The Canadian Mineralogist
Vol. 37, pp. 403-413 (1999)

THE CASE AGAINST OSTWALD RIPENING OF PORPHYROBLASTS

WILLIAM D. CARLSON

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

ABSTRACT

Recently published numerical models of Ostwald ripening greatly overestimate rates of coarsening for garnet porphyroblasts, because of inappropriate choices for values of the input parameters that control diffusional fluxes of Al. More appropriate values compel the conclusion that diffusional fluxes are much too small for this process to modify garnet size-distributions appreciably, because driving forces are negligible for crystals larger than a fraction of a micrometer. Measured crystal-size distributions for garnet porphyroblasts differ in important details from those predicted for Ostwald ripening, but match those predicted by models of thermally activated primary nucleation and growth. Self-similar pseudonormal porphyroblast size-distributions that coarsen with metamorphic grade, previously offered as the principal evidence in favor of Ostwald ripening, are instead the combined consequence of nucleation rates dependent upon the amount of thermal overstepping of reaction and growth rates that are exponential functions of absolute temperature.

Keywords: Ostwald ripening, crystallization, porphyroblast, kinetics.

SOMMAIRE

Les modèles numériques récemment publiés pour décrire le mûrissement d'Ostwald mènent à une surestimation des taux d'augmentation de la granulométrie des porphyroblastes de grenat, à cause d'un choix inapproprié des valeurs des paramètres introduits pour décrire les flux de l'aluminium par diffusion. Des valeurs plus appropriées mènent à la conclusion que les flux seraient beaucoup trop faibles pour que ce processus soit capable de modifier de façon appréciable la distribution de la taille des cristaux de grenat, compte tenu de la force motrice de cette recristallisation où la taille des cristaux dépasse une fraction d'un micromètre. Les distributions mesurées de la taille des porphyroblastes de grenat diffèrent de façon importante dans les détails de celles prédites selon un mûrissement d'Ostwald, mais elles sont tout-à-fait comparables à celles prévues selon la nucléation primaire et la croissance de cristaux par activation thermique. Les distributions de taille de porphyroblastes pseudonormales et auto-semblables, qui deviennent de plus en plus grossières avec l'intensité de la recristallisation métamorphique, qu'on proposait par le passé comme argument en faveur d'un mûrissement d'Ostwald, semblent plutôt maintenant la conséquence combinée des taux de nucléation selon le degré de dépassement du seuil thermique d'une réaction métamorphique et des taux de croissance variant exponentiellement avec la température absolue.

(Traduit par la Rédaction)

Mots-clés: mûrissement d'Ostwald, cristallisation, porphyroblaste, cinétique.

INTRODUCTION

The pioneering studies of Ralph Kretz (1966, 1969, 1973, 1974) made it evident that metamorphic processes at subcrystalline length scales can be revealed by measurement and analysis of macroscopic textural features of metamorphic rocks. In particular, Kretz showed that crystal size distributions (CSDs) of porphyroblasts, to the extent that they are not modified by later processes, contain detailed information on the mechanisms and relative rates of nucleation and growth of crystals. This contribution to the volume in Kretz's honor considers whether coarsening following primary nucleation and growth has an appreciable effect on the size distributions of porphyroblasts in metamorphic rocks, and concludes that it does not.

BACKGROUND

The CSDs that are initially established by any nucleation and growth process can, at least in principle, be coarsened by recrystallization driven by a reduction in interfacial free energy. Joesten (1991) provided a comprehensive review of the kinetics of such grain growth.

---

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

For present purposes, it is important to discriminate between two types of grain coarsening that may occur in geological systems, because each has distinctly different mechanisms and kinetics.

In single-phase systems, grain coarsening driven by reduction in interfacial free energy is widely acknowledged to operate in a variety of metals and monomineralic aggregates. Geological examples include monomineralic aggregates of quartz, calcite, or wollastonite (Joesten 1991) and of clays (*e.g.,* Eberl *et al.* 1990). Even though driving forces are small, coarsening occurs rapidly in single-phase systems, because material residing in a smaller grain needs only to move across a grain boundary into a neighboring larger grain in order to reduce the total interfacial free energy. Thus the required distances of transport are on the order of the width of a single grain boundary, probably only a tiny fraction of a micrometer.

In polyphase systems, coarsening of particles of one phase disseminated throughout a matrix of one or more different phases will also reduce the total interfacial free energy; the term "Ostwald ripening" is commonly used to describe such an increase in grain size of a precipitate phase in metallurgical or ceramic systems. This process, however, must proceed by mechanisms distinctly different from those that produce grain growth in single-phase systems. Coarsening of a dispersed phase requires diffusional transport of material along grain boundaries or grain edges from small crystals to large, over distances on the order of the mean separation between grains of the dispersed phase. In metamorphic rocks, the most rapid form of such transport would involve, in most circumstances, dissolution of components of smaller crystals into an intergranular fluid occupying an interconnected network of grain edges, transport through the network to the surface of a larger grain, and reprecipitation on the larger crystal.

Controversy exists in the recent literature over the relative importance of Ostwald ripening as a factor in determining the CSDs of garnet porphyroblasts in metamorphic rocks. Whereas Cashman & Ferry (1988) and Miyazaki (1991, 1996) have concluded that garnet CSDs are strongly modified or even largely governed by such processes, my coworkers and I have contended that garnet CSDs in typical metamorphic rocks record, with little or no modification by annealing, the original ranges in size resulting from processes of primary nucleation and growth (Carlson 1989, Carlson *et al.* 1995, Denison & Carlson 1997). In this article, the controversy is re-examined in the light of recently published and new numerical simulations of metamorphic crystallization. The implications of Miyazaki's (1996) elegant numerical models of Ostwald ripening are evaluated after careful scrutiny of the values chosen for the input parameters, leading to the conclusion that Ostwald ripening of garnet proceeds far too slowly in metamorphic rocks to materially affect CSDs. The observations that underlie arguments in favor of Ostwald ripening for metamorphic garnet are then assessed, and alternative explanations are offered for them in terms of thermally accelerated, diffusion-controlled nucleation and growth.

