KINETICS OF THE CRYSTALLIZATION OF GARNET AT TWO LOCALITIES NEAR YELLOWKNIFE

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ABSTRACT

The chemical composition of garnet crystals in garnet-biotite-cordierite schist near Yellowknife varies from centre to edge. In a small volume of rock, only the largest crystals have manganese-rich centres, while the composition of the crystal margins, regardless of size, is approximately the same.

The development of compositional zoning is discussed in relation to a simple model of the production of garnet from chlorite. Compositional profiles in crystals of different size are used to derive an expression for the rate of crystal growth. The form of the crystal-size distribution is used to derive an expression for the rate of nucleation. These expressions, in combination, give an equation for the rate of production of garnet, i.e. the reaction rate. This reaction rate was acceleratory, increasing approximately as a function of time raised to the power 5/2. This reaction rate could result from a nearly steady rise in temperature.

INTRODUCTION

The study of metamorphic rocks has made considerable progress during the past few years, and much information is now available on the chemical composition of metamorphic minerals, and on their stability, as determined by experimental methods. Consequently, it is now possible to acquire a fairly satisfactory understanding of the equilibrium relationships within these rocks. In contrast, comparatively little is known concerning the kinetics of the chemical changes that produce minerals during rock metamorphism.

The present study is an attempt to obtain some understanding of the nucleation and growth of garnet crystals in metamorphic rocks. Although it will not be possible to obtain numerical values for the rate constants, it may be possible to obtain information on the form of the growth law from data on compositional zoning within crystals, and on the form of the nucleation law from measurements of crystal size. Two specimens of schist from Yellowknife will serve to illustrate how such information may be extracted from rocks.

OBSERVATIONS

The Yellowknife Group metasedimentary rocks

The Yellowknife Group of volcanic and sedimentary rocks, and their metamorphosed equivalents, occur in the Slave province of the Canadian Shield, and are considered to be Archean in age (Douglas 1970). During the Kenoran Orogeny (2500 m.y.), these rocks were folded, metamorphosed, and intruded by bodies of granite and pegmatite.

Northeast of Yellowknife, the sedimentary rocks consist mainly of greywacke and argillite, and these can be traced through zones of low metamorphic grade into zones of medium grade. The low-grade rocks are characterized by chlorite, white mica, and biotite, and the medium-grade rocks by biotite, cordierite, and less commonly by garnet, andalusite, sillimanite, and staurolite (Henderson & Jolliffe 1941 ; Jolliffe 1942, 1946). A detailed study of these rocks, as found east of Sparrow lake is presently in progress. The metamorphic rocks form very broad aureoles around granite plutons ; metamorphism, folding, and granite emplacement seem to have been essentially contemporaneous.

Near Staple Lake, about 35 km northeast of Yellowknife, a belt of metasedimentary rock, about 7 km wide, lies between the Prosperous Lake granite pluton to the west and the Duncan Lake pluton to the east (Jolliffe 1946; Kretz 1968). A portion of this belt, including the small Staple Lake stock and numerous pegmatite bodies, is shown in Figure 1. The metamorphic rocks at this place consist of quartz, plagioclase, biotite, and one or both of garnet and cordierite. Cummingtonite is less common and andalusite is rare. The metamorphic grade appears to be uniform throughout the area.

Bedding has been preserved in the rocks at Staple Lake, but because the beds are many centimeters thick, volumes of rock of hand-specimen size are apparently homogeneous. A foliation, defined by the parallel arrangement of biotite crystals, and a lineation, defined by the parallel arrangement of elongate aggregates of biotite crystals, are commonly present.

Two specimens of schist were collected for study. One of these, number 285, lies about 600 m west of Staple Lake stock, and the other, number 296, lies about 300 m west of the stock (Fig. 1). The minerals found in these rocks, and the mineral proportions are given in Table 1.

TABLE 1. MINERAL CONTENT OF STUDY SPECIMENS

Specimen:	schist 285	schist 296
plagioclase	60	53
quartz	10	10
biotite	23	33
cordierite	5	<1
garnet	2	4
others[1]	<1	<1

1. tourmaline, zircon, apatite, ilmenite, and retrograde chlorite.

Shape and size of garnet crystals

Different methods were employed to obtain information on the shape and size of garnet crystals within the two rock specimens that were selected for study. In the 'forceful extraction' method, a small volume of rock is carefully disintegrated by use of a vice and small hammer, and by this method approximately 90 per cent of the garnet crystals could be extracted without fracturing them. An examination of the broken fragments, including several half crystals revealed
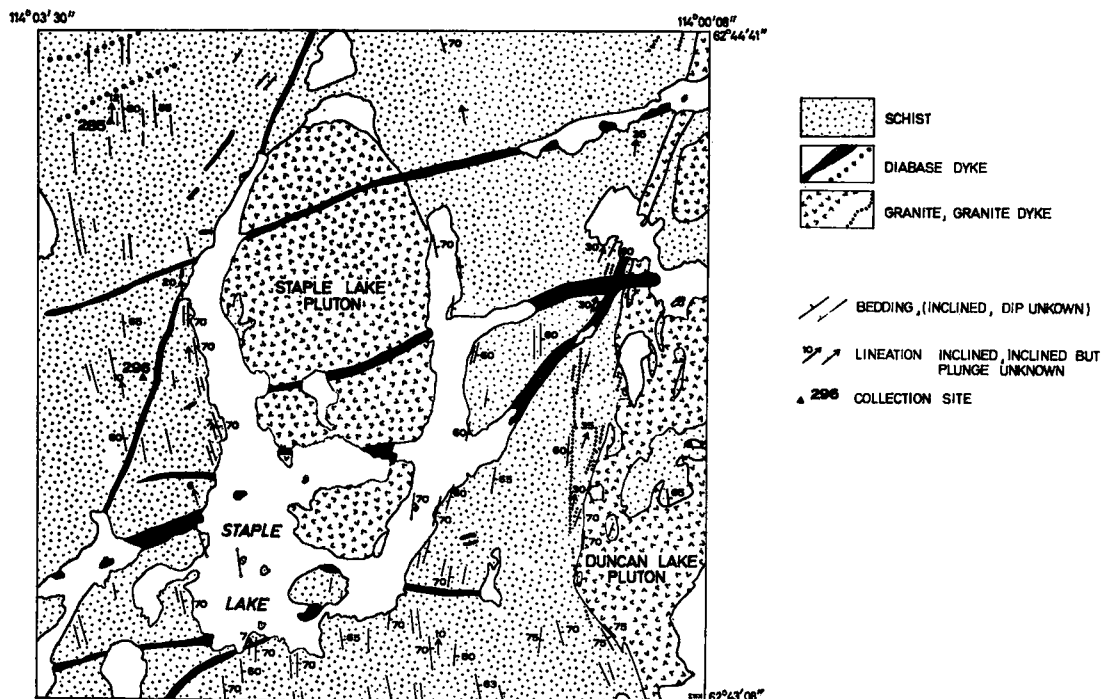

FIG. 1. Geology of the Staple Lake area, showing collecting sites for specimens 285 and 296. The area lies 35 km northeast of Yellowknife.

that crystals of different size had broken; thus the size distribution of the whole crystals is probably representative of the garnet-size distribution within the rock. In the 'thermal extraction' method, small volumes of rock are disintegrated by heating them in air to 600°C for one hour. By this method 99 to 100 per cent of the garnet crystals could be extracted without breaking them. In the 'successive sectioning' method, information on the crystal-size distribution is obtained by cutting numerous parallel sections through a volume of rock, as described previously by the writer (Kretz 1966).

In the first two methods described above, garnet crystals were separated from the remaining minerals by use of tweezers, a magnetic separator, and heavy liquids. This work must be done carefully, to ensure that all of the garnet is separated from the rock sample and to avoid loss of the smallest crystals. After separating the crystals, their diameter can be readily measured by use of a petrographic microscope fitted with a graduated eyepiece.

