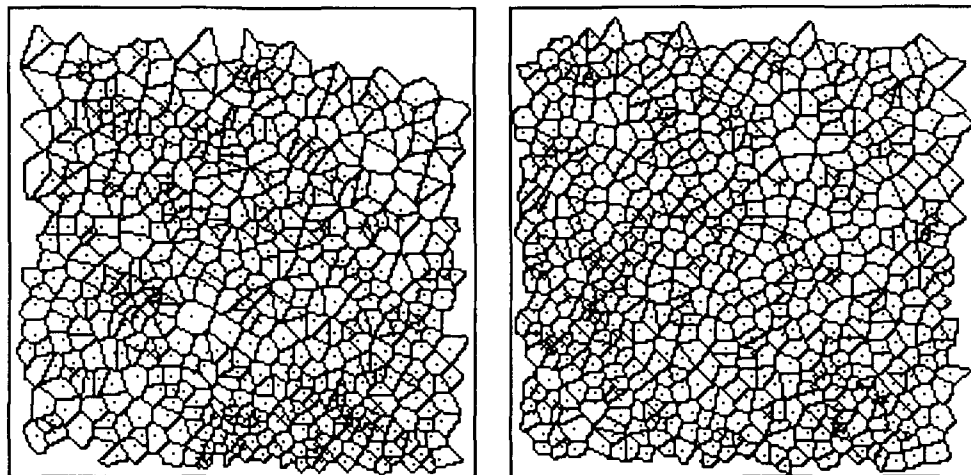
is ignored and the crystals are treated as if they are all growing in isolation from one another.

Thus one's only recourse when analysing natural occurrences is to use equations for the growth of isolated crystals to *estimate* relative times of nucleation from crystal sizes (recognising that this approach will necessarily introduce errors for any individual crystal), and then to rely on the fact that these errors should tend to compensate one another when large numbers of crystals are considered. The compensation arises because the assumption of isolated growth will tend to overestimate growth rates for crystals that are less isolated than the average, but will tend to underestimate growth rates for crystals that are more isolated than the average.

Diffusional domains in rocks of the Picuris Range

To seek meaningful correlations between crystal size and domain size which would, if present, validate the hypothesis of diffusional controls on crystallisation, values of D_H , D_V , and D_M were computed for garnet porphyroblasts in the suite of rocks from the Picuris Range described by Carlson (1989). For each of the specimens in the Picuris Range suite, the radii of garnet porphyroblasts and the locations of their nearly coplanar centres are known to a high level of accuracy. (Details of the data collection process may be found in Carlson, 1989, p. 4.) From these data, D_H is readily calculated. Values for D_V and D_M were computed by considering a square grid of 32,761 points within the analysis area; each such point was assigned to the diffusional domain of a particular crystal on the basis of relative proximity (for D_V) or the relationship given in Equation [1] above (for D_M). The area of each crystal's diffusional domain was then computed by multiplying the number of points assigned to that crystal by the square of the distance between adjacent points. Crystals whose domain boundaries intersected the edge of the analysis area were disregarded, because their actual domain areas are indeterminate. The resolution provided by this calculation is on the order of 1% of the mean domain area; for no sample is the resolution coarser than 2.7% of the mean domain area. Consequently, values of D_H and D_M are precise to within a few percent relative.

Results. Fig. 2 illustrates diffusional domains calculated from the modified Voronoi method for two samples from the Picuris Range suite. Each irregularly shaped region represents the diffusional domain for a single garnet porphyroblast,



Specimen 10

Specimen 11

Fig. 2. Two-dimensional diffusional domains in a pair of specimens from the Picuris Range, calculated using the modified Voronoi method. Dots in the interior of each region represent the measured locations of crystal centres, whereas boundaries between the pseudo-polygonal regions are those calculated on the basis of Equation [1] in the text. Inhomogeneity in the distribution of crystal centres is apparent in Specimen 10 (*left*), with clusters of crystals evident particularly in the lower right portion of the analysis region.

the centre of which is located by a dot in the interior of the domain. Table 1 presents values for the coefficients of linear correlation between porphyroblast volume and domain areas determined by each of the three methods, for all specimens in the Picuris Range suite. Also included are critical values for the correlation coefficients at the 95% confidence level, which depend solely on the number of crystals in each data set. Even using the modified Voronoi method, the correlation coefficients are low, for reasons discussed below. But because the computed correlations exceed the critical values for all samples except Specimen 1, porphyroblast volume and domain area are positively correlated in a statistically significant sense for ten of the eleven specimens.