RATES OF OSTWALD RIPENING OF GARNET DURING METAMORPHISM

Analytical descriptions of the process of Ostwald ripening were first presented by Lifshitz & Slyozov (1961) and by Wagner (1961), and the set of equations governing the time evolution of grain-size distributions driven by reduction in interfacial free energy has thus become known as the LSW (Lifshitz – Slyozov – Wagner) theory. The LSW theory postulates that because of the Gibbs – Thompson effect, the equilibrium concentration of a component at the surface of a crystal is an inverse function of that crystal's radius. As a result, gradients in concentration exist between the surfaces of small crystals and the surfaces of larger crystals, which drive diffusion through the intergranular medium. Diffusion transfers material from small grains to large, thereby producing an overall coarsening of the dispersed particles with a concomitant reduction in their number as the smallest crystals dissolve. An important feature of the LSW theory is its prediction that there exists a single steady-state size distribution (when normalized to mean crystal size and maximum frequency), toward which all initial distributions evolve with time. Once this steady state is achieved, coarsening continues without change in the shape of the normalized size-distribution.

Miyazaki (1996) incorporated the precepts of the LSW theory into numerical simulations of Ostwald ripening, in order to extend the theory to the case of an inhomogeneous initial distribution of crystals, for which the LSW theory provides no analytical solution. As a test of the model, he compared its predictions for a homogeneous case with those of the LSW theory. Because the agreement is good, it is likely that the model correctly captures the qualitative aspects of the behavior of these systems during annealing.

The absolute rates of grain coarsening predicted by Miyazaki's model, however, depend very strongly upon the values chosen for the model's input parameters. The most critical parameters are those that control the material fluxes of dissolved components during annealing, in particular the effective diffusion coefficient through the intergranular medium (D_{eff}), and the effective bulk equilibrium concentration of the dissolved components ($C_{\mathrm{eff}\infty}$). [The value of $C_{\mathrm{eff}\infty}$ is given by the mathematical product of the concentration of dissolved components in equilibrium with an imaginary crystal of infinite radius in a connected intergranular fluid network ($C_{\mathrm{eq}\infty\mathrm{f}}$) and the volume fraction occupied by that fluid (ϕ_{f}).] The discussion that follows indicates that even if the most favorable possible choices are made for these parameters, as was done in Miyazaki (1996), rates of coarsening are able to account for porphyroblast sizes only in very fine-grained metamorphic rocks. If more conservative choices for values of the input parameters are made, rates of coarsening by Ostwald ripening turn out to be many orders of magnitude too slow to have appreciable effects on size distributions of metamorphic garnet.

Annealing rates from Miyazaki (1996)

The most generous assessment of rates of Ostwald ripening would use the set of input parameters employed by Miyazaki (1996) to generate his Figure 1, which is reproduced in Figure 1 here. The diagram is a log–log plot that shows the modeled evolution of the mean grain-size of a population undergoing Ostwald ripening as a function of annealing time at a temperature of 500°C. Curves 1, 4, 5, 6, and 7 all use the same input values for the parameters that control the rates of material transfer; they differ only in the initial sizes and number densities of crystals used in the model. All of these curves converge to a single line after different time-intervals, from which it is possible to estimate the time required to reach a given mean size of crystals by Ostwald ripening of a finer-grained population at 500°C. As an example, the calculations indicate that a mean radius of 100 μm would be reached after ~250,000 years, but that a mean radius of 1 mm would not be achieved until ~250 m.y. had elapsed at 500°C. Curves 2 and 3 each reduce, by a factor of ten, one of the input parameters controlling transport rates (D_{eff} or $C_{\mathrm{eff}\infty}$). These curves are superimposed on one another in a parallel line below the first line; along this lower line, the times required to reach any chosen mean grain-size are a factor of ten larger than along the upper line. Thus ~2500 m.y. would be required to reach a mean crystal radius of 1 mm at 500°C using these parameters.

So even if one accepts at face value the input parameters of Miyazaki (1996) that produce the most rapid coarsening (curves 1, 4, 5, 6, and 7), one must conclude that Ostwald ripening in annealing events lasting a few million years at 500°C would appreciably affect only those populations of garnet crystals whose radii before annealing were smaller than about 100–300 μm. Populations of garnet crystals with mean radii larger than about 300–500 μm, which are common in amphibolite-facies regional metamorphic terranes, almost surely did not originate by coarsening of a population of finer-grained precursor crystals.

It should also be kept in mind, however, that rates of coarsening are proportional to rates of intergranular diffusion, which vary exponentially with temperature. If one assumes an activation energy of 140 kJ•mol^{-1} [based on the activation energy determined for intergranular diffusion of Si by Farver & Yund (1998)], rates of coarsening at 300°C would be nearly 2000 times slower, and those at 700°C would be about 100 times faster. Miyazaki's model therefore predicts that anneal-

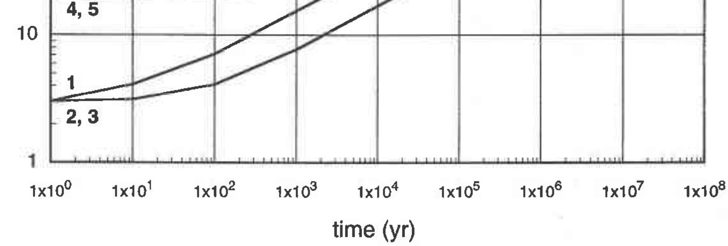

FIG. 1. Relation at 500°C between mean radius (r_{mean}) of garnet crystals and time, as predicted by the LSW theory for Ostwald ripening, redrawn from Miyazaki (1996). Curves 1, 4, 5, 6, and 7 use identical values for all parameters except for initial mean crystal-radius and initial number density. Curves 2 and 3 (superimposed) use the same parameters as curve 1, except that each decreases one of the parameters governing diffusional fluxes by a factor of ten, producing a tenfold increase in the time required to achieve a given mean crystal radius. The analysis of these calculations made in the text argues that the rates of coarsening shown here are overestimated by at least 11 orders of magnitude.

ing at 300°C for a few million years will have appreciable effects only on porphyroblasts with radii smaller than about 10–20 μm, whereas annealing at 700°C for a few million years might produce coarsening of populations with mean radii up to perhaps 1–2 mm.

Overall, the calculations of Miyazaki (1996) indicate that Ostwald ripening could be a viable explanation for garnet CSDs only for populations of very fine-grained porphyroblasts, or perhaps for populations annealed for long times at high temperatures. The calculations reveal a strong dependence of inferred rates of coarsening upon the choices made for values of D_{eff} and $C_{\mathrm{eff}\infty}$. Decreasing either of these parameters by a factor of ten increases the time required for annealing by a factor of ten, sharply reducing the range of possible geological environments in which annealing of dispersed phases can have an appreciable effect. So before accepting a significant role for Ostwald ripening even in those cases for which it appears marginally viable, it would be prudent to examine carefully the values used for the parameters that determine rates of transport.

