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NUMERICAL SIMULATION OF THE DISEQUILIBRIUM GROWTH OF GARNET IN CHLORITE-BEARING ALUMINOUS PELITIC ROCKS

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ABSTRACT

Computer simulation of garnet growth in the assemblage garnet–chlorite–kyanite–muscovite–quartz–water, according to several reaction models, illustrates that the reaction processes controlling growth can be distinguished by compositional-zoning profiles and the dependence of partitioning on bulk composition and grade. Three models produce zoning profiles similar to those described in the literature: (1) reaction–controlled growth, (2) Rayleigh fractionation, and (3) equilibrium growth. However, only the reaction-controlled-growth model explains the variations of garnet-core compositions and the variation of the partitioning coefficient of Mn as functions of bulk composition and sample grade that have been documented in garnet- and staurolite-grade rocks. Sufficient data on intergranular diffusivities do not exist to reject the diffusion-controlled-reaction model, but the assumptions about multicomponent diffusivities required to produce zoning profiles consistent with observation make the success of the model unlikely; published studies on nucleation and growth of garnet also provide evidence against the diffusion-controlled-growth model. The reaction-controlled growth model assumes that (1) the nucleation of garnet is delayed to a temperature above which equilibrium growth would begin, (2) chemical potentials remain nearly uniform in the matrix during growth and (3) diffusion does not occur within garnet. The equilibrium partitioning coefficient assumed in the Rayleigh fractionation model is incorrect for major elements. A disequilibrium-partitioning model is derived here for multicomponent systems that differs from the Rayleigh fractionation model in its prediction that the coefficient is sensitive to bulk composition, extent of crystallization and amount of overstepping. The success of the reaction-controlled-growth model, the commonly euhedral morphology of garnet and published observations on nucleation and growth rate suggest that the rate of garnet growth is limited principally by the reactions at the garnet surface (interface kinetics) and by the dissolution rate of reactant phases. Diffusion-controlled textures or structures can still be generated even if interfacial reactions are the rate-limiting processes, but the mobilities of components in these structures will be underestimated if the effect of interfacial reactions is not taken into account. Simulations of the equilibrium growth of garnet at various locations in a hypothetical contact aureole indicate that: (1) the radial growth-velocity of garnet at the garnet isograd and within the staurolite zone differ by many orders of magnitude, (2) the radial growth-velocity is highest during formation of the core and decreases with time, and (3) rapid equilibrium-growth is followed by a long period of residence near the maximum metamorphic grade. Observations (1) and (2) probably explain the propensity of high-grade rocks to overstep nucleation, and (2) and (3) may explain the apparent equilibrium in the matrix in contrast to the significant dispersion of partition coefficients recorded by garnet cores and their inclusions.

Keywords: crystal growth, garnet, computer simulation, disequilibrium.

SOMMAIRE

D'après une simulation par ordinateur de la croissance du grenat dans l'assemblage grenat–chlorite–disthène–muscovite–quartz–eau, et selon plusieurs modèles de réaction, on peut distinguer les processus de réaction responsables par le profil de la zonation des cristaux et par la dépendance des coefficients de partage de la composition globale et l'intensité du métamorphisme. Trois modèles concordent avec les profils publiés: (1) croissance gouvernée par une réaction, (2) fractionnement de type Rayleigh, et (3) croissance à l'équilibre. Seul le premier de ces modèles rend compte et des variations de composition du noyau des cristaux, et des changements dans le coefficient de partage du Mn en fonction de la composition globale et de l'intensité du métamorphisme, observés dans les roches à grenat et à staurotide. Les données sur la diffusivité intergranulaire ne suffisent pas à infirmer un modèle de réaction à diffusion contrôlée; toutefois, les hypothèses nécessaires concernant les coefficients de diffusivité dans un système à composantes multiples et les résultats déjà publiés sur la nucléation et la croissance du grenat rendent l'acceptation de ce modèle peu probable. Le premier modèle suppose 1) un délai dans la nucléation des cristaux jusqu'à une température supérieure au point de croissance à l'équilibre, 2) une quasi uniformité des potentiels chimiques dans la matrice pendant la croissance, et 3) l'absence de diffusion interne. Les coefficients de partage à l'équilibre, postulés dans le modèle de fractionnement de Rayleigh, sont inadmissibles pour les éléments majeurs. Un modèle de répartition avec déséquilibre, élaboré ici pour les systèmes à multi-composantes, diffère du modèle de Rayleigh lorsqu'il prédit que le coefficient de partage est fonction de la composition globale, du degré de cristallisation et de l'importance de l'emboîtement des réactions. Le succès du premier modèle, l'abondance de cristaux et les observations publiés sur les taux de nucléation et de croissance font supposer que le taux de croissance est limité surtout par la cinétique des réactions à la surface du cristal et de dissolution des réactifs. Les textures ou structures dues à la diffusion peuvent se former même si les réactions à l'interface limitent le taux de croissance, mais la mobilité des composantes sera sous-limitée si l'on néglige l'effet de ces réactions. Une simulation de la croissance à l'équilibre en divers points d'une auréole de contact hypothétique donne les résultats suivants: 1) les vitesses de croissance radiale du cristal à l'isograde du grenat et dans la zone à staurotide diffèrent l'une de l'autre de plusieurs ordres de grandeur, 2) la vitesse de croissance atteint un maximum lors de la formation du noyau et décroît avec le temps, et 3) à toute croissance rapide à l'équilibre succède une longue période statique près du point culminant du métamorphisme. Les observations 1) et 2) expliquent vraisemblablement la tendance des roches fortement métamorphisées à outrepasser la nucléation; 2) et 3) pourraient expliquer l'apparence d'équilibre dans la matrice en dépit de la dispersion importante des coefficients de partage dans le noyau des cristaux et leurs inclusions.

(Traduit par la Rédaction)

Mots-clés: croissance cristalline, grenat, simulation par ordinateur, déséquilibre.

INTRODUCTION

If chemical equilibrium is attained in a metamorphic rock, evidence of its geological history up to that point is lost. Disequilibrium assemblages, on the other hand, offer the opportunity to decipher a record of changing conditions that more clearly constrains tectonic models of metamorphism. The interpretation of disequilibrium assemblages to yield history requires knowledge of the processes by which crystals grow and are destroyed.