The existence of any statistically significant

correlation, however small, is petrologically important. Of the possible crystallisation mechanisms considered above, only diffusion-controlled growth generate any correspondence between crystal size and calculated domain size. For interface-controlled or heat-flow-controlled growth mechanisms, those quantities should be completely uncorrelated. Thus the correlations documented in Table 1 corroborate the evidence from compositional zoning patterns and from crystal size distributions for a diffusion-controlled process of nucleation and growth for these porphyroblasts; such correlations are inconsistent with the possibility that crystallisation rates were dominantly governed by the kinetics of interface reaction or heat flow. Moreover, as is expected for rocks in which a porphyroblastic texture is diffusively generated, the highest

Table 1. Coefficients of linear correlation between crystal volumes and domain areas

Sample	1	2	3	4	5	6	7	8	9	10	11
Critical value	0.17	0.09	0.12	0.09	0.07	0.10	0.09	0.15	0.13	0.08	0.08
D_H	-0.01	0.18	0.14	0.21	0.18	0.16	0.17	0.24	0.08	0.19	0.26
D_V	0.10	0.18	0.11	0.21	0.15	0.24	0.27	0.43	0.24	0.19	0.41
D_M	0.15	0.24	0.14	0.27	0.23	0.29	0.32	0.46	0.30	0.23	0.46

correlation coefficients are generally those for D_M , whereas the coefficients for D_V are in most cases lower, and those for D_H are typically lower still. This may be regarded as further confirmation of the dominance of diffusion kinetics as an influence on these porphyroblastic textures, insofar as the modified Voronoi method is one that approximates most closely the geometry of domains produced by a diffusion-controlled nucleation-and-growth process.

It is not surprising that the correlation between D_M and crystal volume is highly imperfect, with correlation coefficients much less than unity, because inaccuracies may be introduced by diverse violations of the assumptions involved. Most important are the inaccuracies that may arise if nutrients are not homogeneously distributed throughout the precursor matrix, and the inaccuracies inherent in the estimation of relative times of nucleation from crystal radii. It is also possible for inaccuracies to arise if crystal sizes have been modified by processes such as Ostwald ripening (cf. Cashman and Ferry, 1988), although there is no evidence for the operation of such a process in the rocks of the Picuris Range suite. These complications blur the correspondence between crystal size and domain size, reducing the computed correlation between those variables. Nevertheless, statistically significant positive correlations do emerge from the noisy data; they document competition during diffusion-controlled growth.

Ordering and clustering in spatial dispositions

In an inhomogeneous arrangement of porphyroblasts, the effects on growth rates of diffusional competition for nutrients will be intense where crystals cluster in close proximity to one another, but will be mild where crystals are relatively widely and evenly spaced. At the extreme, in a perfectly ordered array of crystals, all of which nucleated simultaneously, the effects of diffusional competition would be negligible. Because natural textures exist that range from substantially ordered (e.g. those in Carlson, 1989) to nearly random (e.g. those in Kretz, 1973) to strongly clustered (e.g. those in Kamineni, 1978), it is important to consider possible mechanisms of ordering and clustering, and to seek a simple means of quantifying the degree of ordering or clustering in a given arrangement of porphyroblasts.

As noted above, all diffusion-controlled nucleation-and-growth processes will impose on the spatial disposition of porphyroblasts a tendency toward ordering, because the development of a diffusively depleted zone around each

growing porphyroblast suppresses further nucleation nearby. This inherent tendency toward ordering may be counteracted, however, by localisation or clustering of crystals that can result from non-uniform arrangements of sites for heterogeneous nucleation and from inhomogeneities in the composition of the matrix of precursors from which the porphyroblasts grow. Because most potential nucleation sites are probably at grain boundaries and edges, non-uniformities in the disposition of nucleation sites may be important in rocks for which the precursor minerals are relatively coarse-grained compared to the spacing between porphyroblasts, but this effect may be negligible for fine-grained precursors in which the porphyroblasts are widely spaced. The effects of inhomogeneity in matrix composition may be very significant for layered metasedimentary rocks, in which bulk compositional variation from layer to layer in the precursor sediments enhances the crystallisation of porphyroblasts in some layers but restricts it in others. Each layer considered separately might exhibit substantial ordering, but at scales that encompass more than one layer, the spatial disposition is characterized by localization or clustering of crystals into regions of favourable bulk composition. Lateral variations in composition will have similar effects.

The most commonly employed means of evaluating quantitatively the degree of ordering or clustering of porphyroblasts is the determination of the mean centre-to-centre separation between nearest neighbours. This evaluation is useful because the suppression of nucleation in the vicinity of early-formed porphyroblasts causes nearest neighbours to be spaced further apart on average than they would be in a random disposition of crystals of the same spatial density, whereas localisation of crystals in regions of favourable matrix composition causes nearest neighbours to be spaced more closely on average than they would be in a random disposition of crystals of the same spatial density. Thus a convenient index of the degree of ordering or clustering is the ratio between the observed mean centre-to-centre separation between nearest neighbours and the mean value of that quantity for a random disposition of the same spatial density, which can be evaluated analytically (cf. Kretz, 1969, p. 50). That ratio is here designated the 'ordering index' and denoted by I . Values of I greater than unity reflect an overall tendency toward ordering, whereas values less than unity reflect an overall tendency toward clustering. Large deviations from unity in either direction signify large departures from a random disposition.