Values for parameters affecting rates of annealing

Because the mechanism envisioned for Ostwald ripening requires diffusional transport of dissolved species through the rock matrix along an interconnected network of grain edges, rates of coarsening depend directly upon: (1) the effective concentration of the dissolved species in the bulk matrix ($C_{\mathrm{eff}\infty}$), which is the mathematical product of the equilibrium solubility, for a hypothetical crystal of infinite radius, of the components in the connected intergranular fluid network ($C_{\mathrm{eq}\infty\mathrm{f}}$) and the volume fraction occupied by that fluid (ϕ_f), and (2) the effective bulk diffusion coefficient of the components through the rock matrix (D_{eff}). Miyazaki (1996), in concert with others (*e.g.*, Carlson *et al.* 1995), regarded the solubility and transport of Al dissolved in an intergranular fluid to be rate-limiting for the growth and dissolution of garnet. Thus to evaluate the required parameters, one needs information on the solubility of Al in the metamorphic fluid during metamorphism, on the volume fraction of fluid occupying the interconnected network of grain edges, and on the effective rate of diffusion of dissolved aluminous species in the intergranular fluid.

Effective concentration of Al. Miyazaki (1996, p. 280) employed a value of 1.7×10^{-7} mole•mm^{-3} for the solubility of Al in his model. This is the value determined by C.W. Burnham (in Clark 1966) for Al in an H_2O-rich fluid in a natural granitic pegmatite at 9.6 kbar and 600°C. However, Miyazaki also made reference (p. 289) to three experimental determinations of Al solubility in fluids equilibrated with metamorphic assemblages, all of which produced values of 10^{-9} mole•mm^{-3}, more than two orders of magnitude smaller: paragonite + albite + quartz at 2 kbar and 400–500°C (Woodland & Walther 1987), quartz + andalusite + muscovite at 2 kbar and 500–600°C (Pascal & Anderson 1989), and microcline + muscovite + quartz at 2 kbar and 400–500°C (Walther & Woodland 1993). No reason was given by Miyazaki for selecting the higher solubility in preference to the lower value arising in common among all three experimental determinations, all of which seem to have the advantage of matching the simulated temperature (and assemblage?) more closely than does the determination that was chosen. Clearly an argument can be made that the effective concentration of Al should be two orders of magnitude smaller than the value employed in the published simulations appearing in Figure 1.

Volume fraction of fluid network. Miyazaki (1996, p. 280) used a value of 10^{-2} for the volume fraction of the fluid network, citing observed porosities of 1% in experimentally equilibrated aggregates of quartz (Farver & Yund 1992), and a computed volume-fraction of about 1% for trapped fluid inclusions in some metamorphic rocks (Nakashima *et al.* 1995). Only a small fraction of the total porosity, however, is likely to represent interconnected diffusional pathways. Farver & Yund (1992, p. 14,026) actually calculated a lower limit of $1.5–2.9 \times 10^{-5}$ for the fraction of the sample volume that is occupied by interconnected pores, and commented that "...the measured [bulk diffusion coefficient] requires that <1% of the porosity was interconnected at any given time." Thus for a total porosity of 10^{-2}, the effective interconnected pore-volume must be less than 10^{-4}; the calculated lower limit would suggest that it could be as low as 10^{-5}.

Moreover, porosities far lower than 10^{-2} are usually encountered in models of metamorphic fluid flow constrained by petrological and isotopic data. Ferry & Dipple (1991), for example, estimated porosity contributing to flow through metacarbonates at the Beaver Brook (New Hampshire) locality to have been between 2×10^{-3} and 5×10^{-4}; Bickle & Baker (1990) estimated that interconnected porosity along grain edges in marble bands on Naxos, Greece was on the order of 10^{-6}. If one considers that decarbonation reactions in these metacarbonate lithologies produce large reductions in solid volumes, leading to transient reaction-enhanced porosity, it seems likely that interconnected porosities in pelitic and mafic units crystallizing garnet are even lower than these estimates for metacarbonates. In any case, both experimental and petrological evidence suggests that the porosity values appropriate to annealing by Ostwald ripening should be smaller than those employed in Miyazaki's model, by at least two orders of magnitude, and perhaps four.

Effective diffusion coefficient. Of all choices made by Miyazaki (1966) for model parameters, the one that is most discrepant with other values in the literature, and that seems most difficult to defend, is the value of the effective diffusion coefficient for Al in the intergranular medium. Miyazaki (1996, p. 280) asserted that the effective diffusivity of cations in metamorphic fluid is similar to that of oxygen, and employed an experimentally determined diffusion coefficient for ^{18}O in a wetted fine-grained quartz aggregate at 450–800°C from Farver & Yund (1992) as a surrogate for Al diffusion. But this value for oxygen diffusion (10^{-13} $m^2 \cdot s^{-1}$) is many orders of magnitude larger than existing estimates for the effective diffusion coefficient for dissolved Al.

Estimates for the effective diffusion coefficient of Al along interconnected grain-edge networks are derived from numerical models of reaction textures in natural metamorphic rocks by both Ashworth (1993) and Carlson *et al.* (1995). Miyazaki (1996, p. 280) dismissed Ashworth's estimate of $10^{-24\pm2}$ $m^2 \cdot s^{-1}$ (at 550–600°C) because it was determined from relatively "dry" coronal textures, in which fluid components were likely present but not abundant. According to Ashworth (1993, p. 331): "It is very unlikely that a fluid phase penetrated all the grain boundaries within the corona... yet the component H_2O was pervasively available for hydration reactions at internal contacts between layers." The inference is that the grain-edge network contained high concentrations of H_2O, but at levels insufficient to segregate a ubiquitous fluid phase. It therefore seems reasonable to consider this estimate as a lower bound, representing fluid-undersaturated conditions, for the effective diffusion coefficient for Al during metamorphic reactions at amphibolite-facies temperatures.

Higher estimates are obtained in circumstances where prograde dehydration reactions are believed to have produced networks of fluid-saturated grain-edges. Carlson *et al.* (1995) modeled garnet crystallization at ~435–625°C in four regional metamorphic rocks and obtained estimates for the effective diffusion coefficient of Al at 500°C of 0.7–5.1 × 10^{-21} $m^2 \cdot s^{-1}$. This result, compared to Ashworth's value (adjusted to 500°C assuming an activation energy of 140 $kJ \cdot mol^{-1}$) of 1.5 × $10^{-25\pm2}$ $m^2 \cdot s^{-1}$, implies that effective diffusion coefficients for Al are roughly four orders of magnitude greater along fluid-saturated grain edges than along fluid-absent H_2O-bearing grain edges.