An impression of the shape of the garnet crystals may be obtained from Figures 2a and 2b. The surface of most of the crystals consists part-
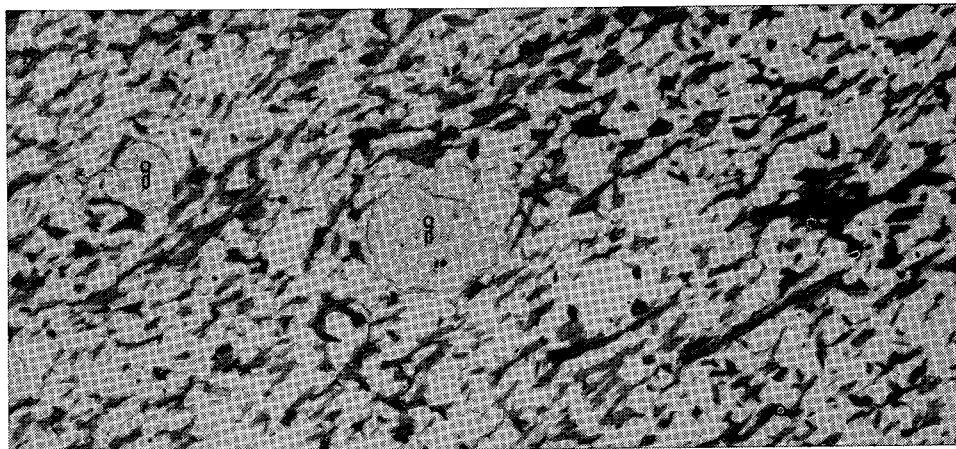

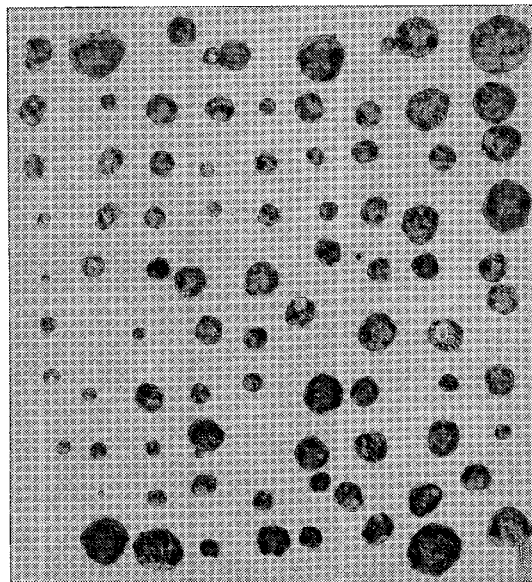Fig. 2a. Section through specimen 296, showing two garnet crystals (g).

Fig. 2b. Flock of garnet crystals extracted from a small volume of specimen 285. The diameter of the largest crystal measures 2.3 mm, and the smallest, 0.2 mm.
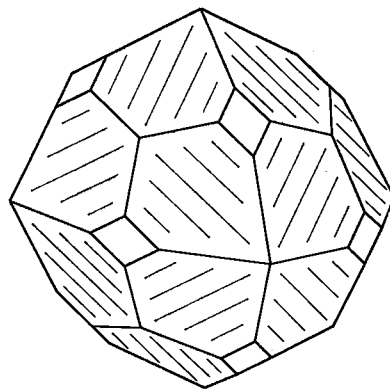

Fig. 3. Idealized shape of garnet crystals in specimens 285 and 296.

ly of crystal faces and partly of more irregular planes. Those crystals from both rocks that show the best development of crystal faces possess a combination of trapezohedral and dodecahedral forms as shown in Figure 3. The trapezohedral faces are typically striated, resulting from an alternation of the two forms. Hence the crystals are nearly spherical in shape.

The crystal-size distribution in a fragment of specimen 285 was previously obtained by use of the 'forceful extraction' method, and the distribution was found to be bimodal as shown in Fi-
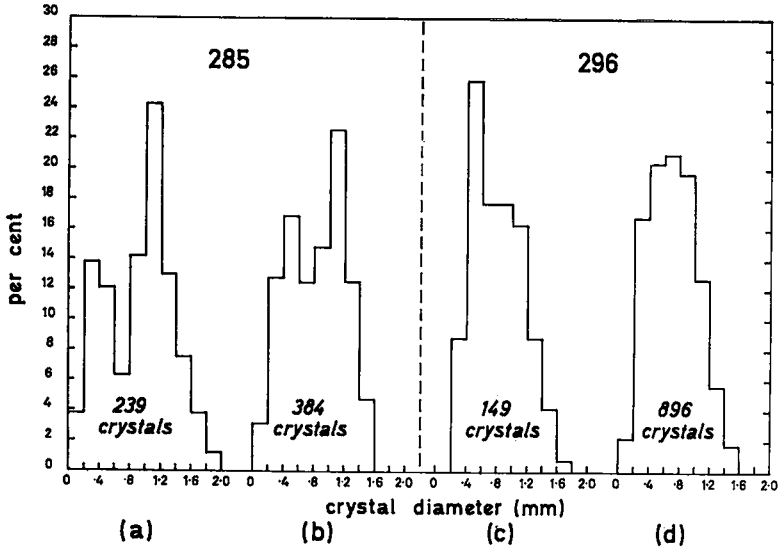

Fig. 4. Histograms of the size of garnet crystals in schists, specimens 285 and 296, duplicate determinations. Method used for a and d, "forceful extraction", for b, "thermal extraction", for c, "successive sectioning". Histograms a and c were previously reported by the writer (1966).

gure 4a. The measurements were repeated, using another fragment from the same hand specimen and the more reliable 'thermal extraction' method, to give the results shown in Table 2 and Figure 4b. The additional data have confirmed that the size distribution is bimodal.

The crystal-size distribution in a fragment of specimen 296 was previously obtained by use of the 'successive sectioning' method, and the distribution was found to be unimodal, as shown in Figure 4c. Note that very small crystals (0 to 0.2 mm diameter) do not appear because of the low probability of intersecting these while sectioning the rock. The 'forceful extraction' method was then applied to another fragment from the same hand specimen, to give the results shown in Table 2 and Figure 4d.

Although specimen 296 contains twice as much garnet as specimen 285, the range in crystal size is about the same in both rocks. However, the nature of the size distribution in the two rocks is distinctly different.

Chemical composition

Crystals of different size were selected from specimen 285 (population of Figure 4a) and

TABLE 2.   DATA ON THE SIZE OF GARNET CRYSTALS

rock specimen	285	296
method of separation	'thermal' extraction	'forceful' extraction
volume of rock, cm^3	13.53	10.58
weight per cent garnet[1]	1.80	3.92
number of whole crystals recovered	384	896
estimated total number of whole crystals	385	985
number of crystals in 1 cubic cm of rock	28	93
smallest crystal, diameter in mm	0.14	0.11
largest crystal, diameter in mm	1.60	1.60
average (modal) size, diameter in mm	0.5,1.1	0.7
histogram, figure	4b	4d

1. not corrected for about 8 per cent (by volume) of inclusions of quartz and ilmenite.

from specimen 296 (population of Figure 4d) for chemical analysis. Sections through the centres of the crystals were obtained by two methods. In the first, which was used for specimen 285, a number of crystals of the same size were dropped into a depression in a mount, the depression was filled with a mounting medium, and the mount was ground down until some of the crystals were intersected. The crystal that gave a section whose diameter was equal to the initial crystal diameter was chosen for analysis. In the second method, which was used for specimen 296, a crystal was dropped into a small upright glass tube filled with a transparent mounting medium, and this was then ground down until half the crystal was removed. Initially, Canada balsam was used as a mounting medium, and it was necessary to remount the crystals. This provided an opportunity for examining the half crystals, and selecting the better ones for analysis, i.e. the ones which were cut exactly through the crystal centres.

An A.R.L. microprobe at Queen's University was used to obtain analysis for iron, manganese, magnesium, and calcium at intervals of 0.1 mm along traverses through the crystal centres. In most instances, two traverses were made at right angles to each other. When the study was begun, a garnet standard was not available, and a garnet from the gneisses of the Otter Lake area, Quebec, previously analysed by emission spectrography and atomic absorption, was used as a 'standard'.
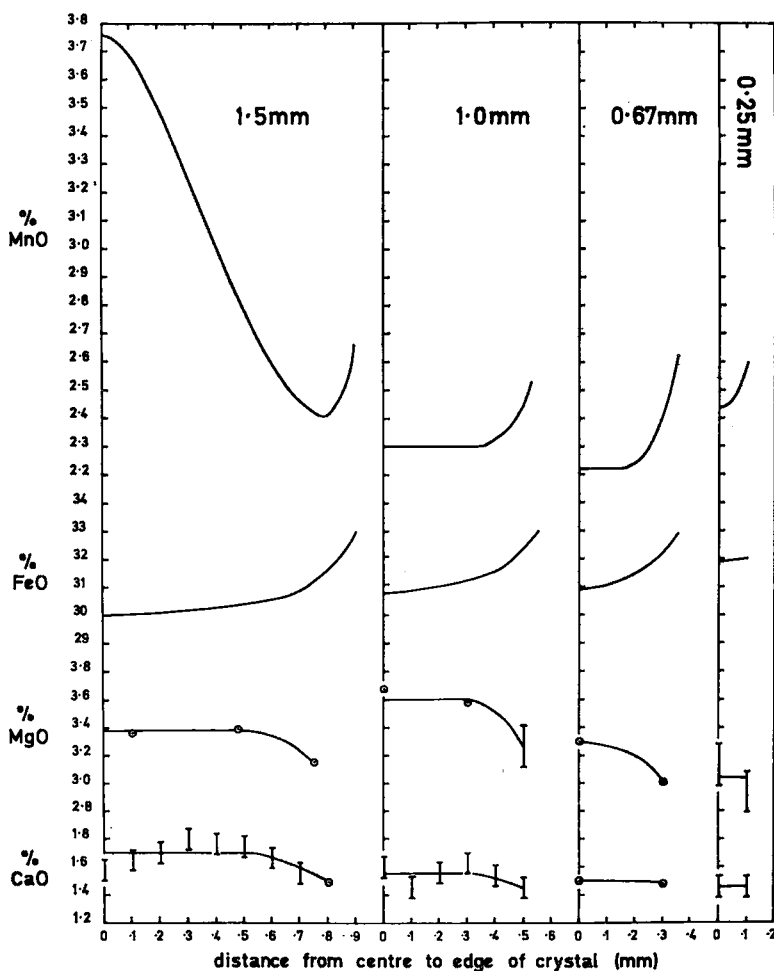

FIG. 5. Chemical profiles from centre to edge of garnet crystals of diameter 1.5 mm, 1.0 mm, 0.67 mm, and 0.25 mm in specimen 285. The Mn and Fe data have been averaged with regard to both distance and concentration. In the Mg and Ca profiles, a vertical bar (length = 2 standard deviations) indicates 1 or 2 readings, and a circle, the mean of 3 to 8 readings.