Simple measures of the degree of ordering or clustering, such as the ordering index I , have important limitations, because the effects of ordering that arise from diffusional competition can be superimposed upon the effects of clustering that arise from inhomogeneities in the precursor. For example, in the suite of rocks from the Picuris Range studied by Carlson (1989), one sample (Specimen 10) yielded a value for I greater than unity, but still exhibited statistically significant tendencies toward clustering under the 'random-point test', a test for departure from randomness that is apparently particularly sensitive to clustering effects. Alternative tests for departures from randomness that were applied to the same specimen are evidently more sensitive to the ordering effects: all of them revealed a significant tendency toward ordering, although the calculated degrees of ordering for Specimen 10 were notably lower than those computed for the other rocks in the same suite (Carlson, 1989, Table 2). Because the mechanisms that produce ordering and clustering may operate simultaneously, it is possible for a spatial disposition to yield a value near unity for the ratio I , even though the disposition arose from partial ordering by diffusively influenced nucleation at sites localised by compositional inhomogeneities in the precursor. An example of such a disposition is provided (in Fig. 5b). Thus a value for I near unity is not apodictic evidence for a random disposition of porphyroblasts; it can arise as a consequence of the superposition of two independent processes that generate an ordered superstructure within one or more clusters of crystals.

Although measures of ordering and clustering more sophisticated than the single parameter I are clearly desirable, this simple measure may have to suffice until more is learned about the relative sensitivity to ordering and clustering of various alternative measures of departures from randomness. Compared to other possible measures based on the quadrat test, the random-point test, or the impingement test (cf. Carlson, 1989, Appendix 1), the ordering index I possesses the notable advantages of being easily calculated and uniquely defined. These advantages justify its adoption here as the preferred measure of the overall dominance of the effects of either ordering or clustering of porphyroblasts.

Simulations of competitive diffusion-controlled growth

Computer simulations of diffusion-controlled porphyroblast crystallisation allow one to explore

the influence of competition for nutrients on measurable textural features in porphyroblastic rocks. Although the simulations presented here are all three-dimensional, they are in many respects analogous to the two-dimensional simulations reported in Carlson (1989, p. 14–16). The reader is referred to that source for a detailed description and justification of the assumptions and simplifications required for mathematical modelling of a natural diffusion-controlled crystallisation process. In brief, these simulations incorporate a nucleation rate that increases exponentially with time in undepleted regions of the rock (but that is zero within all depleted zones), in accordance with a thermal overstepping that increases linearly with time. The exponential increase in the nucleation rate in undepleted regions is governed by a dimensionless input parameter α that is proportional to the activation energy for nucleation (cf. Carlson, 1989, p. 18, Eqn. 11). The nucleation rate is thus computed from

$$\left(\frac{dN}{d\tau}\right) = \left(\frac{dN}{d\tau}\right)_{\tau=0} \cdot \exp(\alpha\tau) \cdot \left(1 - \frac{V_{\text{dpl}}(\tau)}{V_{\text{tot}}}\right) \quad [4]$$

in which N is the number of nuclei, τ is fractional time elapsed since the onset of nucleation, $V_{\text{dpl}}(\tau)$ is the total volume of depleted regions in the rock at time τ , and V_{tot} is the total volume of rock. The depleted zones are postulated to enlarge at a rate inversely proportional to the square root of time, in accordance with a diffusion-limited reaction mechanism. Thus the rate of radial enlargement of the depleted zone surrounding the i -th crystal is given by

$$\left(\frac{dR_i^{\text{dpl}}}{d\tau}\right) = \beta \cdot \frac{K}{\sqrt{\tau - \tau_i}} \quad [5]$$

in which τ_i , β and K have the meanings defined previously. In the simulations, the quantity β is specified as an input parameter, and K is computed from input values for the minimum and maximum crystal radii according to Equation [3] above. As in the prior simulations, input values for the initial nucleation rate $[(dN/d\tau)_{\tau=0}]$ are adjusted by trial-and-error until an appropriate value is found that generates the desired final spatial density of nuclei. Despite these similarities, however, the present simulations are different from those conducted in Carlson (1989) in two important ways.

The first significant difference is that porphyroblast radii in these simulations are not determined as functions of time by the growth-rate law for an isolated crystal. Instead, each crystal is assigned a final volume proportional to the volume of its diffusional domain. Because the relative times of porphyroblast nucleation and the rates of enlargement of the depleted zones are known quantities, every point in the analysis region of the simulation can be uniquely assigned to the diffusional domain of a single porphyroblast, so that each crystal's diffusional domain is uniquely determined in accordance with Equation [1] above. The radius, and thus the volume, of the largest porphyroblast to be produced is specified as an input value, and the ratio between this specified maximum crystal volume and the volume of the largest diffusion domain generated in the simulation is used as a scaling factor to fix the volumes of all other crystals in proportion to the volumes of their respective diffusion domains. Inherent in these procedures is the postulate of a uniform distribution of a fixed quantity of nutrients in the precursor matrix.