Despite their origins in two completely independent approaches, these values appear to be in excellent agreement: the difference between them is consonant with the difference in distance scales over which diffusion was operative in the two cases examined. Whereas the "dry" coronas studied by Ashworth (1993) exhibited diffusive effects over length scales of ~0.1 mm, the diffusional domains in the examples of fluid-saturated garnet crystallization modeled by Carlson *et al.* (1995) are computed to extend over distances of ~10 mm. Because length scales of diffusion are proportional to the square root of the diffusion coefficients, the difference of two orders of magnitude in observed diffusional scales matches well the difference of four orders of magnitude in computed diffusion coefficients.

If one selects the largest value above for the effective diffusion coefficient for Al along interconnected grain edges during garnet growth at 500°C (*i.e.*, 5.1 × 10^{-21} $m^2 \cdot s^{-1}$ from Carlson *et al.* 1995) in preference to the value for ^{18}O diffusion in experimental quartz aggregates (*i.e.*, 10^{-13} $m^2 \cdot s^{-1}$), then one must conclude that the values used by Miyazaki (1996) overestimate Al diffusion rates during Ostwald ripening by at least seven orders of magnitude.

Net effect on coarsening rates. As curves 1, 2, and 3 of Figure 1 show, the rate at which Ostwald ripening can act to modify the CSDs of dispersed phases by coarsening and loss of small crystals is directly proportional to the values of $C_{\mathrm{eff}\infty}$ (= $C_{\mathrm{eq}\infty\mathrm{f}} \cdot \phi_{\mathrm{f}}$) and of D_{eff}. The arguments above lead to the conclusion that in comparison to the values used by Miyazaki, $C_{\mathrm{eq}\infty\mathrm{f}}$ should be smaller by at least two orders of magnitude, ϕ_{f} should be smaller by at least two orders of magnitude, and D_{eff} should be smaller by at least seven orders of magnitude. In combination, these inferences imply that Miyazaki's calculations overestimate rates of garnet annealing by at least 11 orders of magnitude. Because the original model is only marginally able to account for the size distributions of porphyroblasts, even with the most generous possible values for the input parameters, substitution of these more conservative estimates of concentration and rates of transport eliminates Ostwald ripening as a viable mechanism for generating the CSDs of garnet in metamorphic rocks. Partial modification of CSDs by dissolution of the smallest size-fraction is also likely to be negligible, because only crystals with radii of 0.01 to 0.1 μm would be affected at million-year time-scales. For porphyroblasts of typical size, at any reasonable geological time-scale, diffusional fluxes are simply too small for Ostwald ripening to have an appreciable effect.

Driving forces for intergranular diffusion

Is there a contradiction between the above inference that diffusional fluxes during Ostwald ripening are too small to be effective in modifying the size of garnet porphyroblasts, and the prior inference (*e.g.*, Carlson 1989, Carlson & Denison 1992, Denison *et al.* 1997) that intergranular diffusion is the principal process of transport governing garnet crystallization in many metamorphic environments? There is not, for the reason that the driving forces involved differ by many orders of magnitude.

The driving force for Ostwald ripening is a reduction in interfacial free energy upon coarsening. In a steady-state LSW size distribution for Ostwald ripening controlled by matrix grain-boundary diffusion, nearly all crystals (96.7%) are at least half the size of the largest crystal in the distribution [*cf.* Fig. 6 of Joesten (1991), and Fig. 3 below], so for all but a few pairs of crystals, no possible driving force for diffusion would be greater than that produced by a concentration gradient between a crystal and a neighbor twice its size. Application of the Gibbs – Thompson equation (*cf.* Joesten 1991, p. 511) yields a simple expression for the difference in chemical potential ($\Delta\mu$) of a component i at the surfaces of two spherical crystals, one with radius r and the other with radius $2r$: $\Delta\mu = (\gamma\ V)/r$, where γ is the interfacial free energy and V is the molar volume. If one assumes spherical geometry and a value for the interfacial free energy $\gamma_{\text{grt-qtz}}$ of 8.17×10^{-8} kJ•cm^{-2} (Miyazaki 1996, p. 280), this equation gives the straight line in Figure 2, depicting the magnitude of the driving force for Ostwald ripening as a function of grain size.

The driving force for garnet growth governed by intergranular diffusion is the spatial gradient in the chemical affinity for the garnet-forming reaction, which varies over time (*cf.* Carlson 1989, p. 1–3). The chemical affinity ranges spatially from nearly zero at the crystal surface to a maximum at large distances from the crystal, that is, distances beyond the range over which chemical diffusion has been effective, which is on the order of $(D_{\text{eff}} \bullet t)^{1/2}$. In regions unaffected by diffusion, the maximum chemical affinity will increase with time as the equilibrium temperature for the garnet-forming reaction is progressively overstepped in a prograde event. The value for the critical thermal overstepping ($T - T_{\text{eq}}$) needed to initiate reaction is likely on the order of a few degrees, and nucleation and growth of garnet commonly span several tens of degrees. The upper curve in Figure 2 plots the chemical affinity [the difference in free energy between reactants and products, computed from the data of Holland & Powell (1998)] as a function of thermal overstepping at 5 kbar for a model reaction of chlorite [ideal solution between chamosite (their "daphnite") and Fe-substituted amesite (their "Fe-amesite")] and quartz to yield one mole of almandine (T_{eq} = 490°C):

$$^{2}/_{3}\ \mathrm{Fe_{4.5}Al_3Si_{2.5}O_{10}(OH)_8} + {}^{4}/_{3}\ \mathrm{SiO_2}$$
$$= \mathrm{Fe_3Al_2Si_3O_{12}} + {}^{8}/_{3}\ \mathrm{H_2O}.$$

If one takes note in Figure 2 of the logarithmic vertical scale and the logarithmic horizontal scale for crystal size, it is apparent why intergranular diffusion is effective during garnet crystallization, but not during Ostwald ripening: diffusional fluxes are proportional to driving forces, which are orders of magnitude larger for prograde chemical reactions than for reduction of interfacial energy at any geologically relevant scale of crystal size.