The emphasis in this paper is placed on the growth processes of garnet for several reasons: (1) it is a common mineral that forms large crystals, (2) compositional zoning and inclusions that differ from matrix crystals are formed and preserved, (3) the description of the diffusion process is simplified in isotropic crystals, and (4) thermodynamic and experimental data are available. Many investigators have been interested in garnet and have advanced many hypotheses on the growth and zoning of crystals. The preceding paper on simulations of garnet growth under equilibrium conditions (Loomis & Nimick (1982) and this paper on disequilibrium growth processes of garnet in chlorite-bearing, aluminous pelitic rocks contribute to the subject by (1) demonstrating the significant differences between the thermodynamic constraints of the multicomponent system and the binary models usually applied to describe garnet, (2) illustrating the possible effects of nonequilibrium partitioning laws on the popular Rayleigh fractionation model, (3) emphasizing evidence for disequilibrium growth (overstepping), and (4) arguing for the significance of interfacial processes in metamorphic reactions.

The thermodynamic data and methods used to calculate equilibrium partitioning of Mg, Fe and Mn between phases are described in the preceding paper (Loomis & Nimick 1982). As stated there, the simulations of garnet growth are restricted to garnet–chlorite assemblages containing excess aluminum silicate, muscovite and quartz. The total pressure is assumed to be 5 kbar and the water pressure, 4 kbar. The chlorite–garnet assemblage was chosen because garnet often develops first in prograde sequences primarily at the expense of chlorite; this is the simplest assemblage that can be used to produce realistic simulations of garnet growth. Moreover, Mn is an important element responsible for compositional zoning of garnet and, of the major phases present in low-grade rocks, only chlorite usually contains much Mn. Constant mole fractions of "additional" cations (garnet 0.1, chlorite 0.24) in addition to Mg, Fe and Mn are assumed to be present in the phases to make their compositions similar to those occurring naturally and to reduce the extrapolation of compositions from the natural assemblages from which thermodynamic data were derived. The standard bulk composition used to illustrate growth of garnet is reported in Table 3 of Loomis & Nimick (1982). This composition represents a typical Al-rich pelitic rock. One thousand garnet nuclei per mole of oxides, equivalent to approximately 56 nuclei per cm^3 of rock, are assumed to be present. The use of a different or variable number of nuclei would change the radius of the simulated zoning profiles but would have no effect on the compositional history of the first crystals to form.

DISEQUILIBRIUM-GROWTH MODELS

Disequilibrium growth involves several processes that are poorly known in geological systems. Consequently, we only discuss the manner in which these variables might influence growth and suggest the types of evidence that indicates the operation of disequilibrium processes in rocks. Two models of disequilibrium growth of garnet from chlorite are introduced in the next sections, followed by an evaluation of their predicted effect on zoning profiles. The analogous growth-models are discussed in greater detail for the growth of plagioclase from plagioclase melts in Loomis (1981). The measure of disequilibrium in metamorphic reactions analogous to undercooling in igneous systems is usually called "overstepping". It is defined as the actual temperature of growth minus the equilibrium temperature for the phase assemblage for the bulk composition.

Diffusion-controlled reaction

The diffusion-controlled-reaction model is commonly applied to the analysis of metamorphic reactions, although its implications for compositional zoning have not been examined. The model assumes that the rate of reaction is limited *only* by the rate at which components can be transferred among discrete reaction sites determined by nucleation processes. For garnet growth from chlorite, the diffusing elements that control zoning in garnet in the present model are Mg, Fe and Mn. The alternative "reaction-controlled growth" model, discussed below, is appropriate if the diffusion rate of the stoichiometric components Al or Si limit growth rate.

The constraints of the diffusion-controlled-growth model are most easily understood by considering first the binary Mg–Fe system shown by solid curves in Figure 2 of the preceding paper (Loomis & Nimick 1982), where its calculation is described. If the temperature is raised to 775.6 K without any reaction occurring (50 K overstepping), the composition of chlorite (B) is shown by the box in Figure 2 (Loomis & Nimick 1982). At this temperature, garnet nucleates and disequilibrium growth proceeds at constant temperature until equilibrium is achieved throughout the matrix. Because the only process limiting the growth rate of garnet is exchange diffusion of Mg and Fe in the matrix, the initially rapid growth of garnet will drive the chemical potentials of these matrix components *at the garnet surface* to values corresponding to equilibrium at 775.6 K. The compositions of chlorite and garnet corresponding to the local equilibrium situation at the garnet surface are shown as C and G, respectively. In the binary Mg–Fe system, these compositions are unique. Chemical potential gradients