Consequently the analyses must be regarded as possessing only a moderate level of accuracy. The present study is, however, concerned primarily with the detection of differences in composition, and a satisfactory level of precision was obtained. The precision, expressed in terms of one standard deviation, is as follows: FeO, 0.5; MnO, 0.1; MgO, 0.15; CaO, 0.075 weight per cent. The symbol FeO, as used hereafter, refers to total iron expressed as ferrous oxide. The proportion of ferric iron in these samples, as in others of similar origin, is probably small.

The chemical composition of four garnet crystals of diameter 1.5, 1.0, 0.67, and 0.25 mm from specimen 285 is shown in Figure 5. The Mn profiles, obtained from 2 traverses, at right angles to each other, passing through the geometric centres of the crystals are nearly symmetrical; hence the maximum in the profile, the apparent growth centre, coincides approximately with the geometric centre. The Mn and Fe curves of Figure 5 are averages of four profiles from growth centre to crystal edge, both composition and distance having been averaged. The Mg and Ca curves represent the average of two arms of a single traverse across the crystal.
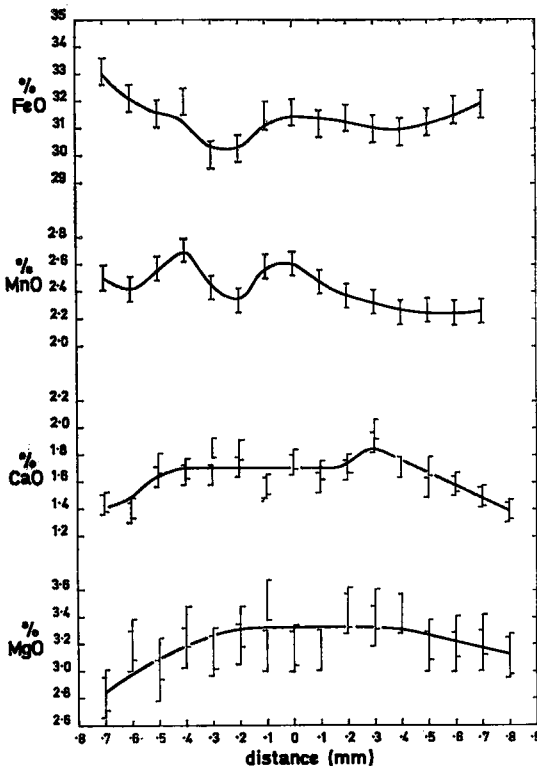
The garnet crystals from specimen 296 are not as strongly zoned as those in 285, and the profiles show a greater irregularity. Not all of the results are presented, but the profiles in a large crystal (1.5 mm diameter) are shown in Figure 6, and the Mn profiles for 7 crystals of progressively smaller size are shown in Figure 7.

The garnet in both specimens has nearly the same chemical composition. The oxide percentages correspond to approximately almandine 72, pyrope 11, spessartine 7, and grossularite 4 weight per cent. In specimen 285, crystals of different size obviously have different compositional characteristics, with greatest variation in composition occurring in the largest crystals.

Three crystals from specimen 285, all of diameter 1.5 mm were analysed, and the three crystals were found to be identical with regard to percent FeO at crystal edge. Also, two small crystals from the same rock fragment were found to have the same chemical composition.

FIG. 6. Chemical profiles across a large garnet crystal (1.5 mm diameter) from specimen 296. Bar length = 2 standard deviations.
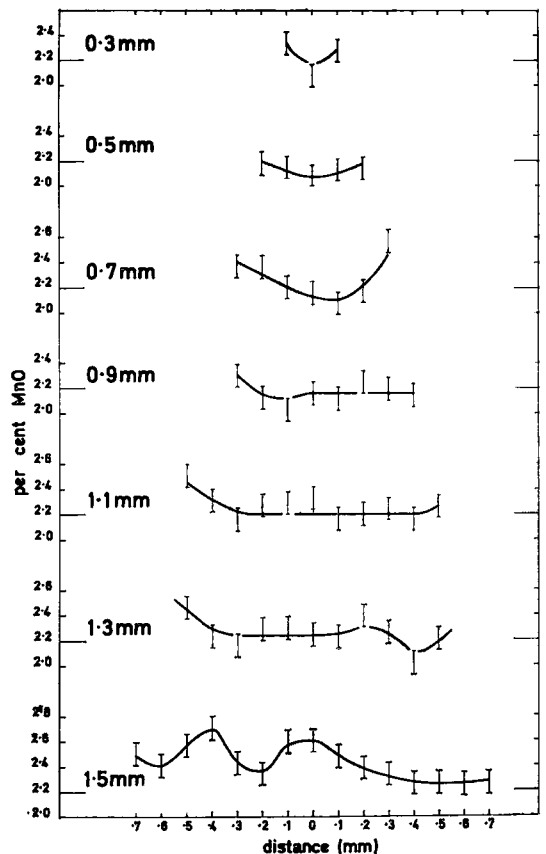

FIG. 7. Mn profiles across 7 garnet crystals from specimen 296. Crystal diameter is indicated. Bar length = 2 standard deviations.

Spatial distribution of garnet crystals

A study was made of the spatial distribution of garnet crystals in specimen 296, and the results, as previously reported by the writer (Kretz 1966) indicate that the garnet crystals are distributed at random. In addition, the size obtained by a garnet crystal was found to be independent of its position in the rock, *i.e.* crystals that occur as clusters are not on the average smaller than crystals that are relatively isolated. This illustrated to some extent by the model shown in Figure 8.
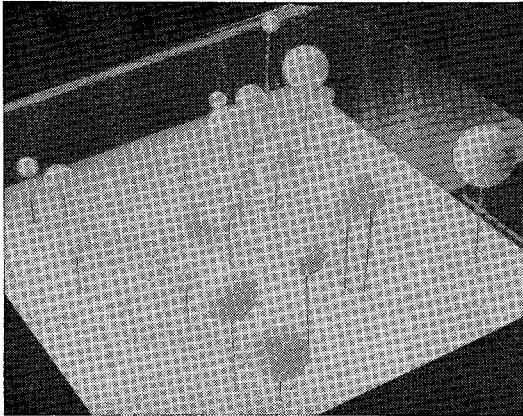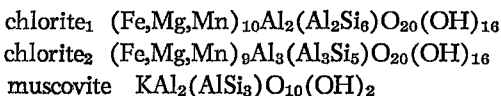

FIG. 8. Model to show the size and distribution of garnet crystals in a small volume of specimen 296. Base is 1 cm × 1 cm.

INTERPRETATION

The garnet-forming reaction

A model of garnet crystallization will now be described and used as an aid in arriving at an understanding of the development of compositional zoning in the garnet crystals from Yellowknife.

Garnet is entirely absent from the least-altered beds of the Yellowknife Group, whereas chlorite is abundantly present, and it seems likely that at least some of the elements presently found in garnet were derived from chlorite. Particularly strong evidence that garnet may form from chlorite was recently presented by Edmunds & Atherton (1971), who described clusters of garnet crystals within aggregates of chlorite. Information on the chemical composition of the chlorite and associated minerals of Yellowknife is not yet available, and it will be necessary to adopt idealized formulas, as follows :

chlorite$_1$ $(Fe,Mg,Mn)_{10}Al_2(Al_2Si_6)O_{20}(OH)_{16}$
chlorite$_2$ $(Fe,Mg,Mn)_9Al_3(Al_3Si_5)O_{20}(OH)_{16}$
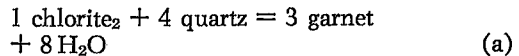muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$

The small amount of calcium in the garnet of the present study, amounting to about 4 per cent grossularite, will be disregarded, and the formula will be written :

garnet $(Fe,Mg,Mn)_3Al_2Si_3O_{12}$

Chemical data on cordierite and biotite from the Yellowknife Group were recently obtained by D.C. Kamineni, and these minerals may be approximately described by the formulas :
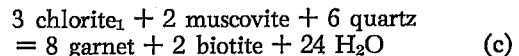
biotite $K(Fe,Mg,Mn)_3(AlSi_3)O_{10}(HO)_2$
cordierite $(Fe,Mg,Mn)_2Al_3(AlSi_5)O_{18}$
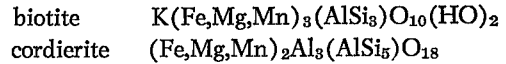
The first reaction to be considered is as follows :