The second significant difference is that the present simulations allow for an inhomogeneous distribution of potential nucleation sites within the analysis region. In the case of garnet porphyroblasts, for example, petrologic evidence often suggests concentration of nuclei in locales probably characterised by high Mn or Al content or perhaps by high ratios of Fe/Mg. In nature, of course, the geometry and distribution of these locales that are relatively favourable for nucleation may be very complex. Their consequences for textural development, however, can be evaluated in a comparatively simple fashion by treating the probability of nucleation as a variable function of distance within the analysis region. If potential sites for nucleation are regarded as homogeneously disposed throughout the precursor matrix, then nucleation should be treated as equally probable everywhere in the analysis region. Alternatively, a single cluster of potential sites for nucleation can be simulated by incorporating a probability function that tends to suppress nucleation at great distances from the centre of the analysis region and to increase the likelihood of nucleation close to the centre. Multiple clusters and concentrations of porphyroblasts in layers can be approximated by specifying probability functions that vary smoothly with one or more of the x , y , and z distances from the origin. But reconnaissance modelling using several of these possibilities demonstrates that the textural effects of diffusional competition do not depend strongly upon the precise geometry of the clustering;

instead, they correlate most strongly and rather simply with the magnitude of the ordering index I . For this reason, the simulations discussed below have used a probability function that localises crystals to varying degrees in a single cluster near the centre of the cubic analysis region. The relative probability of nucleation P decreases outward from the centre of the analysis region according to

$$P = (1 - r)^c \quad [6]$$

in which c is a non-negative number specified as an input parameter, and r is distance from the centre of the analysis region divided by the maximum possible distance (half the length of the body diagonal of the cubic analysis region). It should be emphasised that the function given in Equation [6] has no theoretical basis, and no physical meaning should be attached to the value of c . This function is merely a convenient means of generating spatial dispositions that exhibit variable degrees of ordering and clustering as measured by the ordering index I . As illustrated in Fig. 3, larger values of c concentrate the nuclei more strongly toward the centre of the volume, leading to more densely clustered distributions and smaller values of the ordering index I .

Implications of diffusional competition for quantitative textural analysis

Several intriguing questions are posed by the above demonstration for rocks of the Picuris Range that diffusional competition among growing porphyroblasts exerts a discernible influence on the development of some porphyroblastic

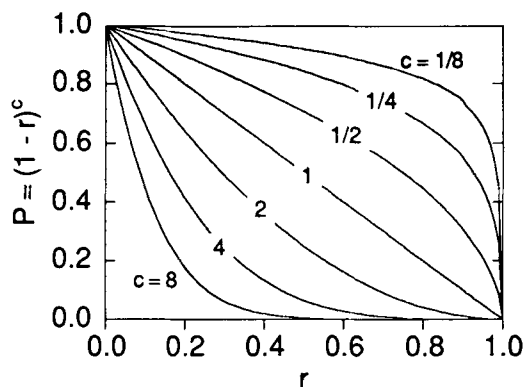


FIG. 3. Probability P of nucleation as a function of fractional distance r from centre of the analysis region according to the relation $P = (1 - r)^c$. Larger values of c concentrate nuclei more strongly toward the centre of the analysis region.

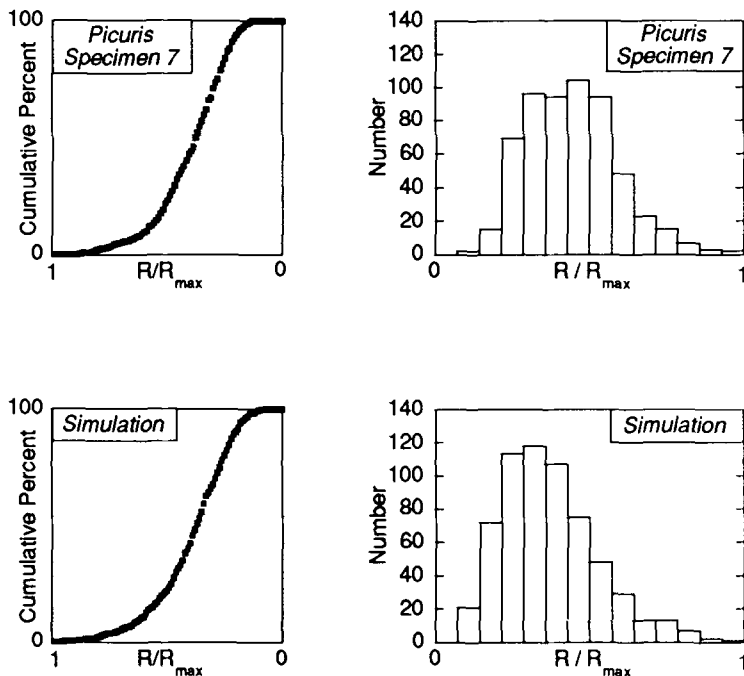


Fig. 4. Comparison of crystal size distributions for porphyroblastic garnet in typical specimen of quartzose pelitic schist from the Picuris Range (*top*) and for typical simulation of competitive diffusion-controlled nucleation and growth (*bottom*). Sigmoidal shape in cumulative size distributions (*left*) is characteristic of many metamorphic minerals in diverse rock suites. Histograms (*right*) display characteristic pseudo-normal shapes with positive skewness.

textures. Are the crystal size distributions generated by a process of competitive diffusion-controlled growth consistent with those observed in typical metamorphic textures? Are crystal size distributions and compositional zoning patterns more strongly affected by diffusional competition when porphyroblasts are strongly clustered? Are the inaccuracies introduced by the estimation of relative nucleation times from crystal sizes significant factors affecting the extraction of quantitative kinetic parameters from porphyroblastic textures? These questions are addressed below by analysing computer simulations of a competitive diffusion-controlled process of porphyroblast nucleation and growth.