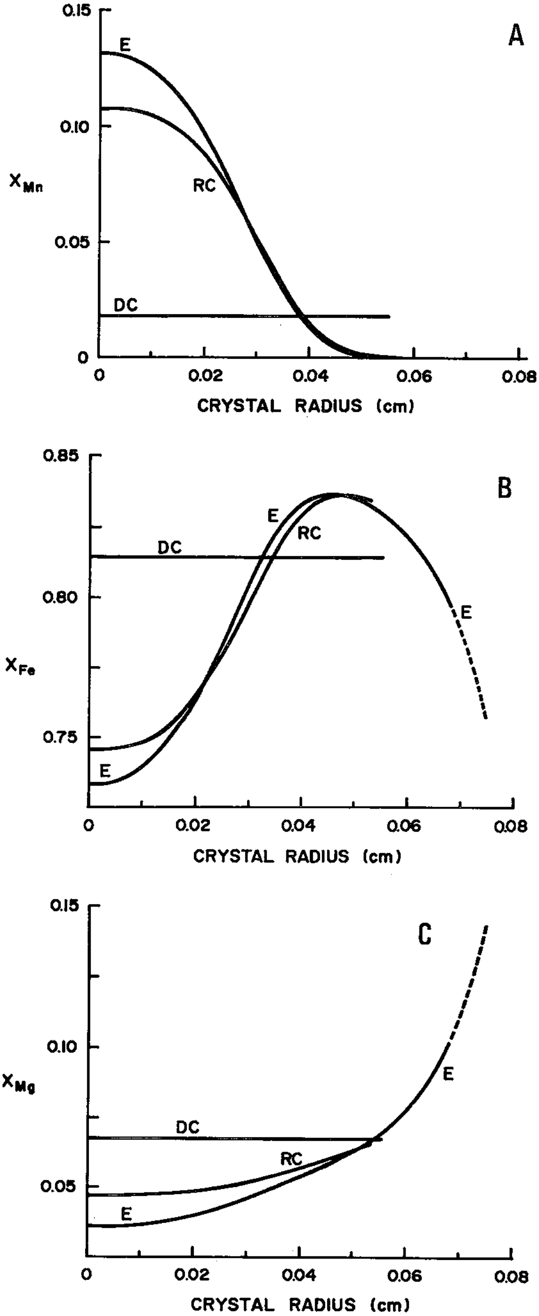

FIG. 1. Computed zoning profiles for the pelitic bulk composition in Table 3 of Loomis & Nimick (1982) according to the following models: E equilibrium growth between 725.6 and 835 K (dashed where metastable), DC diffusion-controlled growth at 50 K overstepping (775.6 K), and RC reaction-controlled growth at 50 K overstepping (775.6 K). A Mn profiles, B Fe profiles, C Mg profiles.

of Mg and Fe are established in the matrix between the garnet–chlorite equilibrium condition at the surface of the garnet and the chemical potentials of these elements, as defined by the composition of chlorite away from the garnet (B in Fig. 2 of Loomis & Nimick 1982). If chlorite is present in the region around garnet, its composition should vary from C at the garnet surface to B out in the matrix. The rate of garnet growth will decline with time as diffusion gradients diminish, and growth will stop when all remaining chlorite in the matrix reaches composition C. The garnet produced will be homogeneous with a composition G.

If temperature varies after garnet nucleates, the compositions of garnet (G) and chlorite (C) that reflect the local equilibrium state at the garnet surface will vary according to the requirement of the phase diagram. Large variations in temperature during growth would be necessary to induce significant zoning. Only isothermal growth is considered here.

The isothermal growth of garnet by a diffusion-controlled model is less well defined in the ternary system because the equilibrium compositions of garnet and chlorite depend on bulk composition as well as temperature. The simplest simulation is shown in Figure 1 as profile DC. The equilibrium composition of garnet at each step of growth was calculated using the *bulk composition of the matrix.* The equilibrium compositions of garnet and chlorite are shown as G_2 and C_2, respectively, on Figure 3 of the preceding paper; these equilibrium compositions at 775.6 K can be contrasted with those for the same bulk composition at 725.6 K (G_1 and C_1), representing the initial conditions for equilibrium growth of garnet. The computed profile is unzoned because components are removed from the matrix by garnet in proportion to their equilibrium partitioning into this phase.

The actual constraints on relative diffusion rates implied by the simulation shown in Figure 1 are not easily determined. Presumably, a bell-shaped Mn profile might be generated if the diffusion exchange of Mn and Mg were much faster than Fe and Mg. At the initiation of growth, the inhibited diffusion of Fe toward garnet would raise the "apparent" bulk composition content of Mn and stabilize an equilibrium composition of garnet enriched in Mn and deficient in Fe. Eventually Mn would be depleted in the matrix, however, and the composition of garnet would migrate toward a Fe-rich composition. Unfortunately, quantitative simulation of the growth of garnet crystals controlled by multicomponent diffusion processes in spherical co-ordinates is beyond our current ability. Whereas it may theoretically be possible to generate a bell-shaped Mn profile using unequal diffusivities of Mg, Fe and Mn, the assumption that Mn diffuses many times faster than Fe seems unlikely. The data of Blackburn (1968) on compositional variations of garnet in high-grade metamorphic rocks suggest that Mn equilibrated over only a slightly larger volume than Fe, although both do show more extensive equilibration than Mg. A more likely prediction of zoning would be that the Mg content of garnet would be depressed initially, raising both Fe and Mn values; subsequent fractionation of the matrix would cause both Fe and Mn to fall as Mg rises. Other observations that argue against the importance of diffusion control of garnet growth are discussed in the section below on processes of disequilibrium growth.

Reaction-controlled-growth model and disequilibrium partitioning

This model assumes that the rate of garnet growth is limited by factors *in addition* to the diffusion of Mg, Fe and Mn in the rock matrix. Consequently, diffusion gradients of Mg, Fe and Mn in the matrix will be reduced. In the end-member case investigated here, it is assumed that the rate of growth is sufficiently slow that chemical potential gradients of Mg, Fe and Mn in the matrix are eliminated. This assumption is identical with that for the basic Rayleigh fractionation model (Hollister 1966). Several processes could restrict the rate of garnet growth in this way and will be considered in the section on processes of disequilibrium reaction.

Two consequences of the reaction-controlled-growth model are: (1) local equilibrium at the crystal face is *not* maintained, and (2) the crystal composition can be influenced by crystallographic factors if growth is interface-controlled. The absence of local equilibrium at the crystal interface adds uncertainty to our interpretation of partitioning of elements between phases.

A partitioning model commonly used for Mn in garnet is Rayleigh fractionation (Hollister 1966, Atherton 1968), in which a partitioning coefficient $K_E(i)$ indicates the relative mass or mole fraction of component i in the crystal of interest (x) and the matrix phase(s) (m): $K_E(i) = X_i^x / X_i^m$. It is commonly assumed that K_E for partitioning between two phases is primarily a function of temperature, and that changes of K_E may reflect changing temperature because constant K_E is expected for isothermal growth. Only Hollister (1966, 1969a) recognized that it is necessary to assume that Mn is a minor component in order to regard K_E as constant. Unfortunately, many of the assumptions regarding the behavior of K_E during equilibrium and disequilibrium growth are incorrect.

If we assume ideal solution of components in the phases, K_E is indeed a function only of temperature *at equilibrium*. However, the equilibrium value of K_E cannot be correct for a disequilibrium system. This can be easily illustrated by arbitrarily defining the composition of the matrix phase (chlorite) and using the equilibrium K_E for each element to calculate the composition of garnet; the result is a sum of mole fractions unequal to one. Thus, the element-partitioning constant is a function of the matrix composition. The Rayleigh fractionation model, as implemented above, appears to work if only one component is calculated or if a trace element is considered, because mass or molar abundance problems are not obvious. In practical applications, the complications of non-ideal solution and varying relative abundances of multiple matrix-phases (Hollister 1969a) also obfuscate comparison of data and simulations.