1 chlorite$_2$ + 4 quartz = 3 garnet
+ 8 H$_2$O   (a)

This reaction, with reference to Fe and Mn end members, has been experimentally reproduced by Hsu (1968). In the Yellowknife rocks, biotite is invariably associated with garnet, and cordierite is commonly present, and these minerals were evidently also derived from chlorite, possibly as follows :

4 chlorite$_2$ + 6 muscovite + 25 quartz
= 9 cordierite + 6 biotite + 32 H$_2$O   (b)
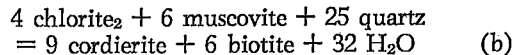
A more normal (less aluminous) chlorite may yield garnet and biotite :

3 chlorite$_1$ + 2 muscovite + 6 quartz
= 8 garnet + 2 biotite + 24 H$_2$O   (c)

Perhaps the actual reaction that has taken place in the specimens from Yellowknife is, in simplified form, a combination of (b) and (c) :

(chlorite$_1$, chlorite$_2$) + muscovite + quartz
= garnet + biotite + cordierite + H$_2$O   (d)
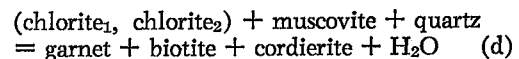
In the Yellowknife area, garnet is only found above the cordierite isograd, and the possibility exists that garnet has formed from cordierite or biotite, or both :

3 cordierite + 2 biotite
= 4 garnet + 2 muscovite   (e)
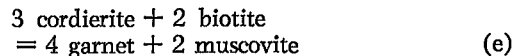
However, cordierite and biotite appear to be stable and compatible to the highest grade of metamorphism, adjacent the granite plutons. Moreover, muscovite which would be a product of this reaction, is rarely present with garnet. Reaction (e) is therefore considered to be unlikely relative to the above reactions which involve chlorite.

Let us first consider the most simple garnet-forming reaction, namely (a) above, and suppose that no magnesium is present, *i.e.* the reaction is

$(Fe,Mn)_9Al_3(Al_3Si_5)O_{20}(OH)_{16} + 4\ SiO_2$
$= (Fe,Mn)_9Al_6Si_9O_{36} + 8H_2O$ (f)
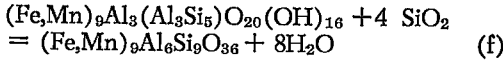
This reaction, for Fe and Mn end members, is univariant, provided that the pressure acting on all phases is the same. The univariant boundary curves were recently located by Hsu (1968), and are shown in Figure 9. When the pressure is 2000 bars, and the system is buffered by iron-quartz-fayalite, iron chlorite will break down to form iron garnet at $542 \pm 5°C$, and manganese chlorite will break down to form manganese garnet at $405 \pm 5°C$.
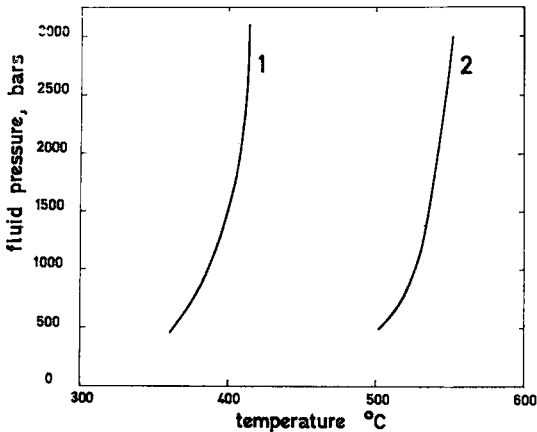

FIG. 9. Boundary curves for the chlorite-garnet reaction (f) with reference to Mn end members (1) and iron end members, (2) (Iron-quartz-fayalite buffer), as determined by Hsu (1968).

Consider now an Fe-Mn chlorite solid solution reacting with quartz to form an Fe-Mn garnet solid solution (reaction f) at pressure $P = 2000$ bars. At the reaction temperature, chlorite and garnet will be in a state of equilibrium, which is characterized by two equilibrium constants:

$$K_{Fe} = a_{Fe\ gar}/a_{Fe\ chl}$$
$$= \exp(-\Delta G_{Fe}/RT) \quad (1a)$$

$$K_{Mn} = a_{Mn\ gar}/a_{Mn\ chl}$$
$$= \exp(-\Delta G_{Mn}/RT) \quad (1b)$$

Here a is activity and the subscripts refer to end members (reaction f), T is absolute temperature, R is the gas constant, and ΔG_{Fe} and ΔG_{Mn} refer to the change in molar Gibbs free energy for (f) in terms of the Fe and Mn end members respectively.

Assume now that both chlorite and garnet may be regarded as ideal solutions. Then the activity terms in (1) may be replaced by mole fraction terms, such as [Fe gar], etc. Equations (1a) and (1b) may now be differentiated with respect to

T at constant P, and then integrated from the reaction temperatures for the end members (T_{Fe}, T_{Mn}) to T, in the normal manner, to obtain

[Fe gar]/[Fe chl] $= \exp\{(-\Delta H_{Fe}/R)$
$[(1/T) - (1/T_{Fe})]\}$ (2a)

[Mn gar]/[Mn chl] $= \exp\{(-\Delta H_{Mn}/R)$
$[(1/T) - (1/T_{Mn})]\}$ (2b)

Here ΔH_{Fe} and ΔH_{Mn} refer to the change of molar enthalpy of (f) for the Fe and Mn end members. Solving explicitly for [Fe gar] and [Fe chl] as functions of temperature, we obtain the following expressions, in which e^{Fe} and e^{Mn}
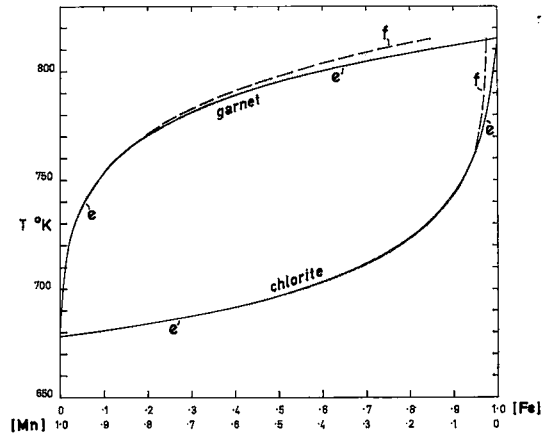

FIG. 10. Curves to show the dependance of composition on temperature in a simple model of garnet crystallization. Curves e refer to equilibrium P = 2000 bars.
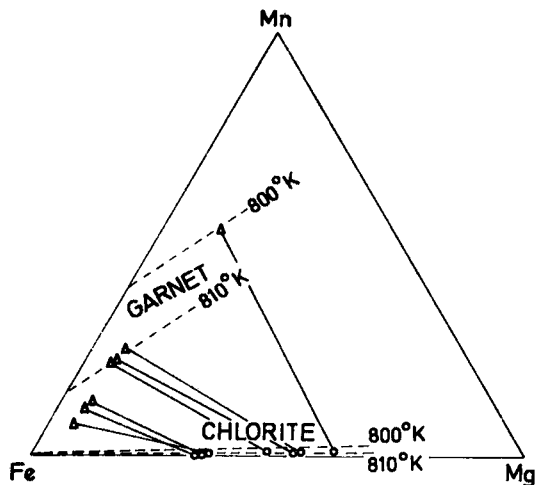

FIG. 11. Tentative location of isotherms on the chlorite and garnet composition planes at 2000 bars pressure, based on data of Figure 10. Data on coexisting chlorite and garnet are from Albee (1965).

denote the exponential terms in (2a) and (2b) respectively:

$$[\text{Fe gar}] = (1 - e^{-\text{Mn}})/(e^{-\text{Fe}} - e^{-\text{Mn}}) \quad (3a)$$

$$[\text{Fe chl}] = (1 - e^{\text{Mn}})/(e^{\text{Fe}} - e^{\text{Mn}}) \quad (3b)$$

These equations show how the composition of garnet and chlorite change as a function of temperature at constant pressure; they are, incidently, entirely analogous to the equation for the liquidus and solidus curves in the plagioclase system.

The equations cannot be used unless some information is available concerning the heat of the reaction for the Fe and Mn end members. These values may be estimated from the following equations:

$$\partial \ln P_{\text{Fe}}^x / \partial(1/T) = -\Delta H_{\text{Fe}}/R \quad (4a)$$

$$\partial \ln P_{\text{Mn}}^x / \partial(1/T) = -\Delta H_{\text{Mn}}/R \quad (4b)$$

where P^x refers to the fugacity of H_2O. When the boundary curves of Figure 9 are replotted in terms of ln fugacity and $1/T$, nearly straight lines are obtained at higher temperatures. ΔH may be estimated from the slope of these lines, to give $\Delta H_{\text{Fe}} = 44$ kcal mole^{-1} and $\Delta H_{\text{Mn}} \parallel$ 34 kcal mole^{-1}.