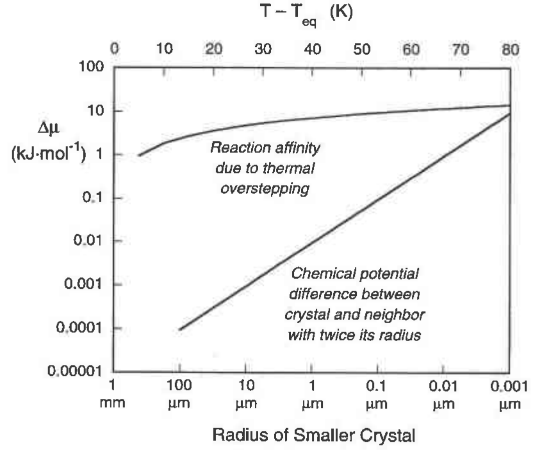

FIG. 2. Comparison of magnitudes of driving forces for diffusion (differences in chemical potential) produced by reduction in interfacial free energy and by chemical affinity due to thermal overstepping of prograde reaction. Note logarithmic scale for difference in chemical potential. Differences in chemical potential between neighboring crystals in populations with mean radii of 0.1 to 1 mm are on the order of 0.01 to 0.1 J•mol^{-1}; chemical potential differences between reactants and products for overstepping in the range 5–50°C are on the order of 1,000 to 10,000 J•mol^{-1}. This immense difference in the magnitude of the driving force accounts for the effectiveness of intergranular diffusion as a mechanism of prograde reaction despite its ineffectiveness in achieving reductions in interfacial free energy by Ostwald ripening.

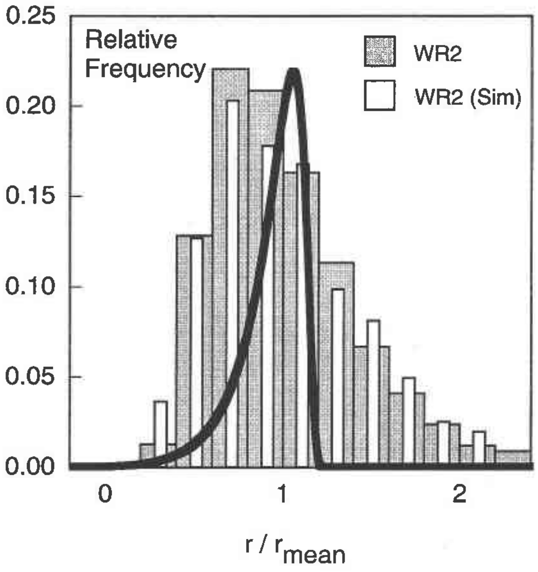

FIG. 3. Comparison of natural, modeled, and theoretical CSDs. Gray histogram: CSD for natural population of garnet crystals in amphibolite from Llano Uplift, Texas (sample WR2). White histogram: CSD generated by numerical model of diffusion-controlled nucleation and growth. Black line: CSD predicted by LSW theory for Ostwald ripening controlled by grain-boundary diffusion. Data for histograms from Carlson *et al.* (1995).

ALTERNATIVE ORIGIN FOR SELF-SIMILAR, PSEUDONORMAL CSDs THAT COARSEN WITH GRADE

The notion that size distributions of garnet porphyroblasts were either generated by Ostwald ripening (Miyazaki 1991) or strongly modified by it (Cashman & Ferry 1988) is based principally on (1) a presumed similarity in shape between the measured CSDs of porphyroblasts and the CSD predicted by the LSW theory, or (2) the observation that with increasing grade, mean grain-size increases without much change of shape of the normalized CSD, while the number density of crystals decreases. If Ostwald ripening does not appreciably affect porphyroblast sizes, one is forced to reconsider the degree of similarity of measured and theoretical CSDs, and to seek an alternative origin for self-similar, pseudonormal CSDs that coarsen with grade. As shown below, measured size-distributions for porphyroblasts actually depart significantly from the predictions of the LSW theory, whereas pseudonormal size-distributions (which match measured CSDs and which coarsen with increasing metamorphic grade yet remain self-similar) arise naturally from the kinetics of crystallization governed by thermally activated nucleation and growth.

Comparison of natural CSDs to predictions of LSW theory

Important but underappreciated differences exist between natural CSDs for porphyroblasts and CSDs predicted by the LSW theory. As illustrated in Figure 3, measured and theoretical distributions differ markedly in skewness, maximum crystal size, and degree of dispersion about their mean values. The consistency and the magnitude of these differences suggest that Ostwald ripening is not a principal determinant of porphyroblast size.

The first vital difference is that natural CSDs commonly, though not invariably, display positive skewness (*e.g.*, Kretz 1966, Figs. 1, 3, 5, and 8, Cashman & Ferry 1988, Fig. 2, Denison & Carlson 1997, Figs. 2 and 3), whereas the CSDs predicted by LSW theory are negatively skewed (*e.g.*, Joesten 1991, Fig. 6; Miyazaki 1996, Fig. 5). A second, particularly striking difference is that the LSW theory predicts vanishingly small percentages of crystals with radii greater than about 1.5 times the mean radius, contradicting the observation that crystals with radii greater than this limit are abundant in natural distributions. For instance, numerous large crystals (ranging in radius up to three times the mean) are evident in Figure 10 of Cashman & Ferry (1988); crystals larger than the LSW limit are also numerous in all of the natural CSDs cited above. A third conspicuous difference is that most natural CSDs exhibit considerably greater dispersion about their mean than is permitted under LSW theory. The LSW theory predicts that 94% of the crystals should fall in the range $0.75 < r/r_{\text{mean}} < 1.25$. In the specimens examined by Denison & Carlson (1997), however, only 37–68% (typically ~50%) of the crystals fall into that range. Although a large volume-fraction of crystals will broaden the LSW distribution, this effect is too small to account for the observed dispersion except at volume fractions approaching unity; moreover, this broadening has a negligible effect on the number of large crystals ($r/r_{\text{mean}} > 1.5$) and does not alter the distribution's negative skewness (Joesten 1991, p. 524). Miyazaki (1996, p. 125) explained this discrepancy as the result of heterogeneity in the spatial distribution of garnet, causing local fluctuations in mean concentration, but even the narrow CSDs in his Figure 3 are all (except perhaps one) broader than the LSW prediction; in addition, the broader CSDs in Denison & Carlson (1997) are found in all specimens, regardless of the degree of spatial heterogeneity in crystal locations.

Given these striking and widespread discrepancies, the claim that size distributions of natural porphyroblasts correspond to the predictions of the LSW theory is tenuous, and probably an overgeneralization that cannot be substantiated in detail. As shown below, other mechanisms of crystallization produce CSDs that match natural distributions more closely.