Hopper & Uhlmann (1974) have proposed three models of nonequilibrium partitioning for binary systems based on thermodynamic reasoning; the application of these models to the growth of plagioclase is evaluated by Loomis (1981). Of these, the first is pursued here because it is analogous to the Rayleigh fractionation model, the second is an approximation that produces a result equivalent to the diffusion-controlled simulations presented above, and the third usually requires too many thermodynamic data for general use.

The disequilibrium-partitioning model requires that the free energy of the system be reduced a maximum amount for a given amount of reaction, a model compatible with the assumptions of irreversible thermodynamics. I will extend the model to systems of n components and evaluate it in terms of simple thermodynamic quantities as follows. The system comprises an assemblage containing the solid-solution crystal of interest, denoted x (garnet) and a matrix assemblage m (chlorite). The energy per mole of the solid-solution phases are:

$$g_x = \sum_i X_i^x \mu_i^x,\ i = 1,n \tag{1}$$

$$g_m = \sum_i X_i^m \mu_i^m,\ i = 1,n$$

The chemical potentials μ are defined for ideal solution by, for example,

$$\mu_i^x = \mu_i^{x,o} + \mathrm{RT}\ln X_i^x\ i = 1,\ n, \tag{2}$$

where $\mu_i^{x,o}$ refers to a standard state at the temperature and pressure of growth. Following Hopper & Uhlmann, the m and x assemblages are formed from an initial m assemblage, where m had the composition X_i^0. The free energy of reaction to form N moles of x and M moles of m from one mole of m of the initial composition is:

$$\Delta G = Ng_x(X_i^x) + Mg_m(X_i^m) - g_m(X_i^0) + \Delta G_E, \tag{3}$$

where ΔG_E represents the change in free energy attributable to other phases. The mass-balance constraints for each component i are:

$$NX_i^x + MX_i^m = X_i^o \tag{4}$$

The value of ΔG is maximized as a function of crystal composition for a fixed amount of reaction (N and M constant) and fixed initial X_i^0 by requiring

$$\left(\frac{\partial \Delta G}{\partial X_i^x}\right)_{X_j^x} = 0, \qquad i = 1,\ n-1, \tag{5}$$

where X_j^x signifies that all mole fractions except $j = i$ are constant. Only n-1 components are independent in a crystal owing to the constraint

$$\sum_i X_i = 1. \tag{6}$$

Expanding (5)

$$\left(\frac{\partial \Delta G}{\partial X_i^x}\right)_{X_j^x} = \left(\frac{\partial \Delta G}{\partial X_i^x}\right)_{X_i^m} + \left(\frac{\partial \Delta G}{\partial X_i^m}\right)_{X_i^x} \frac{\partial X_i^m}{\partial X_i^x},\ \mathrm{i} = 1,\ n-1,$$

using (4) to evaluate the last term, and introducing (3) we find

$$\left(\frac{\partial g_x}{\partial X_i^x}\right)_{X_j^x} = \left(\frac{\partial g_m}{\partial X_i^x}\right)_{X_j^m} \quad i = 1,\ n-1. \tag{7}$$

This is a generalization of the result for the binary system. Explicitly solving (7) by introducing (1) and (2), the general constraint can be formulated as

$$\frac{X_i^x\, X_n^m}{X_n^x\, X_i^m} = \exp\left[\frac{-(\mu^{x,o} - \mu_i^{m,o}) + (\mu_n^{x,o} - \mu_n^{m,o})}{RT}\right]$$

$$i = 1, n - 1. \qquad (8)$$

Equation (8) is simply a statement of the equilibrium distribution-coefficient $K_D{}^{i-n}$ for binary exchange of each component i and the dependent component n. It implies that $K_D{}^{i-n}$ for binary exchange during disequilibrium growth is the same as for equilibrium at the same temperature. The right-hand side of (8) can be evaluated from thermodynamic data. Then the composition of phase x for a defined composition of phase m is found as follows. For each component i

$$K_E^{i-n} = \frac{X_i^x}{X_n^x} = K_D^{i-n}\frac{X_i^m}{X_n^m}, \; i = 1, n - 1. \qquad (9)$$

Expanding (6), we can write

$$X_n^x + \sum_i X_n^x \frac{X_i^x}{X_n^x} = 1, \qquad i = 1, n - 1. (10)$$

Combining (9) and (10), the value of $X_n{}^x$ is found:

$$X_n^x = \frac{1}{1 + \sum_i K_E^{i-n}}, \; i = 1, n - 1. \qquad (11)$$

Subsequently, the other components are found from (9)

$$X_i^x = X_i^x K_E^{i-n}. \qquad (12)$$

There is a significant difference between this disequilibrium-partitioning model based on thermodynamic assumptions and the partitioning model usually assumed in Rayleigh fractionation calculations: the former model requires that K_E for an element change as the composition of the source phase changes, even for isothermal growth. Consequently, the compositional zoning of garnet will reflect a variable K_E during growth. Furthermore, the value of K_E at the beginning of growth calculated by the disequilibrium partitioning model will differ from the equilibrium partitioning K_E assumed in the Rayleigh calculation, and the calculated composition of garnet for a given composition of matrix will differ.

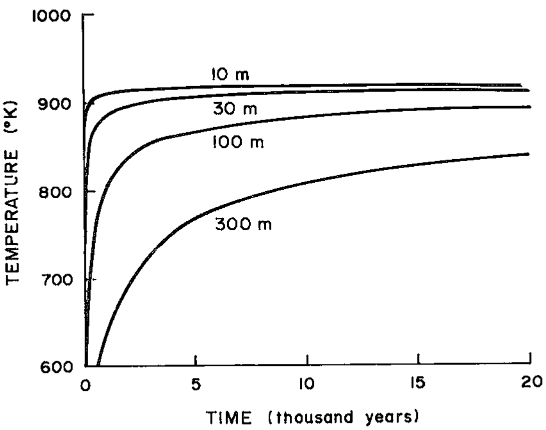

FIG. 2. Thermal history curves computed for points at the indicated horizontal distance from the midpoint of the side of an intrusive body 5 x 5 km in cross section and extending 20 km downward and vertically. Regional temperature 300°C, intrusion temperature 1000°C, thermal diffusivity 0.0079 cm^2/s.