Equations 3a and 3b may now be plotted, as shown in Figure 10, curves e.

The model can be extended to allow for the presence of magnesium in both minerals. The chlorite and garnet curves in Figure 10 then become surfaces, and at a given temperature, tie lines can be drawn from points on the chlorite plane to points on the garnet plane. Such lines are shown in Figure 11, which contains data on coexisting chlorite and garnet reported by Albee (1965). Isotherms can also be drawn on the chlorite and garnet planes, as shown in a tentative manner in Figure 11.

The main features of the model are as follows: Mg-Fe chlorite, containing a small amount of Mn will, at approximately 800°K, begin to break down to produce Mn-Fe garnet containing a small amount of Mg. With increasing temperature, a state of equilibrium or near-equilibrium will be maintained if garnet crystallizes at the expense of chlorite, and if both minerals constantly change in composition. The garnet must increase in Fe relative to Mn, while the chlorite increases in Mg relative to Fe. If no Mg is present, both minerals must increase in Fe relative to Mn (Fig. 10).

Compositional zoning

The above model concerning the production of garnet from chlorite will now be called on to account for the gross features of compositional

variation in the garnet crystals of specimen 285 (Fig. 5). We shall use the model in its simplest form as illustrated in Figure 10. Since both chlorite and garnet must change in composition during reaction, if near-equilibrium is maintained, different possibilities may be considered in relation to departure from equilibrium. Such departures are most likely to appear when the growth rate is rapid relative to the rate at which diffusion takes place in the crystals, in order to maintain homogeneity.

Four possibilities will be considered

a) Near-equilibrium crystallization; 'complete' diffusion in chlorite and garnet (Fig. 12a). In this case the rate of crystal growth is sufficiently slow to permit both phases to maintain homogeneity; consequently the garnet crystals produced by the reaction will not be zoned.

b) 'Complete' diffusion in chlorite; no diffusion in garnet (Fig. 12b). It is clear from Figure 10 that garnet crystals so produced will have their central portions enriched in Mn. This kind of reaction has been discussed in detail by Pfann (1952) who derived an equation to express the change in composition with distance in the phase within which no diffusion takes place. In terms of garnet and chlorite, the equation is:

$$[\text{Mn gar}] = \lambda [\text{Mn chl}]_0 (1 - g)^{\lambda - 1} \quad (5)$$

where $\lambda = [\text{Mn gar}]/[\text{Mn chl}]$, $[\text{Mn chl}]_0$ is the initial concentration of Mn in chlorite, and g is the extent of reaction expressed as a fraction. This equation was previously used by Hollister (1966) and Atherton (1968) to account for the Mn profiles in the garnet crystals that they had examined.

Equation (5) was derived on the assumption that λ is independent of temperature. With reference to the garnet-forming reaction λ would be constant only if the garnet and chlorite curves in Figure 10, near the Fe end of the diagram, are essentially straight lines. In Figure 10, λ does not remain constant, but varies from 13 at 760°K to 48 at 810°K.

c) Restricted diffusion in chlorite, no diffusion in garnet, steady state (Fig. 12c). The possibility that a steady state condition may arise, in which the composition of both reactant and product become constant while the reaction progresses, was considered by Chalmers (1964). This condition cannot develop unless the composition (Fe/Mn ratio) of product (garnet) arrives and stays at the valve of the initial composition of the reactant (chlorite).

A change in the rate of growth of a garnet crystal may cause a change in the composition at the edge of the crystal (*c.f.* Chalmers 1964, fig. 5.13, p. 138). A decrease in the rate of growth

will cause the Mn content to increase, as might be deduced from examination of Figure 12c. This possibility has been advocated by Edmunds & Atherton (1971) to account for the increase in Mn content found in the outer margins of some garnet crystals.

d) Restricted diffusion in chlorite, restricted or no diffusion in garnet, non steady state (Fig. 12d). The Mn content at the edge of a growing garnet crystal need not level off at the initial Mn content of the chlorite, and it could in fact continue to decrease, as shown in Figure 12d. If diffusion in chlorite is restricted, the Mn content of the edge of the chlorite crystal will fall below the value in the centre, and when the remaining chlorite finally breaks down to provide Fe and Mn for the outer rims of the garnet crystals, this outer rim will show a rise in Mn content.

This can be confirmed by the following calculation based on non-equilibrium crystallization in the simple model of Figure 10. Begin with a single crystal of chlorite of composition [Mn chl] = 0.05, and let a single, nearly spherical crystal of garnet form as a product of the chlorite-garnet reaction. Let the outer edges of the chlorite and garnet crystals maintain the composition required by equilibrium, and let the mean composition of the minerals be represented by curves f, Figure 10. These curves imply restricted diffusion in both minerals. Then the resulting Mn profile in the garnet crystal will be as shown in Figure 13. If a reaction of this kind was in fact responsible for the rise in the Mn profile in the garnet crystals of specimen 285 (Fig. 5), then a
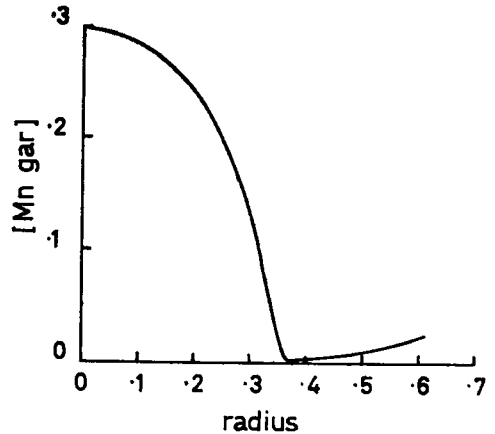
FIG. 13. Mn profiles in garnet obtained from the simple model of garnet crystallization of Figure 10, under the conditions indicated in Figure 12d. The profile was derived from curves f in Figure 10, which show the average composition of garnet and chlorite as a function of temperature.

FIG. 12. Four possibilities concerning changes in the composition of chlorite and garnet during reaction of chlorite to form garnet: (a) "complete" diffusion in chlorite and garnet; (b) "complete" diffusion in chlorite, no diffusion in garnet; (c) restricted diffusion in chlorite, no diffusion in garnet (steady state); (d) restricted diffusion in chlorite, no or restricted diffusion in garnet (non-steady state).

KINETICS OF THE CRYSTALLIZATION OF GARNET

large proportion of the garnet has crystallized at temperatures above those at which chlorite is stable.

Models of crystal growth

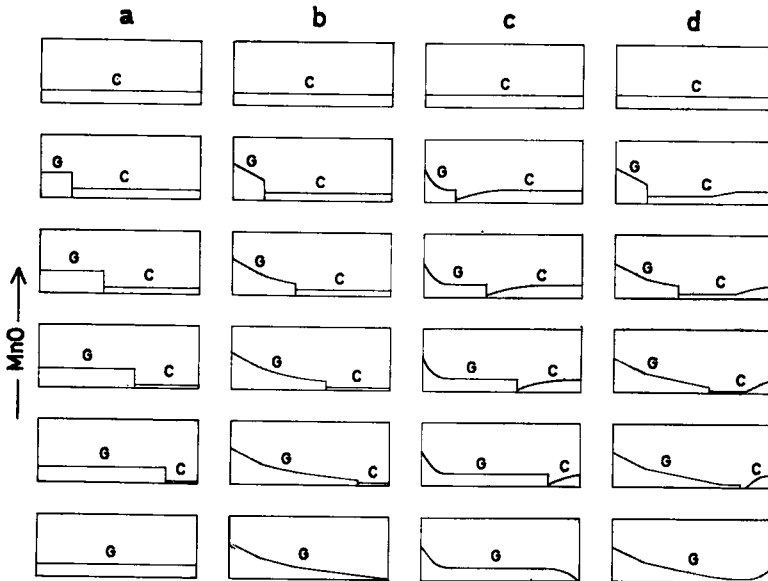Before attempting to extract some information concerning crystal growth from the compositional data, it is appropriate to briefly consider some models of crystal growth. To this end we shall assume that the crystals are spherical in shape, with radius r, surface area a, and volume v. Also, let t denote time, and let k_1, k_2, k_3 be rate constants.

In the first model, the radius of a crystal increases at a constant rate, and a point on the surface of the crystal advances at a constant speed. In the third model, the rate of increase of volume is constant, and (disregarding possible changes in density) the amount of material delivered to the surface of the crystal in unit time remains constant. The second model, in which the rate of increase of surface area remains constant, represents a growth rate intermediate between 1 and 3. The three models are compared in Table 3 and Figure 14.

The history of growth of a single crystal may conceivably be quite eventful, and numerous possibilities exist concerning its rate of growth, which may remain steady or may fluctuate. This could be illustrated by drawing, in Figure 14, numerous lines between the two points which represent the beginning and end of growth. The slopes of these lines need not always be positive; a zero slope would indicate a period of no growth, and a negative slope a period of dissolution.