Crystal size distributions. Competitive growth under diffusional kinetic control, even when idealised as in the simulations presented here, generates crystal size distributions closely similar to those that characterise many metamorphic minerals from diverse metamorphic environments. Fig. 4 presents a comparison between a typical crystal size distribution measured in one of the rocks of the Picuris Range suite, and the size distribution produced by a typical simulation of a

competitive diffusion-controlled process of crystallisation. The similarities are evident: both histograms are pseudo-normal with distinct positive skewness and with comparable dispersion about their means; both cumulative size frequency distribution curves are sigmoidal, typical of porphyroblasts in regional and some contact metamorphic environments [cf. Fig. 13 of Carlson (1989), which plots data from Kretz (1966)]. Note that Fig. 4 does not represent an attempt to replicate the measured size distribution by adjusting the input parameters for the simulation; if that were done, a simulated size distribution nearly identical to the measured one could be produced. The point of Fig. 4 is rather to illustrate that crystal size distributions consistent with those that typify many metamorphic rocks arise from a process of diffusion-controlled nucleation and growth, in which the textural development is governed by (i) suppression of later nucleation near early-formed porphyroblasts and (ii) competition for nutrients among adjacent porphyroblasts.

Alternative explanations for the origin of these skewed pseudo-normal size distributions have

been proposed. For example, Cashman and Ferry (1988) claim that initial size distributions produced by constant rates of nucleation and growth are subsequently strongly modified by Ostwald ripening, leading to loss of small crystals. Waters (1990) argues that these size distributions can also be ascribed to changes in nucleation rates that result from variations in the thermal overstepping of the porphyroblast-producing reaction. Both of these mechanisms could operate in conjunction with the mechanisms of diffusively influenced nucleation and diffusion-controlled growth advocated here and in Carlson (1989); in fact it is likely that all of these processes operate in nature and that all influence porphyroblastic textures to some degree. The existence of several meritorious alternative explanations for the crystal size distributions commonly encountered in metamorphic rocks is a compelling reason to seek independent textural confirmation of the operation of each of these proposed mechanisms, because a comprehensive model for the nucleation and growth of porphyroblasts must account not only for typical crystal size distributions, but also for the spatial disposition of crystals and their compositional zoning patterns.

To contrast the textural effects of diffusional competition for nutrients in ordered and clustered arrangements, the size distributions generated in three simulations are shown in Fig. 5. All three simulations used identical input values for α (10.0) and for the maximum and minimum crystal radii, and all domain volumes were calculated at the same high level of resolution (less than 0.1% of the mean domain volume). Initial nucleation rates were adjusted by trial-and-error to yield nearly equal numbers of nuclei (550 ± 60) in each simulation. Holding these values constant in all three simulations allows one to isolate the effects of ordering and clustering. The magnitude of those effects is controlled in the simulations by the input values for β and c , and monitored by the resulting ordering index I . Larger values of β impose greater diffusional ordering on the simulation, whereas larger values of c intensify the effects of clustering. For each part of Fig. 5, the value of the ordering index I is specified, and a visual indication of the extent of clustering is afforded by a small diagram that shows the position of each crystal centre (but not the size of the crystal) projected onto a single plane.

In Fig. 5, the close similarity of the crystal size distributions spanning a wide range of values of the ordering index I demonstrates that diffusional competition for nutrients has relatively small effects on the overall size frequencies, compared to the variation in sizes that arises naturally from

the dispersal of nucleation events over time. The simulations do produce a slight broadening of the