The effect of disequilibrium partitioning, according to the model above, on the growth of garnet from chlorite at 775.6 K (50 K overstepping of the beginning of growth under equilibrium conditions) is illustrated in Figure 1 (curves RC). The profile was computed by assuming, at each growth step, that matrix chlorite had a composition determined by the bulk composition of the matrix, and that the composition of garnet at each step was derived from the chlorite composition by equations 11 and 12.

COMPARISON OF ZONING PRODUCED BY GROWTH MODELS

The simulated profiles of equilibrium-growth zoning in Figure 1 (curve E) reproduced from the preceding paper (Loomis & Nimick 1982) are comparable to the profiles described by Hollister (1966, 1969a). The bell-shaped Mn profile, the small compensating rise of Mg and the large rise of Fe with growth are similar. The late-stage zoning of Mg and Fe predicted by the simulations is not found in Hollister's samples because the garnet crystals did not grow this large, and the appearance of biotite and staurolite add complicating reactions. In view of the importance of bulk composition and nucleation factors, it is remarkable that even the MnO core composition of garnet (6–7 wt.% in the natural examples, and ~ 5.7 wt. % in the simulations) and width of the Mn bell-shaped profile (0.08–0.1 cm in natural examples and ~0.08 cm in the simulations) are similar. We can conclude that there is no obvious discrepancy between the simulated and the natural profiles of zoning that cannot be explained by bulk composition or nucleation.

The disequilibrium profiles in Figure 1 represent two end-member models of disequilibrium growth at 50 K overstepping of nucleation. The diffusion-controlled model (DC) assumes that diffusion of Mg, Fe and Mn in the intergranular medium is the important rate-limiting step, whereas the reaction-controlled model (RC) assumes that intergranular diffusion of these components is infinitely fast. Comparison of the simulated profiles in Figure 1 with the equilibrium-growth-model curves and natural profiles indicates that *if* disequilibrium growth of garnet occurs, (1) the reaction-controlled-growth model easily accounts for observed zoning features, whereas (2) the diffusion-controlled-growth model *may* be able to produce the observed profiles only *if* the diffusion rate of Mn is much faster than that of Fe in the matrix. The suitability of the reaction-controlled-growth model for simulating zoning in garnet was essentially arrived at by Hollister (1966) and Atherton (1968) based on their successful approximation of Mn zoning profiles by the Rayleigh fractionation model.

To determine whether disequilibrium-growth models can explain other aspects of garnet zoning that are not explained by equilibrium processes, the following sections will focus on the variation of zoning patterns with bulk composition and metamorphic grade. Data do not exist to evaluate the effect of these variables on relative rates of diffusion in the matrix; therefore, only the reaction-controlled-growth model is considered.

The effect of bulk Mn and overstepping on Mn partitioning

Table 1 summarizes partitioning data for Mn for three bulk compositions that produce garnet under both equilibrium and disequilibrium (reaction-controlled growth) conditions in the garnet–chlorite system. Several observations are pertinent to the interpretation of compositional variations in garnet. Firstly, the bulk composition has little effect on K_E(Mn) for the first appearance of garnet under equilibrium conditions, despite the large effect of bulk composition on this isograd temperature. Nearly ideal mixing of Mn and Fe, and their similar interaction with Mg (Ganguly & Kennedy 1974), suggest that nonideal mixing considerations would not significantly change this result. Similarly, K_E changes little over a large range of temperature during equilibrium growth.

TABLE 1. PARTITIONING OF Mn BETWEEN GARNET AND CHLORITE AS A FUNCTION OF Mn CONTENT OF THE SYSTEM AND TEMPERATURE

BULK Mn (moles)		TEMPERATURE (°K)	ΔT (°K)	INITIAL K_E(Mn)	FINAL K_E(Mn)
.0004	(E)	725.6 - 834.6	0	43.3	43.9
	(D)	775.6	50.0	35.5	43.5
.0008	(E)	695.8 - 834.0	0	42.4	43.9
	(D)	745.8	50.0	35.3	43.4
	(D)	775.6	79.8	31.8	43.5
.0012	(E)	668.7 - 834.7	0	40.8	43.9
	(D)	718.7	50.0	34.6	43.3
	(D)	775.6	106.9	28.9	43.5

Fe and Mg contents of all bulk compositions are .06 and .04 moles, respectively. E designates equilibrium growth between the two temperatures, D designates isothermal, reaction-controlled growth at the indicated temperature. The overstepping at the beginning of disequilibrium growth is indicated by ΔT. K_E is defined in the text.

Secondly, K_E(Mn) for the initial composition of garnet (INITIAL K_E) to nucleate under disequilibrium conditions decreases with the amount of overstepping. A given amount of overstepping affects K_E in a similar way in all compositions. Since increasing bulk Mn content depresses the equilibrium temperature of the garnet isograd and increases overstepping, the value of K_E in garnet crystals growing at the same temperature will be inversely proportional to the bulk Mn content (*cf.*, 775.6 K growth for the three compositions in Table 1).

Thirdly, K_E(Mn) is predicted to increase markedly during isothermal growth but reaches a fairly constant value (FINAL K_E) as Mn is depleted. The increase of K_E can be correlated with decreasing overstepping as the matrix is fractionated toward an equilibrium composition. K_E converges to a nearly uniform value at the end of growth in all examples in Table 1 because it becomes a trace element after depletion, and Henry's law can be applied.

In general, these observations suggest that the *equilibrium* value of K_E(Mn) is insensitive to temperature and, as required by ideal solution, to bulk composition. In contrast, the value of K_E(Mn) during *disequilibrium* growth is sensitive to overstepping, which is related, in turn, to growth temperature and to bulk composition. The following paragraphs discuss how these predictions of the reaction-controlled-growth model can explain certain observations on garnet zoning not possible using the equilibrium-growth or Rayleigh fractionation models.