Comparison of natural CSDs to predictions of models for diffusion-controlled crystallization

Recent work has shown that processes of garnet nucleation and growth governed by rates of intergranular diffusion are commonplace in regional metamorphic rocks across a range of bulk compositions and regional metamorphic environments (*e.g.*, Carlson 1989, Denison & Carlson 1997). The defining characteristic of diffusion-controlled crystallization is the presence of local gradients in the chemical affinity for the garnet-forming reaction within the intergranular medium around growing crystals. During growth, a diffusionally depleted zone develops around each crystal, within which nucleation is suppressed by the low chemical affinity for reaction. These depleted zones increase in size as the crystals within them grow, gradually reducing the fraction of the rock within which nucleation is possible. As the depleted zones enlarge, they eventually impinge and coalesce, but even where local coalescence is complete, residual gradients in chemical affinity for reaction still persist; further diffusion of nutrients in response to these residual gradients generates an increment of growth even after nucleation has essentially ceased. For a more complete description of this entire process, see Carlson (1989, p. 1–3.)

Numerical simulations of this process closely replicate the CSDs and many other textural features measured in natural samples (Carlson *et al.* 1995, their Fig. 5). The general form of the CSD that arises from this process is a positively skewed, pseudonormal frequency distribution, the precise shape of which reflects the interplay of several factors. Nucleation during a prograde crystallization event takes place in undepleted portions of the rock at a rate that increases exponentially with the extent of thermal overstepping of the equilibrium curve for the reaction. Thus in the early stages of reaction, when most of the rock volume is undepleted, nucleation rates rise steadily, because the undepleted portions of the rock are increasingly out of internal equilibrium from the time that a discontinuous reaction boundary is first crossed or a multivariant reaction band for a continuous reaction is first entered. This thermal increase in net rate of nucleation is progressively counterbalanced by the gradual elimination of undepleted regions in the rock, as the diffusionally depleted zones enlarge with time; thus the net rate of nucleation reaches a maximum, then declines rapidly to zero as the undepleted volume-fraction shrinks. The early steady rise in nucleation rate combines with a rapid cessation of nucleation when depleted zones coalesce to produce a positively skewed CSD. The precise temperature–time history determines the degree of skewness (*cf.* Carlson *et al.* 1995, Fig. 7). Growth driven by residual chemical-affinity gradients after nucleation ceases accounts for the fact that the minimum crystal-size for the population is not vanishingly small.

Figure 3 offers a visual comparison between a typical natural CSD, the model CSD produced by numerical simulation of thermally accelerated, diffusion-controlled nucleation and growth, and the predictions of the LSW theory for Ostwald ripening controlled by matrix grain-boundary diffusion. It illustrates that observed porphyroblast size-distributions can be explained by the operation of primary nucleation and growth processes without Ostwald ripening, and that numerical models of such processes generate CSDs that match those measured in many natural occurrences more closely than does the LSW distribution.

Changes in CSDs with increasing metamorphic grade

One feature of garnet size-distributions that makes Ostwald ripening seem attractive is the common observation that mean sizes of crystals may increase with grade while crystal number densities decrease, as documented, for example, by Cashman & Ferry (1988). Annealing subsequent to primary crystallization might be thought to produce more pronounced coarsening and more substantial reduction in numbers of crystals in higher-grade rocks, because "high-grade portions of metamorphic terranes are hotter and cool over longer periods than low-grade portions" (Cashman & Ferry 1988, p. 411).

But an increase in grain size with grade is a predictable consequence of primary nucleation and growth taking place over a range of temperatures. The explanation for an increase in porphyroblast sizes with grade may lie in the fact that nucleation rates increase exponentially with the degree of thermal overstepping of the

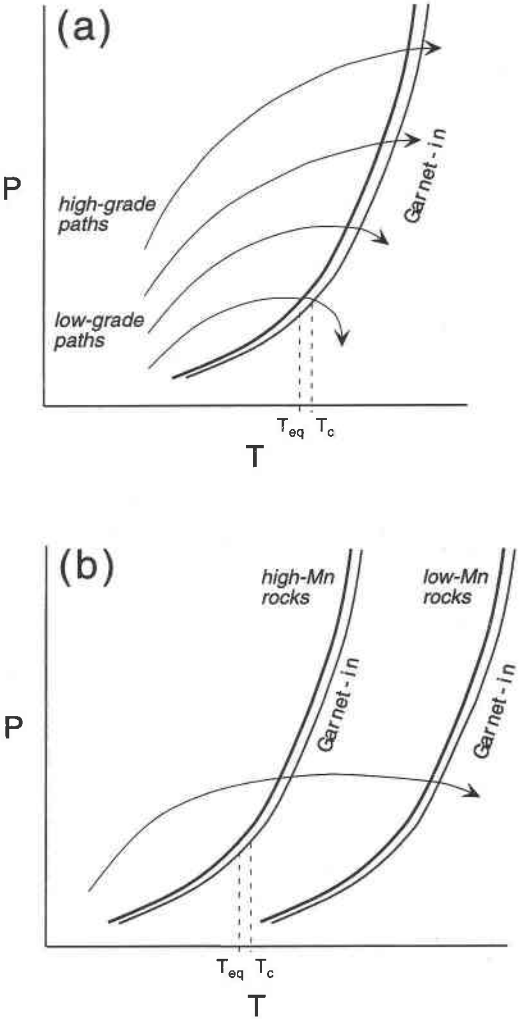

FIG. 4. (a) Schematic P–T diagram illustrating general increase for a prograde sequence of P–T paths of the equilibrium temperature for a typical garnet-in reaction (T_{eq}) and the critical temperature of overstepping required to initiate nucleation (T_c). Because the driving force for nucleation is a function of the thermal overstepping ($T - T_{eq}$), rates of nucleation are nearly equivalent for a given amount of overstepping along low-grade and high-grade paths. In contrast, rates of growth depend exponentially upon absolute temperature, such that crystal growth is much faster for a given amount of overstepping along high-grade paths. Thus reduction of reaction affinity along low-grade P–T paths is accomplished by a prolonged interval of nucleation that yields large numbers of slow-growing crystals, whereas reduction of reaction affinity along high-grade P–T paths can be accommodated by rapid growth on crystals that nucleate soon after T_c is reached. (b) Diagram illustrating that similar variations in the temperature at the onset of garnet crystallization may arise from the effects of bulk composition, leading to variations in mean grain-size for rocks that reach equivalent peak conditions.

reaction, whereas diffusion rates (which control crystal growth) increase exponentially with absolute temperature. As a result, overstepping a reaction by 10°C at 400°C will produce the same rate of nucleation as would overstepping a reaction by 10°C at 550°C, but diffusion rates at 400°C will be roughly 100 times slower than those at 550°C (assuming an activation energy of 140 kJ•mol^{-1}). Consequently, growth of existing crystals is a far less efficient means of restoring equilibrium at 400°C than at 550°C. Many crystals growing slowly at low temperature are needed to produce the same total reduction in reaction affinity as a few crystals growing rapidly at high temperature. Thus the kinetics at high temperature favor rapid growth on existing nuclei, whereas the kinetics at low temperature favor nucleation of new, slowly growing crystals. The end result is to produce fewer, larger crystals at higher grade.