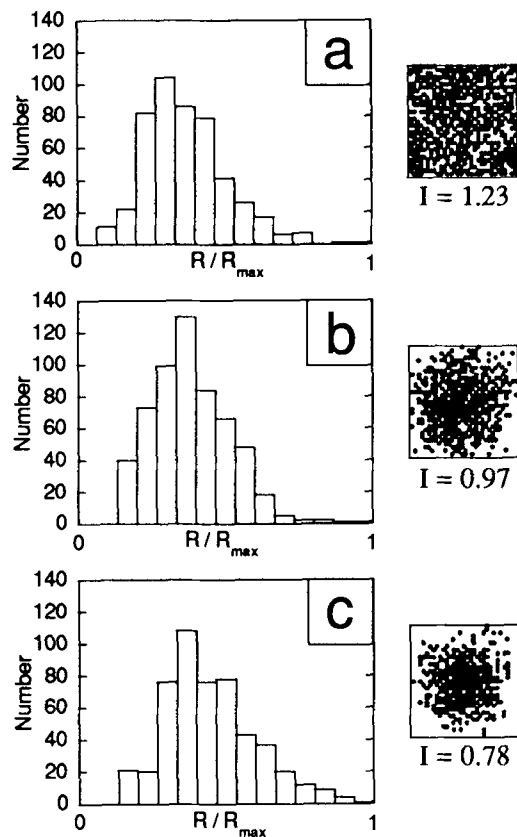


FIG. 5. Effects of ordering and clustering on size distributions produced by competitive diffusion-controlled nucleation and growth. Results are shown for three simulations for which input conditions were virtually identical except for variations in values of the diffusion-ordering parameter β and the clustering parameter c . Small diagrams at right give visual indication of degree of ordering/clustering by projecting locations of all crystal centres (dots) onto a single plane. Values of the ordering index I are also shown. The overall similarity of the histograms demonstrates that ordering/clustering of porphyroblasts has relatively insignificant effects on crystal size distributions. (a) Simulation using $\beta = 3.0$, $c = 0.0$. Ordering index I has value 1.23, comparable to that calculated for most of the natural specimens in the Picuris Range suite. (b) Simulation using $\beta = 2.0$, $c = 4.0$. The value of the ordering index is nearly unity, which would characterise a random disposition, even though the simulation superimposes effects of diffusional ordering on a clustered arrangement of nucleation sites. (c) Simulation using $\beta = 1.0$, $c = 6.0$. This distribution best illustrates the slight broadening that results from tight clustering of nucleation sites.

crystal size distribution for more clustered dispositions: standard deviations of the size distributions in Fig. 5a, b, and c (for which the maximum radius is in every case 0.15 cm) increase from 0.021 cm to 0.022 cm to 0.025 cm. This steady increase is easily explicable. A perfectly ordered arrangement of porphyroblasts would yield a pseudo-normal distribution reflecting the range of nucleation times. Relative to that perfectly ordered disposition, clustering will cause the crystals in any given size class to be spread out over adjacent size classes, with more-isolated crystals entering larger size classes, and less-isolated crystals entering smaller ones. The net effect is to disperse the size distribution somewhat more broadly about its mean. As the comparison in Fig. 5 shows, however, the overall effect is a minor one: crystal size distributions appear to be relatively insensitive to the degree of ordering or clustering in the spatial disposition of porphyroblasts.

Diffusion domains. Each computer simulation yields locations of crystal centres and radii that can be treated in the same way as data from natural specimens to approximate the domains from which each growing crystal extracted its nutrients. This makes it possible to use the simulations to assess the accuracy of the modified Voronoi method for identification of diffusional domains. Fig. 6 illustrates the degree of correspondence between the volumes of the 'actual'

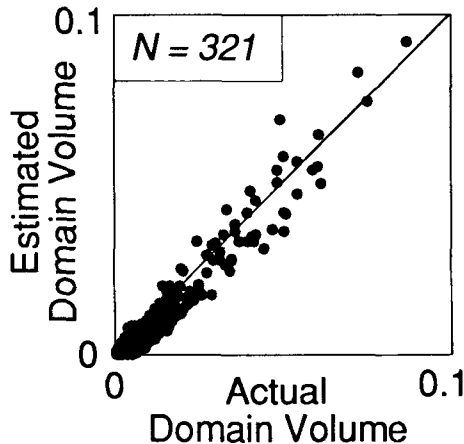


FIG. 6. Correspondence between sizes of 'actual' diffusional domains generated in typical simulation with estimated sizes computed by application of the modified Voronoi method to crystal size and location data from the simulation. Diagonal line indicates perfect correspondence between 'actual' and estimated domain sizes. (Vertical and horizontal axes are scaled in cm^3 , but that scaling is arbitrary, controlled only by the choice of input parameters.)

diffusional domains generated by a typical simulation and the volumes estimated from the modified Voronoi method. In general, the degree of correspondence is quite good, as illustrated by the proximity of the plotted points to the diagonal line indicating perfect agreement between the simulated and the estimated domain volumes. This high level of agreement is found in simulations across a wide range of values for the ordering index I . Thus the inaccuracies that are inherent in the estimation of relative nucleation times from crystal sizes probably do not have significantly deleterious effects on our ability to identify diffusional domains for porphyroblasts in metamorphic rocks using the modified Voronoi method.

Evaluation of kinetic parameters. Carlson (1989) demonstrated that it is possible to obtain quantitative estimates of the activation energy for porphyroblast nucleation by fitting values of the nucleation parameter α to cumulative crystal size distribution curves. Because the model equations presented in that work account only indirectly for the effects of diffusional competition for nutrients during growth, it is important to evaluate the magnitude of the inaccuracies introduced by the use in those equations of average growth-rate parameters. This was done by again treating data on crystal location and sizes from simulations in the same way as data from natural specimens, using the procedure described in Carlson (1989, p. 14–16) to extract values of α and β for each simulation; these values were then compared to the values actually used as input to control the simulation.

Table 2 presents the results of this analysis for three simulations using identical input values of α and β , but different values of the clustering parameter c . Input values of α can be recovered by the fitting procedure with reasonable accuracy. Values of β , however, are evidently overestimated by a factor of two or more when the equations for isolated growth are used; the error is greater in more strongly clustered dispositions.