The effect of bulk composition on K_E(Mn) provides an explanation for the observation of Hollister (1969b) that the fractionation factor analogous to K_E (he used wt. % instead of mole %) for the core composition of garnet decreased apparently systematically with increase of the bulk Mn content of the rock. The five samples examined by Hollister were from the same staurolite-grade outcrop and can be assumed to have experienced the same thermal history. The data presented in Table 1 indicate that K_E should not be affected significantly by bulk composition if the garnet crystals began growing at their equilibrium temperatures. Similarly, if they all grew at the same amount of overstepping of their respective equilibrium-temperatures, a significant trend of K_E with bulk composition would not be visible. However, if all garnet crystals nucleated at approximately the same temperature under disequilibrium conditions, K_E (core composition) would decrease significantly with bulk Mn because the amount of overstepping would be greater in rocks enriched in Mn.

Additional support for the overstepping model comes from the data of Atherton (1968). Using bulk-rock and measured garnet-core compositions, he found that K_E(Mn) decreases with increasing metamorphic grade. Whereas diffusion within garnet would result in greater relaxation of Mn curves at a progressively higher grade, it is unlikely that significant diffusion occurred between the garnet- and staurolite-isograd temperatures because (1) complex zoning of Ca and Mg is preserved in the core region of some zoning profiles, (2) estimates of the exchange diffusivity of Mg and Fe in garnet based on the data of Lasaga *et al.* (1977), Loomis (1978) and Elphick *et al.* (1981) indicate that little relaxation of profiles should occur, and (3) Yardley (1977) and Woodsworth (1977) found that evidence of homogenization of garnet crystals was restricted to higher-grade rocks. The decreasing value of nucleation K_E with grade is easily explained if the amount of overstepping at the initiation of garnet growth increased monotonically with maximum grade.

A final observation is that of Hollister (1966, Fig. 2); discrepancies between his Rayleigh fractionation simulations and measured profiles suggested to him that K_E(Mn) varied during growth. The variation of K_E during isothermal growth predicted by the disequilibrium-partitioning model developed here improves the fit between simulated and observed profiles.

Mg and Fe zoning

Hollister (1969a, p. 1484) compared the zoning profiles of garnet in chlorite-bearing assemblages from different metamorphic grades and noted that (1) the zoning of Mg/Fe ratio is small in the central part of each grain of garnet, (2) the profiles of garnet grains from different grades do not overlap, and (3) the average Mg/Fe ratio increases with grade. The Mg/(Mg + Fe) ratio in garnet cores for biotite, biotite + staurolite, and biotite + sillimanite assemblages are 0.038, 0.099 and 0.153, respectively. Based on these data, he suggested that garnet crystals found at high grades did not nucleate at the same temperature as their lower-grade counterparts, but that they grew directly at higher temperature. Bulk compositions of garnet obtained by Atherton (1968) also show an average increase of Mg/Fe with distance above the garnet isograd (samples 4 to 13).

The possibility that Mg/(Mg + Fe) ratio in the garnet core is controlled by the bulk-rock composition can be evaluated. Considering the garnet–chlorite equilibrium approximated in Figure 2 (Loomis & Nimick 1982), it is apparent that there would have to be a systematic increase of bulk Mg/(Mg + Fe) to very high values to explain the systematic shift of garnet-core composition. Moreover, the temperature of first appearance of garnet would be shifted to values approximating the staurolite isograd itself. The possibility that increasing Mn content of the bulk composition in higher-grade samples could increase the ratio Mg/(Mg + Fe) can be discounted, because the data presented by Hollister (1969a, Figs. 8, 19) indicate that the concentration of Mn in a garnet core declines with grade; Atherton (1968) also documented this trend in his samples.

The systematic variation of Mg/(Mg + Fe) with grade documented by Hollister (1969a) can be explained by a progressive increase of overstepping with grade. For the bulk composition modeled, the ratio Mg/(Mg + Fe) in the garnet core is predicted to increase from 0.047 to 0.061 with 50 K of overstepping according to the reaction-controlled-growth model.

DISEQUILIBRIUM-REACTION PROCESSES

Disequilibrium is created whenever growth or reaction rates of crystals do not keep pace with changing environmental conditions. Disequilibrium growth is accepted in some igneous systems, but has been slow to be acknowledged in metamorphic cases. One argument is that metamorphic reactions occur over long periods of time, and equilibrium is more likely to be achieved. Yet, the grain size and nucleation density in metamorphic rocks, measures of the relative ease of growth and transport processes, are similar to those in igneous rocks. Thus, the disequilibrium processes that govern the growth of crystals in igneous systems may well play a role in metamorphic rocks.

Several factors could restrict the rate of growth of garnet. First is limited rate of diffusion of components in intergranular medium. If diffusion of Mg, Fe and Mn are the rate-limiting steps, the reaction model is here called "diffusion-controlled growth". If the diffusion of Al or Si is the rate-limiting step, the appropriate reaction model is "reaction-controlled growth". As discussed previously, it may be possible to generate zoning patterns similar to those observed with the diffusion-controlled-growth model if Mn has a much higher diffusivity than Fe. Because the Al content of garnet is nearly stoichiometric in pelitic rocks (and ferric iron cannot be distinguished with the microprobe), there is no direct evidence of the significance of Al diffusion recorded in compositional zoning. Textural evidence has been cited to support the contention that the limited diffusivity of Al controls inclusions within crystals, local mineral assemblages and, to some extent, the morphology of aluminous crystals in metamorphic rocks (*e.g.*, Carmichael 1969, Fisher 1970); however, other work suggests that Al is not as immobile as commonly assumed (Foster 1977, 1981).

The evidence against the significant control of diffusion of Al and Si on garnet nucleation and growth rate is impressive. Careful study of the distribution and size of garnet crystals in several types of rocks yielded the unanimous conclusion that nucleation was random and that growth was not controlled by competition for components with neighboring garnet crystals (Jones & Galwey 1964, Galwey & Jones 1966, Kretz 1966, 1973). Galwey & Jones found that nucleation density in rocks with similar thermal histories lacks correlation with the amount of garnet crystallized; this observation suggests that nucleation of garnet is not controlled by the supply of its constituents in the matrix. The progressively increasing rate of nucleation with time, found by the authors cited above, probably does not correlate with the supply of garnet constituents by reaction, as exemplified by the curve in Figures 4 and 5 of Loomis & Nimick (1982). Finally, it seems unlikely that the rates of intergranular diffusion of Mn and Fe are much slower than those of Al or Si, and that the relative diffusivity of Mn and Fe will be of the correct magnitude, and have the correct dependence on bulk composition and temperature, to match the observations discussed above.