Growth law deduced from compositional zoning in crystals of different sizes

It is obvious that mineral-forming reactions in metamorphic rocks bring about a certain amount of rearrangement of atoms within small volumes of rock, and that these atoms must possess at least a transient mobility. As a reaction is in progress, a small fraction of the material involved in the reaction must be in an activated

state, i.e. in the process of moving from a position in the reactant crystals to a position in the product crystals. This is a common aspect of chemical reactions in general.

In metamorphic rocks, the activated complex is visualized as an aggregate of atoms and molecules in motion, and is thought of as constituting a separate phase, which is concentrated along grain boundaries. We shall now assume that the atoms and molecules in this phase, as it existed in the study specimens, possessed a sufficient mobility to permit the garnet which was crystallizing from this phase at different points in a small volume of rock to everywhere be of the same chemical composition. Evidence in support of this assumption exists in Figure 5, which shows that the composition of garnet at the margins of the crystals, regardless of their size, is everywhere nearly identical.

If the above assumption is even approximately true, then an examination of the chemical profiles for crystals of different size within specimen 285, as shown in figure 5, will indicate that all of the four crystals could not have started their growth at the same time, but that progressively smaller crystals evidently began their growth at progressively later points in time. Thus the crystal of 0.67 mm diameter evidently began its growth when garnet of composition 31 per cent FeO was crystallizing in the rock, and when the 1.5 mm diameter crystal had grown to a radius of 0.7 mm. From this point in time to the time when crystal growth stopped, the smaller crystal grew (in terms of radius) 0.35 mm while the larger grew 0.20 mm. The two crystals were

TABLE 3. THREE MODELS OF CRYSTAL GROWTH[1]

	1	2	3
dr/dt	k_1	$k_2/8\pi r$	k_3/a
da/dt	$8\pi r k_1$	k_2	$(2/r)k_3$
dv/dt	ak_1	$(r/2)k_2$	k_3

1. Crystals assumed to be spherical with radius r, area a, and volume v; t is time and k_1, k_2, k_3 are rate constants.
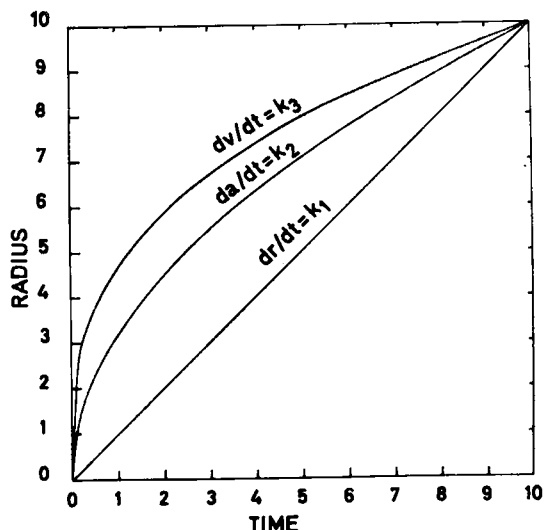

FIG. 14. Increase of radius with time in the three models of crystals growth listed in Table 3.

therefore evidently not growing according to the first growth law, which demands that, for a given interval of time, the radius of the two crystals must have increased by the same amount. This illustrates the kind of reasoning which may be followed to obtain information on crystal growth in metamorphic rocks.

Before proceeding further, a second assumption must be stated, namely that the compositional profiles have not changed significantly since their original development. Evidence in support of an assumption of this kind is found in the data of Edmunds & Atherton (1971) which showed that compositional profiles which developed during regional metamorphism survived a later contact metamorphism.

In the rocks of the present study, the rate of diffusion of cations in the garnet crystals is so small that profiles were not eliminated or levelled off in a time interval of abount 2.5×10^9 years.

Now let x denote some aspect of the composition of garnet material crystallizing at time t within a small volume of rock; x may be the ratio Fe/Fe + Mn for example. Then:

$$x = f(t) \qquad (6)$$

$$dx/dt = f_1(x) \qquad (7)$$

where $f(t)$ and $f_1(x)$ are unspecified functions of time and composition respectively.

Now:

$$dx/dr = (dx/dt)/dr/dt) \qquad (8)$$

By substitution of $dr/dt = k_1$, i.e. the equation for growth model 1, together with equation (7) into (8):

$$dx/dr = (1/k_1) f_1(x) \qquad \text{growth model 1} \quad (9)$$

Similarly

$$dx/da = (1/k_2) f_2(x) \qquad \text{growth model 2} \quad (10)$$

$$dx/dv = (1/k_3) f_3(x) \qquad \text{growth model 3} \quad (11)$$

Thus for any value of x there will be a fixed and corresponding value of dx/dr, dx/da, or dx/dv, regardless of crystal size, depending on whether the growth law which was followed was 1, 2, or 3, respectively.

In order to determine which of the three growth laws is best satisfied by the compositional data of specimen 285, the FeO concentration of the four crystals of different size has been plotted against a measure of size, namely radius or distance (Fig. 15a), area (Fig. 15b) and volume (Fig. 15c). In Figure 15b, the curves, being profiles for crystals of different size, are closer to being parallel, i.e. *having the same slope for* select values of per cent FeO, than in the remaining two figures. Actually, the curves ought
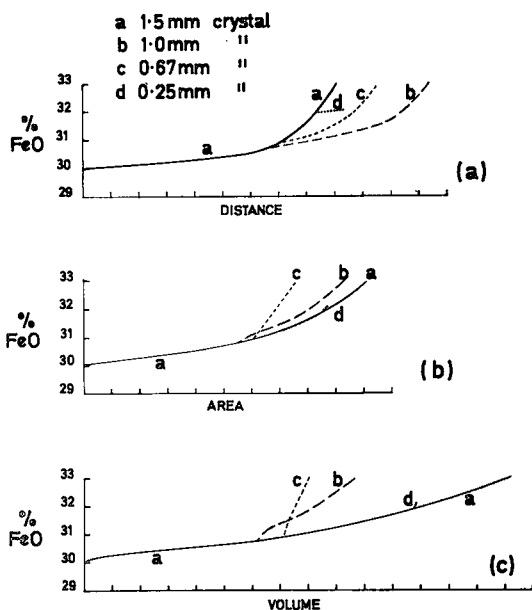

Fig. 15. Iron profiles in garnet crystals from specimen 285, replotted to test crystal-growth models. (a) test of growth model 1; (b) test of growth model 2; (c) test of growth model 3. Data from Figure 5.

to coincide, but a slight error in the determination of FeO in the centre of a crystal would cause a slight shift of the whole profile curve for that crystal. Hence the data from specimen 285 are in fairly good agreement with the second growth model, in which the rate of increase of area with respect to time is constant.

Nucleation law deduced from crystal-size distribution

The procedure to be followed in deriving an expression for the nucleation rate, i.e. the rate of appearance of crystals in a specified volume of rock, based on the crystal-size distribution and an assumption concerning the growth rate was previously described by the writer (Kretz 1966). The procedure is illustrated in Table 4, where the crystal-size distribution for specimen 285 (Fig. 4b) is used together with the growth law $dr/dt = k_1$, to obtain a relationship between the number of crystals (n) and time (t). The main feature of the procedure is that radius in mm is divided by the rate constant k_1 to obtain units of time. A time scale is then set up, which begins at the beginning of growth of the largest crystal and ends at the completion of growth of the largest as well as all other crystals. The resulting relationship between n and t is shown by curve a in Figure 16; the nucleation rate, dn/dt, may be identified as the slope of this curve.

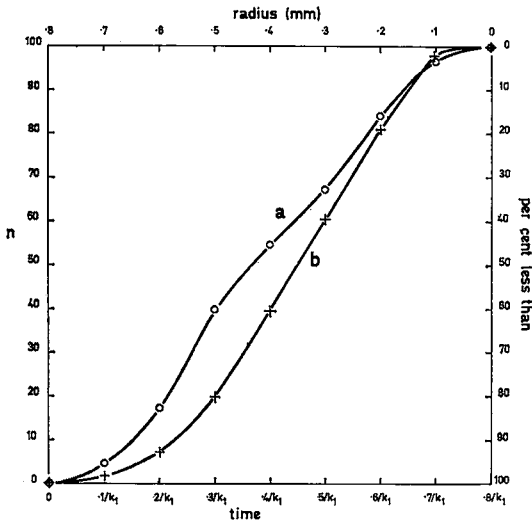The result of a similar calculation for specimen 296 is shown as curve b in Figure 16.

FIG. 16. Plot of number of garnet crystals (n) against time (t) for specimen 285 (curve a, Table 4) and 296 (curve b), on the assumption of $dr/dt = k_1$ (growth model 1).

In order to derive an expression for the nucleation rate when the second and third growth laws are considered, it is necessary to obtain histograms for the crystal-size distribution where size is measured in terms of area and volume. Such histograms, for specimen 285, are shown in Figure 17, together with the diameter histogram. In constructing these figures, a larger-than-normal number of classes was employed in order

to preserve the multimodal character of the distribution. Note that the histograms for area and volume appear to possess a mode (at a) in addition to the two modes (at b and c) which are the dominant features of the diameter histogram.