Table 2. Kinetic parameters

Simulation No.	1	2	3
α (input)	7.5	7.5	7.5
β (input)	2.0	2.0	2.0
c (input)	0.0	4.0	8.0
I	1.13	1.00	0.81
α (fitted)	8.7	8.5	8.2
β (fitted)	3.7	4.0	4.4

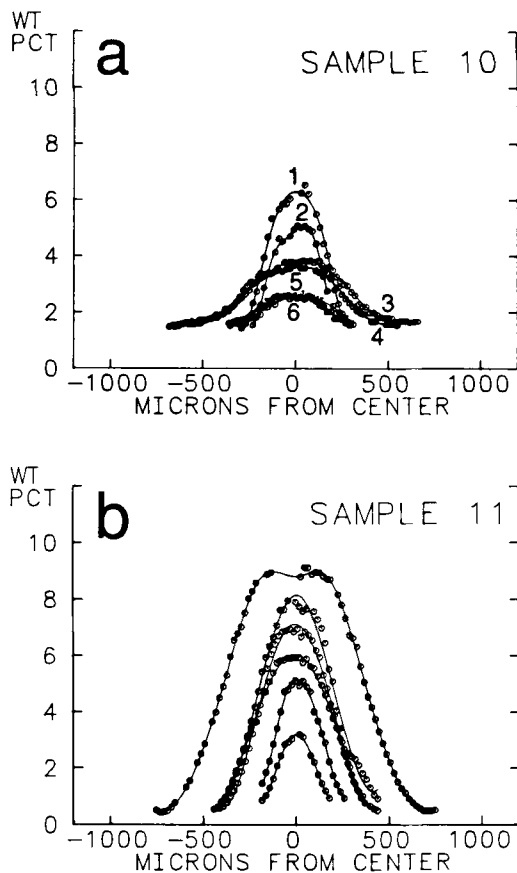


Fig. 7. Concentration profiles for garnets (*a*) in Specimen 10 and (*b*) in Specimen 11 from the Picuris Range suite. Data for MnO are shown for six garnets in each specimen. *Dots* are compositions measured by electron probe microanalysis; *curves* are cubic-spline smoothing functions fitted to the measured analyses. Numbers beside profiles in part (*a*) refer to specific crystals discussed in the text.

Compositional zoning profiles. The effects of competition for nutrients on the chemical zoning of porphyroblasts may be apparent in the contrasting behaviour of garnet porphyroblasts in two samples from the Picuris Range suite. The critical observation requiring explanation is shown in Fig. 7, which presents zoning profiles for Mn in centrally sectioned garnets from two specimens in that suite. In Specimen 11, the zoning profiles for six garnets of different size show central MnO contents that decrease systematically from large crystals to small ones (Fig. 7*b*). This correlation between size and central Mn content is typical of most specimens from the

Picuris Range suite. In Specimen 10, however, the highest central MnO contents are found in garnets of intermediate size (Fig. 7*a*). These differences between specimens are also evident in zoning profiles for Fe and Mg.

The differences between the zoning patterns in Fig. 7*a* and *b* are correlated with contrasting spatial dispositions of the porphyroblasts in the two specimens. In Specimen 11, the ordering index *I* has a value of 1.27, reflecting the strong tendency toward ordering that characterises most other analysed specimens from the Picuris Range. But in Specimen 10, the ordering index has a value of only 1.14, a ratio that is anomalously low by comparison to the other analysed specimens; Specimen 10 also exhibits a statistically significant tendency toward clustering under the 'random-point' test of departure from randomness, and inhomogeneity in the distribution of crystal centres can be statistically verified in this specimen. In the context of the simulations described above, these observations can be explained by processes operating during competitive diffusion-controlled nucleation and growth. Specifically, the hypothesis is advanced here that in Specimen 10, early nucleation in manganese-rich portions of the precursor served to localise clusters of crystals; crystals within these clusters then failed to grow to the large sizes of their more isolated counterparts because of increased competition for nutrients within the clusters.

The instantaneous growth rate of each garnet crystal must depend upon the local abundance of the slowest-diffusing nutrient components in the nearby diffusion field and upon the intensity of competition for those nutrients. But the intensity of the diffusional competition depends in turn upon the local spatial density of nuclei, which might be controlled by other compositional factors that directly affect the probability of nucleation, such as the local abundance of Mn (or perhaps the local Fe/Mg ratio). If sources for the reactant species that instigate nucleation are distributed inhomogeneously in the precursor matrix, then one might expect clusters of early-nucleated crystals to form in the regions of favourable composition. If, however the slowest-diffusing nutrient components are not proportionately enriched in the precursor within the same local area, then more intense competition will diminish overall growth rates in those regions. Zoning patterns like those in Fig. 7*a* may then be interpreted as the result of lower overall growth rates for earlier-formed crystals growing in clusters localised by higher-than-average MnO content in the matrix (crystals 1 and 2), and of higher overall growth rates for later-formed

crystals growing in more isolated environments (crystals 3, 4, 5, and 6).

When data like those in Fig. 7a are plotted on a normalised radius-rate diagram (Kretz, 1974; Finlay and Kerr, 1987; Carlson, 1989), they produce a meaningless scatter, because competition for nutrients within clusters violates the assumption inherent in the normalised radius-rate analysis that all crystals obey an identical growth-rate law. This illustrates that strong clustering may severely disrupt the systematics of diffusionally controlled compositional zoning patterns, so that the porphyroblasts do not contain in their radius-rate relations any evidence of diffusional controls on their growth. It is therefore prudent to restrict the application of normalised radius-rate analysis to rocks in which the spatial dispositions are relatively homogeneous and yield relatively high values of the ordering index *I*.