A second factor controlling the rate of garnet growth is the interfacial process whereby a garnet crystal is formed from the intergranular medium. The significant influence of interfacial processes on the growth of metamorphic crystals is evident from the presence of crystal faces, which imply anisotropic growth. The morphology of a crystal whose growth is controlled solely by diffusion will depend on the source of its constituent components and rejection of others, whereas interface processes allow the internal structure of the crystal to control morphology. Anisotropic interface kinetics can increase the stability of crystal faces against the tendency for instabilities to form in response to external thermal or compositional gradients. Kirkpatrick (1975) has reviewed the various types of interface-controlled mechanisms of growth.

A third factor that could control the rate of garnet growth is the process of dissolution of reactant minerals. The rate of dissolution can be controlled by diffusion within dissolving crystals or by interface kinetics. From a number of detailed studies of disequilibrium reactions in high-grade metamorphic rocks, I have concluded that dissolution of kyanite or sillimanite and intragranular diffusion within reactant garnet are far more effective at limiting rate of reaction than intergranular diffusion (Loomis 1976, 1977, 1979). Both aluminum silicate minerals develop euhedral forms by anisotropic growth, suggesting that interfacial processes are significant factors in their reaction. In the present example of garnet and water forming from chlorite, kyanite and quartz, the dissolution rate of kyanite could be expected to be the process-limiting rate of reaction.

I believe that there is ample evidence of the significant control of interfacial processes on the growth of garnet reported in the literature. Prograde garnet crystals are commonly euhedral, indicating that the interfacial processes responsible for anisotropic growth must have some rate-limiting effect. Kretz (1973) compared zoning profiles in several garnet crystals of varying sizes to correlate growth rate with an extensive property of the crystals. His data (Kretz 1973, Fig. 4) indicate that the rate of change of garnet growth falls slightly below that expected if growth rate were controlled by surface area, but far above that expected if growth were controlled by diffusion in the matrix. Growth rate proportional to surface area would be expected if only interface nucleation processes controlled growth, because the probability of nucleating a new crystal layer would be proportional to the surface area. Kretz (1966) suggested that the activation energy for interface growth is not greatly different than that for nucleation based on the relationship of grain-size distribution to median grain-size. This result is reasonable if garnet grows by a surface-nucleation mechanism. In addition, there is enough evidence of the recalcitrant dissolution of aluminum silicates cited previously and of their metastability (*e.g.*, in rock samples cited here and by Hollister 1969b) to propose that dissolution of kyanite and sillimanite may delay nucleation and limit the rate of growth of garnet.

RATES OF CRYSTAL GROWTH IN CONTACT METAMORPHISM

The comparison of garnet-growth simulations with natural profiles and partitioning data suggests that garnet grains found in rocks above the garnet isograd may have nucleated with significant overstepping. The equilibrium-growth simulations described in the preceding paper (Loomis & Nimick 1982) and a simple thermal model of contact metamorphism can be used to gain some idea of the relative growth-rates of crystals that must be achieved to maintain equilibrium in various parts of a metamorphic terrane.

Figures 4 and 5 of the preceding work (Loomis & Nimick 1982) show the volume of garnet growth by the equilibrium model as a function of temperature. They demonstrate that increasing Mn in the bulk composition should cause the appearance of garnet at an increasingly lower temperature, but that the volume of garnet grown is small until almandine-rich compositions become stable. The profiles in Figure 1 (this paper) exaggerate the apparent volume of Mn-rich garnet owing to the spherical geometry of the crystal.

Figure 2 shows the computed thermal history that would be experienced by rocks at four distances from a hypothetical intrusion emplaced at 1000°C in rocks with a regional temperature of 300°C. The intrusive body measures 5 x 5 km in horizontal cross section and extends above and below the sample plane a large distance (20 km). The metamorphic samples are located 10, 30, 100, and 300 m from the edge of the body. The model neglects possible complications of convective motions of water and magma, and the effect of metamorphic reaction on heat flow.

The thermal model of Figure 2 can be combined with our equilibrium-growth simulations to compute the growth rate of garnet at each point. These computations are presented in Figure 3 in terms of the radial velocity of growth of garnet spheres as a function of the amount of growth for each of the four hypothetical samples. I have neglected any differ-

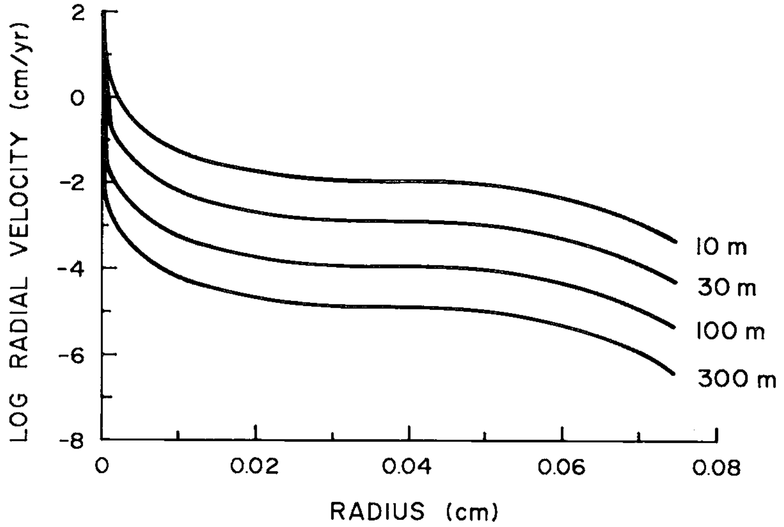

FIG. 3. Computed velocity of radial growth of garnet according to the equilibrium-growth simulation and the thermal history of Figure 2.

ence in nucleation rate. The information in Figures 2 and 3 is useful to critically evaluate the various models of garnet growth. The figures show that the growth rate of a crystal must vary almost three orders of magnitude over a distance of 290 m in this hypothetical aureole to maintain equilibrium. Rocks just beyond the garnet isograd in temperature would develop garnet at rates orders of magnitude slower yet. Whereas the equilibrium-growth model demands these large variations in growth rate, there is not a compensating variation of mobility of components. The rate of surface reactions, the mobility of components along grain boundaries and the rate of diffusion of components through crystals should be similar in *all* samples during the simulated growth-event, because the temperature at each stage of growth is *identical* in all samples at equilibrium. If there is any tendency toward disequilibrium during growth in contact-metamorphic rocks, it is apparent that kinetic constraints on growth will be greatly exaggerated during development of high-grade rocks.