The size data are now processed according to the procedure outlined in Table 4, to give three nucleation-rate curves, as shown in Figure 18. Curves 1, 2, and 3, are obtained by adopting growth models 1, 2, and 3 respectively, as given in Table 3.

The position of the modes, a, b, and c, is indicated in Figure 18. A mode, which corre-

TABLE 4. PROCEDURE TO OBTAIN A RELATIONSHIP BETWEEN NUMBER OF CRYSTALS (n) AND TIME (t) FROM CRYSTAL-SIZE DISTRIBUTION (FIG. 4b) AND ASSUMPTION OF CONSTANT RATE OF LINEAR GROWTH ($dr/dt = k_1$)

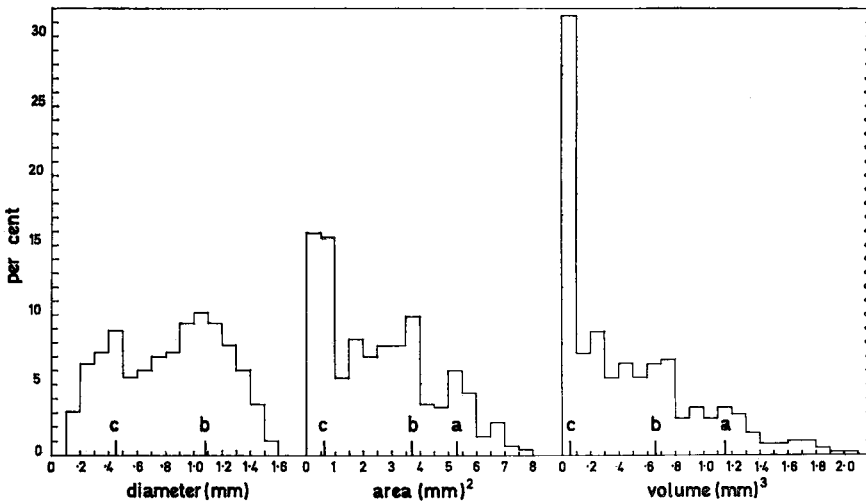| crystal diam. (mm)	crystal radius r	class mid-point r	no. of crystals	% of crystals	duration of growth time units	$\frac{t}{\text{time scale, time units}}$	$\frac{n}{\text{number of crystals at time } t}$
0	0					$.8/k_1$	96.9+3.1=100.0
		.05	12	3.1	$.05/k_1$		
.2	.1					$.7/k_1$	84.1+12.8=96.9
		.15	49	12.8	$.15/k_1$		
.4	.2					$.6/k_1$	67.2+16.9=84.1
		.25	65	16.9	$.25/k_1$		
.6	.3					$.5/k_1$	54.6+12.5=67.2
		.35	48	12.5	$.35/k_1$		
.8	.4					$.4/k_1$	39.8+14.8=54.6
		.45	57	14.8	$.45/k_1$		
1.0	.5					$.3/k_1$	17.2+22.7=39.8
		.55	87	22.7	$.55/k_1$		
1.2	.6					$.2/k_1$	4.7+12.5=17.2
		.65	48	12.5	$.65/k_1$		
1.4	.7					$.1/k_1$	4.7
		.75	18	4.7	$.75/k_1$		
1.6	.8					$.0/k_1$	0

FIG. 17. Histogram of crystal-size distribution in specimen 285, in relation to diameter (a), area (b) and volume (c).

sponds to a period during which a relatively large number of crystals was produced, shows up as an inflection point on the nucleation curve.

Owing to the bimodal or trimodal nature of the garnet-size distribution, the nucleation curves are irregular. However the general trend of curves 2 and 3 can be approximately expressed by power-law equations, while curve 1 can perhaps be regarded as being approximately a straight line. The approximate equations of these curves are as follows:

$$1 : n = 47.6\, k_1 t \qquad (12)$$

$$2 : n = 1.35\, (k_2 t)^{2.07} \qquad (13)$$

$$3 : n = 11.7\, (k_3 t)^{2.58} \qquad (14)$$

and these are shown as broken lines in figure 18. Expression for the nucleation rate are obtained by differentiation of these equations:

$$1.\ dn/dt = 47.6\, k_1 \qquad (15)$$

$$2.\ dn/dt = 2.79\, k_2^{2.07} t^{1.07} \simeq 2.8\, k_2^2 t \qquad (16)$$

$$3.\ dn/dt = 30.19\, k_3^{2.58} t^{1.58} \simeq 30\, k_3^{2.6} t^{1.6} \qquad (17)$$

Since the compositional data for garnet in specimen 285 is in better agreement with growth model 2 than with models 1 and 3, the nucleation rate expressed by curve 2 in Figure 18 is preferred. The curve shows that nucleation rate increased slowly at first, reached a maximum value late in the period of garnet crystallization, and finally declined. This can be understood by referring again to the simple crystallization model shown in Figure 10, and by plotting the per cent of garnet crystallized under conditions of near-equilibrium against temperature, making use of the lever rule. This plot is shown in
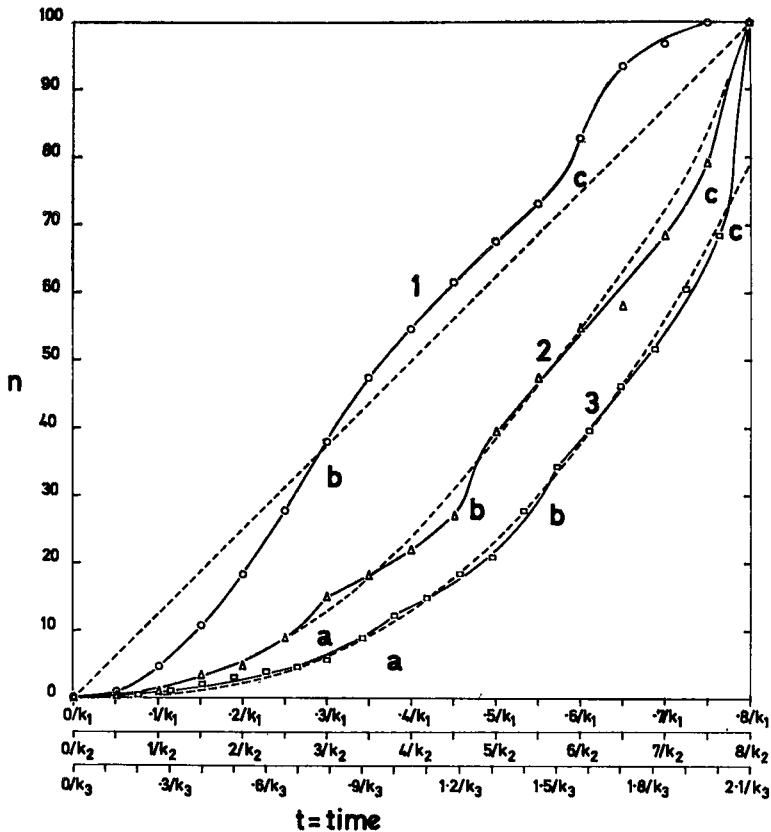
FIG. 18. Nucleation rate curves for garnet in specimen 285, based on crystal-size distribution (Fig. 17) and three models of crystal growth (Table 3). The relationship between n and t may be approximately expressed by equations (12), (13), and (14) which are plotted as broken lines. n is per cent of garnet crystals, or number of crystals in a volume of rock that ultimately contains 100 crystals. The three scales on the abscissa relate from top to bottom to curves 1 to 3 respectively.

FIG. 19. Per cent of garnet crystallized (y) as a function of temperature (T) during near-equilibrium crystallization in the simple model of Figure 10.

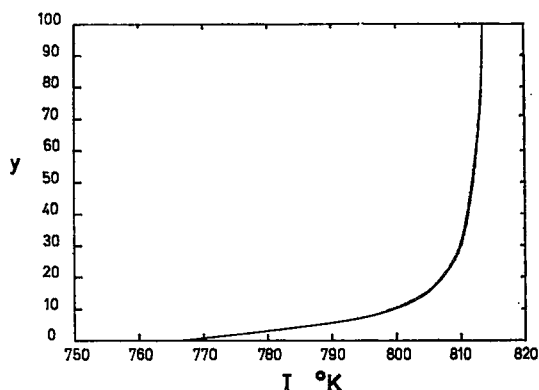Figure 19. If temperature were to increase at a uniform rate, the amount of garnet produced would increase rapidly with time, and the rate of nucleation would probably increase accordingly. If the rate of increase of temperature is sufficiently rapid to bring about a considerable departure from near-equilibrium, (overstepping), the rate of garnet production would probably increase even more rapidly during the latter stages of crystallization. Finally, however, the nucleation rate must decrease to zero, and the shape of curve 2 (Fig. 18) shows that this must happen (relatively) very quickly, during a very small fraction of the time of crystallization. One may notice, finally that a lower limit exists in the range of crystal size (Table 2) ; hence crystal growth evidently continued for a short period of time following the termination of the period of nucleation.