Similarly, crystals with zoning patterns like those shown in Fig. 7a will produce the largest inaccuracies in attempts to estimate domain sizes from crystal sizes. For example, crystals 1 and 6 have nearly equal radii, so they would be assigned the same relative time of nucleation by the modified Voronoi method, even though their distinctly different central MnO contents suggest that crystal 1 nucleated much earlier in the crystallisation interval than did crystal 6. This mandates caution when attempting to identify diffusional domains in rocks with inhomogeneous dispositions of porphyroblasts.

Summary

When rates of porphyroblast crystallisation are governed by the kinetics of intergranular diffusion, adjacent porphyroblasts must compete with one another for nutrients during nucleation and growth. Diffusion-controlled crystallisation should therefore be characterised by textures in which a positive correlation exists between the volume of a porphyroblast and the volume of the diffusion domain from which it extracted its nutrients. In contrast, interface-controlled or heat-flow-controlled crystallisation should produce textures in which no such correlation exists. Among possible methods of identifying diffusional domains, the approach that corresponds most closely to a natural diffusion-controlled process is the modified Voronoi method, in which estimates of relative nucleation times are assigned to porphyroblasts on the basis of their size and a diffusion-controlled growth-rate law for isolated crystals. In rocks of the Picuris Range, statistically significant correlations exist between porphyroblast volume and domain

size. This documents the existence of competition among porphyroblasts for nutrients during diffusion-controlled growth and corroborates evidence from spatial dispositions, compositional zoning patterns, and crystal size distributions that rates of intergranular diffusion dominated the textural development of these rocks. Computer simulations of competitive diffusion-controlled nucleation and growth suggest that although the effects of diffusional competition on crystal size distributions and on the quantitative inferences drawn from them are relatively minor, such competition may alter patterns of compositional zoning in porphyroblasts sufficiently to disrupt the systematic radius-rate relations that normally characterise thermally accelerated diffusion-controlled growth.

Acknowledgements

This work was influenced by papers presented in September 1990 at the stimulating conference on mineral textures in Manchester, England, and by discussions there with many of those who attended, so I would like to express my gratitude to the speakers and participants, and in particular to Giles Droop and David Polya for organising the meeting. I also wish to thank the institutions that made it possible for me to attend the symposium, in particular the Metamorphic Studies Group of the Mineralogical Society of Great Britain. Informal reviews of the manuscript by Cambria Johnson and Robert Folk are sincerely appreciated. This research was supported by a grant to the author from the Texas Advanced Research Program (no. 003658-147). The Geology Foundation of the University of Texas helped to defray costs of publication.

References

- Boots, B. N. and Murdoch, D. J. (1983) The spatial arrangement of random Voronoi polygons. *Comput. Geosci.*, **9**, 351–65.
- Carlson, W. D. (1989) The significance of intergranular diffusion to the mechanisms and kinetics of porphyroblast crystallization. *Contrib. Mineral. Petrol.*, **103**, 1–24.
- Cashman, K. V. and Ferry, J. M. (1988) Crystal size distribution (CSD) in rocks and the kinetics and dynamics of crystallisation. III. Metamorphic crystallization. *Ibid.* **99**, 401–15.
- Evans, D. G. and Jones, S. M. (1987) Detecting Voronoi (area-of-influence) polygons. *Math. Geol.*, **19**, 401–15.
- Finlay, C. A. and Kerr, A. (1987) Evidence for differences in growth rate among garnets in pelitic schists from northern Sutherland, Scotland. *Mineral. Mag.*, **51**, 569–76.
- Gilbert, E. N. (1962) Random subdivisions of space into crystals. *Ann. Mat. Stat.*, **33**, 958–72.

- Hayes, W. B. and Koch, G. S. (1984) Constructing and analysing area-of-influence polygons by computer. *Comput. Geosci.*, **10**, 411–30.
- Kamineni, D. C. (1978) A study of some garnet aggregates from Yellowknife, Canada. *Neues Jahrb. Mineral. Mh.*, 44–62.
- Kretz, R. (1966) Grain size distribution for certain metamorphic minerals in relation to nucleation and growth. *J. Geol.*, **74**, 147–73.
- (1969) On the spatial distribution of crystals in rocks. *Lithos*, **2**, 39–66.
- (1973) Kinetics of the crystallization of garnet at two localities near Yellowknife. *Can. Mineral.*, **12**, 1–20.
- (1974) Some models for the rate of crystallization of garnet in metamorphic rocks. *Lithos*, **7**, 123–31.
- Trevius, E. B. and Kovnurko, G. M. (1985) Metric characteristics and distribution of mineral grains in rocks and their genetic analysis (by example of garnet from northern Kazakhstan eclogites) [in Russian]. Notes of the All-Union Mineralogical Society, *Zap. Vses. Mineral. Obschch.*, **114**, 313–22.
- Waters, D. (1990) Nucleation and overstepping in prograde metamorphic reactions: Implications for overall reaction rates and crystal size distributions (abstract). *Mineral Textures*, Programme with Abstracts, Joint meeting of the applied Mineralogy Group and Metamorphic Studies Group of the Mineralogical Society, and the Mineral Deposits Studies Group of the Geological Society, Manchester, England, September 1990.

[Revised manuscript received 4 March 1991]