Another observation from Figure 3 is that the greatest growth-velocity of a garnet crystallizing at equilibrium occurs early in its growth history, and that the slowest velocity probably occurs near the termination of growth. This trend of growth rate will probably be enhanced under disequilibrium as the matrix is fractionated. If we accept radial growth-velocity at equilibrium to be a rough guide to the rate at which equilibration processes (diffusion and interface reactions) must occur in the matrix, then the greatest opportunity for disequilibrium obtains early in the growth history and the least near the end of growth. Maximum disequilibrium at the beginning of growth may explain the large variations of K_E for garnet cores measured in natural samples.

A final observation of possible kinetic significance in Figure 2 is that each sample in the hypothetical aureole experiences prolonged residence at its maximum temperature after passing through the equilibrium-growth interval of garnet. Consequently, we should be careful to distinguish between the rapidly changing conditions at which garnet might have grown and the stable conditions at the "isograd" temperature where the matrix phases (and possibly garnet) had a long time to reach equilibrium. The long period of annealing at high temperature and slow growth-rate at the end of garnet growth could explain why equilibrium partitioning of components is so common between garnet rims and matrix phases, but that K_E for garnet cores, and core composition, zoning morphology and inclusion compositions show significant dispersion.

CONCLUSIONS

The computer simulations of garnet growth compared here provide a basis for estimating the effects of equilibrium and disequilibrium processes on garnet growth in chlorite- and biotite-bearing assemblages. Both the equilibrium-growth and the reaction-controlled-growth models predict zoning morphologies consistent with those observed in garnet- and staurolite-zone rocks. Although both models differ from the Rayleigh fractionation model applied by Hollister (1966), their success in predicting observed profiles confirms the basic assumptions of the Rayleigh model, namely: (1) equilibration within garnet is limited during growth, and (2) the chemical potentials of Mg, Fe and Mn components remain nearly uniform in the matrix.

The equilibrium growth, reaction-controlled growth, and Rayleigh fractionation models differ substantially in their predictions of effects of temperature of growth and bulk composition on partitioning of elements between garnet and the matrix. The disequilibrium partitioning law used here suggests that partitioning can be used as a measure of overstepping, where overstepping is a function of temperature, bulk composition and extent of reaction. In contrast, the equilibrium growth and the Rayleigh fractionation models are distinguished by the insensitivity of partitioning to bulk composition and extent of reaction. The trends of partitioning of Mn, Fe and Mg as a function of grade, bulk composition and extent of crystallization reported by Hollister (1966, 1969a) and Atherton (1968) are consistent only with the reaction-controlled-growth model and the inference that the extent of overstepping during nucleation of garnet increased in direct relation to the ultimate grade of the sample. If garnet does grow according to the disequilibrium-partitioning law developed here and at progressively greater overstepping with grade, the amount of diffusion that has been inferred to occur from the derease of gradients in zoning profiles with grade (*e.g.*, Woodsworth 1977, Yardley 1977) is overestimated because growth profiles similar to those of lower-grade samples were never created.

Sufficient data do not exist to determine whether the diffusion-controlled-growth model, in which only the diffusivity of Mg, Fe and Mn control the growth rate, can explain the observed zoning profiles and effects of bulk composition and grade on K_E. However, it seems unlikely that the relative rate of intergranular diffusion of Mn and Fe will be found to vary with temperature and composition in exactly the correct way to produce the observed effects. Moreover, the studies of garnet nucleation and growth rate discussed in the preceding section do not support models of diffusion-controlled growth.

Kinetic processes at the garnet surface and possibly the interfacial processes that control the dissolution rate of aluminum silicate minerals are probably the most important reaction steps that limit the nucleation and growth rate of garnet. The existence of an interface control of reaction rate does *not* require that textures controlled by Al–Si diffusion cannot be formed. Dissolution, diffusion and interface-controlled growth act in series and may all exert a limiting effect on growth rate. The effect of discontinuities in chemical potentials at crystal interfaces serves to *reduce* the gradient of these chemical potentials in the matrix, the amount of reduction being proportional to the extent of interface control. But diffusion gradients will still exist and influence mineralogy through their control of bulk composition. Thus, the existence of diffusion-controlled structures does not prove that reaction rate is *not* dominantly controlled by interface kinetics, as I have emphasized before (Loomis 1976). It does mean, though, that the mobility of components estimated from such structures will be *underestimated* because the actual gradient of a chemical potential is less than it is estimated to be if the rate of reaction is assumed to be controlled solely by diffusion. The explanation of the creation of obvious diffusion-structures in an initially homogeneous rock is basically a problem in nucleation.

The model of garnet formation adopted here was essentially established by the work of Kretz (1966, 1973) and Hollister (1966, 1969a). The model assumes that garnet nucleates slowly with increasing overstepping, so that most crystals nucleate at significant overstepping. The model is based on the concept that nucleation of garnet, interface-controlled growth of garnet and diffusion within garnet are processes with high activation-energies relative to intergranular diffusion. The same model can probably be applied to kyanite and sillimanite (Loomis 1972), and probably to several other minerals.

Comparisons of the predictions of the disequilibrium-partitioning model and observed trends of K_E with grade and bulk composition suggest that in contact-metamorphosed rocks, (1) overstepping increases with the ultimate grade of the sample, and (2) the temperature at which most garnet grains nucleate may be similar in an outcrop and does not depend on bulk composition. These conclusions indicate that garnet development is controlled principally by thermal history. The observations are readily explained by Figure 2 if we assume that the sluggish nucleation of garnet delays the development of most crystals long enough that "plateau" temperatures are reached.

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