As shown schematically in Figure 4a, the onset of garnet crystallization may tend to occur at higher temperatures in higher-grade rocks, because normal clockwise *P–T* trajectories encounter a typical garnet-in reaction at different pressures and temperatures along its positive slope. Of course, porphyroblasts in high-grade rocks are not observed universally to be coarser than those in low-grade rocks; any effect of grade on grain size can be masked or mimicked by differences in the relative abundance of favorable sites of nucleation, for example, as well as by effects of bulk composition. As shown schematically in Figure 4b, differences in bulk composition may produce differences in the temperature of onset of garnet crystallization that could lead to different CSDs in rocks that traverse the same *P*–T path, for reasons identical to those above.

Here I consider the prediction that, with all other factors being equal, primary nucleation and growth of porphyroblasts over a range of temperatures will lead to an increase in grain size with grade. This prediction has been tested by simulating diffusion-controlled nucleation and growth using the time-explicit numerical model described in Carlson *et al.* (1995). All simulations used identical input parameters, except for the

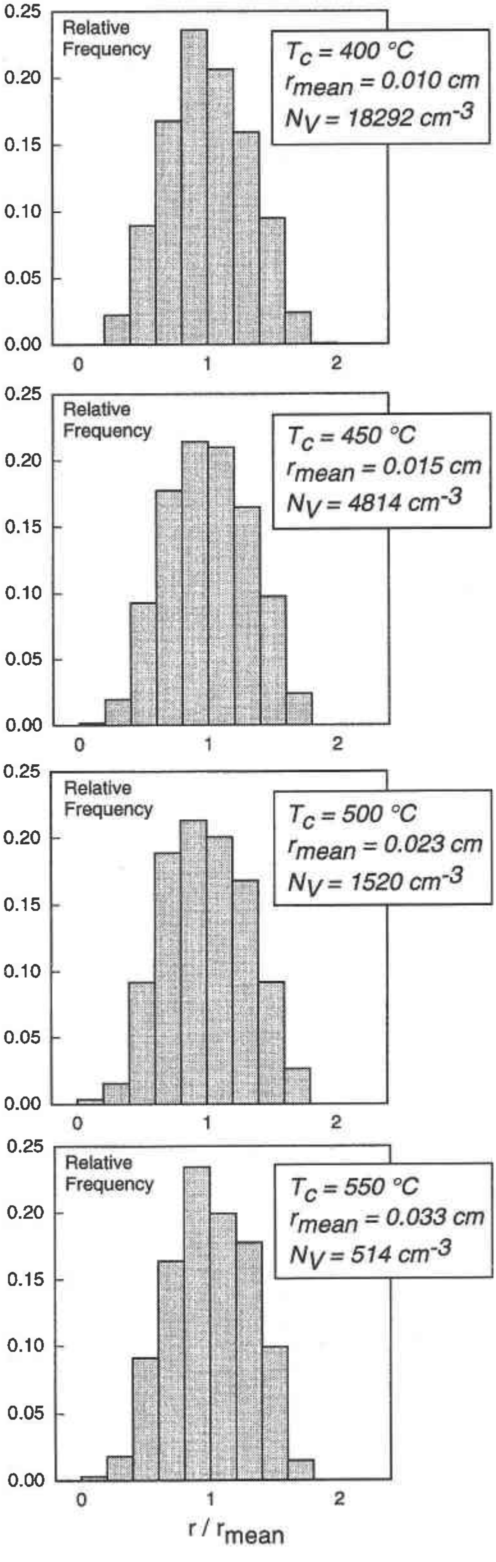

FIG. 5. Comparison of frequency distributions of crystal size produced by primary nucleation and growth processes initiated at different temperatures (T_c), as computed by the numerical model of Carlson *et al.* (1995). Vertical axes are normalized to maximum frequency, and horizontal axes are normalized to mean crystal radius. If plotted in this way, the CSDs are seen to be self-similar across a range of grade, while clearly increasing in mean radius (r_{mean}) and decreasing in crystal number density (N_V). Except for the value of T_c, all simulations used identical input parameters: initial rate of nucleation $[dN/dt]_{t=0} = 1 \times 10^{-4}$ s^{-1}•cm^{-3}; thermal dependence factor for nucleation $\kappa = 0.07$ K^{-1}; effective diffusion coefficient at infinite temperature $D_\infty = 1 \times 10^{-7}$ cm^2•s^{-1}; activation energy for diffusion $Q_D = 140$ kJ•mol^{-1}; heating rate $dT/dt = 10$ K•Ma^{-1}; volume fraction of garnet = 10%.

value of the temperature at which crystallization began. These simulations were designed to reproduce the general character of the prograde sequence of samples studied by Cashman & Ferry (1988), so they correspond broadly to the range of temperatures and grain sizes reported there. The CSDs generated by the model are shown, plotted on normalized axes, in Figure 5. All of them are slightly positively skewed pseudonormal distributions; when plotted on normalized axes, they are nearly identical to one another, demonstrating self-similarity across a range of grade. The mean grain-size increases steadily with increasing grade, whereas the crystal number density decreases, in a manner closely analogous to that reported by Cashman & Ferry (1988). The temperature intervals over which nucleation and growth were found to take place ($T_c - T_{95}$, as defined in Carlson *et al.* 1995), for a constant heating rate of 10°C/m.y., were 400–482°C, 450–512°C, 500–542°C, and 550–581°C; thus crystallization beginning at 400°C required 8.2 m.y. to complete, while the same amount of crystallization beginning at 550°C required 3.1 m.y. to complete.

These simulations confirm the prediction that lower temperatures require a more prolonged interval of growth on smaller but more numerous crystals, all other factors being equal. Together, they demonstrate that processes of thermally accelerated diffusion-controlled nucleation and growth can produce self-similar CSDs that coarsen with grade, an observation formerly attributed to Ostwald ripening.

Finally, it is worth noting that any growth mechanism for which the kinetics increase exponentially with absolute temperature will produce this coarsening with grade, given nucleation rates that increase with thermal overstepping. In particular, an interface-controlled mechanism of growth [see examples in Daniel & Spear (1997) and Spear & Daniel (1997)], if it obeys a thermally activated (Arrhenius-type) rate law, will generate the same contrast between rapid growth of existing crystals at high temperatures and nucleation of new, slowly growing crystals at low temperatures.

CONCLUSION

Re-evaluations of published models of Ostwald ripening using more appropriate estimates for parameters governing the diffusional flux of Al, coupled with assessment of the magnitude of the relevant driving forces, require the conclusion that coarsening of garnet porphyroblasts driven by reduction in interfacial free energy cannot have an appreciable effect on porphyroblast sizes. Instead, observations of self-similar pseudonormal CSDs that coarsen with metamorphic grade are explained by thermally dependent mechanisms of primary nucleation and growth: an exponential increase in rates of growth with increasing temperature, combined with rates of nucleation that are functions of reaction overstepping rather than absolute temperature, produce less numerous but larger crystals at higher grade.

ACKNOWLEDGEMENTS

Richard Ketcham was instrumental in creating the time-explicit numerical model for diffusion-controlled nucleation and growth. David Hirsch performed some enlightening preliminary calculations on the relative magnitudes of driving forces. They are also thanked, along with Cambria Denison and James Rougvie, for providing comments on an early version of the manuscript. Helpful reviews were provided by Ray Joesten and Stuart Raeburn. This work was supported by NSF Grant EAR–9417764 to the author, and by the Geology Foundation of the University of Texas at Austin.

REFERENCES

ASHWORTH, J.R. (1993): Fluid-absent diffusion kinetics of Al inferred from retrograde metamorphic coronas. *Am. Mineral.* **78**, 331-337.

BICKLE, M.J. & BAKER, J. (1990): Advective-diffusive transport of isotopic fronts: an example from Naxos, Greece. *Earth Planet. Sci. Lett.* **97**, 78-93.

CARLSON, W.D. (1989): The significance of intergranular diffusion to the mechanisms and kinetics of porphyroblast crystallization. *Contrib. Mineral. Petrol.* **103**, 1-24.

________ & DENISON, C. (1992): Mechanisms of porphyroblast crystallization: results from high-resolution computed X-ray tomography. *Science* **257**, 1236-1239.

________, ________ & KETCHAM, R.A. (1995): Controls on the nucleation and growth of porphyroblasts: kinetics from natural textures and numerical models. *Geol. J.* **30**, 207-225.

CASHMAN, K.V. & FERRY, J.M. (1988): Crystal size distribution (CSD) in rocks and the kinetics and dynamics of crystallization. III. Metamorphic crystallization. *Contrib. Mineral. Petrol.* **99**, 401-415.

CLARK, S.P., JR. (1966): Solubility. *In* Handbook of Physical Constants (S.P. Clark, Jr., ed.). *Geol. Soc. Am., Mem.* **97**, 415-436.

DANIEL, C.G. & SPEAR, F.S. (1997): The interface-controlled growth of garnet in regional metamorphic rocks from NW Connecticut. *Geol. Soc. Am., Abstr. Programs* **29**, 338.

DENISON, C. & CARLSON, W.D. (1997): Three-dimensional quantitative textural analysis of metamorphic rocks using high-resolution computed X-ray tomography. II. Application to natural samples. *J. Metamorphic Geol.* **15**, 45-57.

________, ________ & KETCHAM, R.A. (1997): Three-dimensional quantitative textural analysis of metamorphic rocks using high-resolution computed X-ray tomography. I. Methods and techniques. *J. Metamorphic Geol.* **15**, 29-44.

EBERL, D.D., ŚRODOŃ, J., KRALIK, M., TAYLOR, B.E. & PETERMAN, Z.E. (1990): Ostwald ripening of clays and metamorphic minerals. *Science* **248**, 474-477.

FARVER, J.R. & YUND, R.A. (1992): Oxygen diffusion in fine-grained quartz aggregates with wetted and non-wetted microstructure. *J. Geophys. Res.* **97**, 14017-14029.

________ & ________ (1998): Bulk diffusion of selected cations in a natural quartz aggregate. *Eos, Trans. Am. Geophys Union* **79**, 369 (abstr.).

FERRY, J.M. & DIPPLE, G.M. (1991): Fluid flow, mineral reactions, and metasomatism. *Geology* **19**, 211-214.

HOLLAND, T.J.B. & POWELL, R. (1998): An internally consistent thermodynamic data set for phases of petrological interest. *J. Metamorphic Geol.* **16**, 309-343.

JOESTEN, R.L. (1991): Kinetics of coarsening and diffusion-controlled mineral growth. *In* Contact Metamorphism (D.M. Kerrick, ed.). *Rev. Mineral.* **26**, 507-582.

KRETZ, R. (1966): Grain-size distribution for certain metamorphic minerals in relation to nucleation and growth. *J. Geol.* **74**, 147-173.

________ (1969): On the spatial distribution of crystals in rocks. *Lithos* **2**, 39-69.

________ (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**, 123-131.

LIFSHITZ, I.M. & SLYOZOV, V.V. (1961): The kinetics of precipitation from supersaturated solid solutions. *J. Phys. Chem. Solids* **19**, 35-50.

MIYAZAKI, K. (1991): Ostwald ripening of garnet in high P/T metamorphic rocks. *Contrib. Mineral. Petrol.* **108**, 118-128.

________ (1996): A numerical simulation of textural evolution due to Ostwald ripening in metamorphic rocks: a case for small amount of volume of dispersed crystals. *Geochim. Cosmochim. Acta* **60**, 277-290.

NAKASHIMA, S., MATAYOSHI, H., YUKO, T., MICHIBAYASHI, K., MASUDA, T., KUROKI, N., YAMAGISHI, H., ITO, Y. & NAKAMURA, A. (1995): Infrared microspectroscopy analysis of water distribution in deformed and metamorphosed rocks. *Tectonophys.* **245**, 263-276.

PASCAL, M.L. & ANDERSON, G.M. (1989): Speciation of Al, Si, and K in supercritical solutions: experimental study and interpretation. *Geochim. Cosmochim. Acta* **53**, 1843-1855.

SPEAR, F.S. & DANIEL, C.G. (1997): Garnet growth in the garnet zone. *Geol. Soc. Am., Abstr. Programs* **29**, 338.

WAGNER, C. (1961): Theorie der Alterung von Niederschlagen durch Umlosen. *Z. Elektrochem.* **65**, 581-591.

WALTHER, J.V. & WOODLAND, A.B. (1993): Experimental determination and interpretation of the solubility of the assemblage microcline, muscovite, and quartz in supercritical H_2O. *Geochim. Cosmochim. Acta* **57**, 2431-2437.

WOODLAND, A.B. & WALTHER, J.V. (1987): Experimental determination of the solubility of the assemblage paragonite, albite, and quartz in supercritical H_2O. *Geochim. Cosmochim. Acta* **51**, 365- 372.

Received November 3, 1997, revised manuscript accepted July 28, 1998.