The reaction rate

Expressions for the growth rate and nucleation rate may be combined to obtain an expression for the reaction rate. The equation is :

$$V(t)=\int_{u=0}^{u=t} v(t,u)\left[dn/dt\right]_{t=u} du \qquad (18)$$

Where $V(t)$ is the volume of the product at the time of observation, t, v (t,u) is the volume of a crystal that began growth at time u when observed at time t, and dn/dt is the nucleation rate. Now with reference to garnet in specimen 285, the favoured

growth rate is

$$da/dt = k_2 \qquad (19)$$

$$dv/dt = rk_2/2 \qquad (20)$$

But since

$$r= \left[(k_2 t)/(4\pi)\right]^{\frac{1}{2}} \qquad (21)$$

$$dv/dt=(k_2^{3/2}t^{\frac{1}{2}})/(4\pi^{\frac{1}{2}}) \qquad (22)$$

Also, the favoured nucleation rate is, approximately,

$$dn/dt= 2.8 \, k_2^2 t \qquad (23)$$

By substitution of (22) and (23) into (18):

$$V(t)=\int_{u=0}^{u=t}\left[\int_{s=u}^{s=t}(k_2^{3/2}s^{\frac{1}{2}})/(4\pi^{\frac{1}{2}})ds\right]$$
$$\left[2.8k_2^2 u\right] du \qquad (24)$$

where s is time. Upon integration,

$$V(t)=(11.2/210\pi^{\frac{1}{2}})k_2^{7/2}t^{7/2} \qquad (25)$$

The relationship between volume of garnet produced, $V(t)$, and time, t, for an arbitrary value of k_2 is shown in Figure 20. The reaction rate is described by differentiation of (25):

$$dV(t)/dt=(7/2)(11.2/210\pi^{\frac{1}{2}})k_2^{7/2}t^{5/2}$$

that is, dV/dt is proportional to t raised to the power 5/2.

The general form of the reaction-rate equation can be understood by referring once again to the simple model of garnet crystallization as expressed by figure 10, and by comparing figures 19 and 20. An acceleration in the reaction, as shown in Figure 20 would naturally result from nearly uniform rate of increase of temperature.
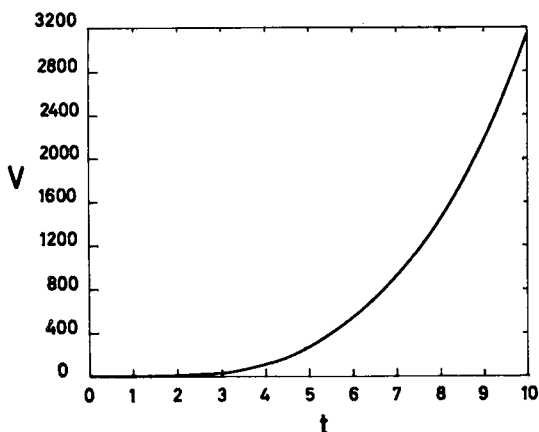

FIG. 20. Reaction rate curve (equation 25) for an arbitrary value of the rate constant k_2.

Nucleation sites

The observation that the garnet crystals in specimen 296 are randomly distributed indicates that the number of potential nucleation sites per cm³ of rock was large but not necessarily infinite. Thus the sites may have been restricted to interfaces between chlorite and quartz, for example, but since the rock was fine-grained, nucleation restricted to these planes could easily produce a distribution of product crystals that is nearly random. It is not possible to determine at present whether the actual selection of sites was determined by slight differences among the potential sites with regard to the energy required for nucleation, or whether the selection was governed by fluctuations in the energy and composition of the activated complex.

Growth mechanism

The presence of crystal faces and growth steps on the garnet crystals of the present study indicates that crystal growth progressed, at least in part, by the spreading of layers on surfaces of preferred crystallographic orientation. It is somewhat surprising that this process takes place in metamorphic rocks, where the growing crystals are constantly surrounded by crystalline material such as quartz and feldspar.

An important aspect of crystal growth in metamorphic rocks is that the solid material that lies in the path of crystal growth must be removed. The symmetrical nature of the composition profiles indicates that this material was removed with equal ease in all directions. However, quartz and ilmenite, which form the most common inclusions in the garnet crystals, were obviously removed with greater difficulty than feldspar and biotite. The large garnet crystal shown in Figure 2a was evidently in the process of engulfing a grain of quartz when crystallization stopped. The favoured interpretation concerning the removal of the material that was lying in the path of crystal growth is that a chemical break-down or dissolution of this material took place at the garnet interface. The atoms thus entered the activated phase and migrated away from the garnet, being deposited elsewhere in the rock. However, once these atoms have entered the activated phase, they would be indistinguishable from atoms that came from chlorite, and it seems likely, therefore, that the garnet-forming reaction as discussed above cannot be entirely isolated from the reaction by which feldspar, biotite, etc. were relocated in the rock as a result of garnet growth.

DISCUSSION

Zoning in garnet crystals

During the past few years, compositionally zoned garnet crystals have been reported from low-grade and medium-grade metamorphic rocks in many parts of the world, for example by Banno (1965), de Béthune et al. (1965), Atherton & Edmunds (1966), Harte & Henley (1966), Hollister (1966), Brown (1967), Linthout & Westra (1968), Dudley (1969), and Okrusch (1971), and the phenomenon appears to be a very common one. In contrast, garnet crystals in rocks of high-grade regional metamorphism are evidently only very slightly zoned or are homogeneous (Himmelberg & Phinney 1967; Blackburn 1968).

In nearly all of the zoned garnet crystals described to date, there is a general decrease of Mn content and an increase of Fe content along a traverse from the centre of the crystal to the margin, while considerable variation has been found in the Mg and Ca profiles. The composition profiles, particularly with reference to Mn, have been most frequently interpreted as the result of the ability of garnet to selectively extract Mn from the reactant phase during crystal growth. This interpretation was first discussed in some detail by Hollister (1966) and by Atherton (1968), and is analogous to the interpretation commonly employed to account for zoning in plagioclase crystals in igneous rocks. Most frequently, crystal growth has been considered to take place while the metamorphic grade or the temperature was increasing.

Some more complex profiles have been found by de Béthune et al. (1968), by Lithout & Westra (1968), and by Edmunds & Atherton (1971), and these have been accounted for by fluctuation in metamorphic grade or in temperature.

The Hollister-Atherton interpretation of compositional zoning in garnet is presently adopted, but their model, as expressed by equation 5, is considered to contain too many restrictions. In particular, the assumption that the concentration ratio, λ, remains constant seems unreasonable, and has been shown above to be capable of considerable variation. Moreover, due consideration has not been given in the past to compositional profiles in crystals of different size. Hence the writer has not attempted to express the profiles of the Yellowknife crystals in terms of equation 5.

The curious increase in the Mn content that is sometimes found in the outer margins of garnet crystals has attracted much attention and some quite different interpretations have been advanced to account for it. The possibility that

a decrease in growth rate might bring about an increase in the concentration ratio λ was hinted at by Hollister (1966) and was developed in some detail by Edmunds & Atherton (1971). This model was described above. A second interpretation is that the garnet crystal, after growing to a certain size, experienced dissolution, during which Fe and Mg were extracted from the crystal in advance of the dissolution 'front', causing Mn to be concentrated in that region. This interpretation was employed by Evans & Guidotti (1966), de Béthune et al. (1968), and Grant & Weiblen (1971). A third interpretation, due to Drake (1968), is expressed in terms of a change, during crystal growth, of the position of the garnet-chlorite tie line, resulting from the appearance of another phase, in this case, staurolite.

With reference to the Yellowknife rocks, the favored interpretation is illustrated in Figure 12d, above, and is similar to that of Edmunds & Atherton (1971). It does not, however, depend upon a change in the rate of crystal growth, only on a restriction on diffusion in chlorite during the reaction.

It is surprising that compositionally zoned garnet crystals that formed during metamorphism did not subsequently become homogenized by diffusion. The subject was discussed by Mueller (1967), who pointed out that plastic strain, which would lower the energy barrier associated with diffusion, would be much less in isolated garnet crystals than in the chlorite crystals of a chlorite-rich matrix. In any case, the diffusion coefficient for Fe-Mn exchange diffusion in garnet must be very small, and the temperature below which diffusion becomes negligible may be at, or even above, the temperature of garnet crystallization in low- and medium-grade metamorphic rocks. Diffusion may take place, however, at the higher temperatures of high-grade regional metamorphism, and the crystals found in these rocks may have been zoned initially, but were homogenized by diffusion, as suggested by Blackburn (1968).

An unexpected finding of the present study is that the Mn profiles in the garnet crystals of the specimens are not the same. The specimens are separated by a relatively small distance (Fig. 1) compared to the width of the metamorphic zones, and it is unreasonable to suppose that the rate of heating of the two specimens was much different. More data are needed before a satisfactory answer to this question can be found. One possibility is that the garnet crystals in specimen 296 were homogenized to some extent by a later rise in temperature caused by the intrusion of the near-by diabase dike.

Crystal size

Abundant and valuable information on the size of garnet crystals in metamorphic rocks were presented in papers by Galwey & Jones (1963, 1966) and by Jones & Galwey (1964, 1966). Numerous crystal-size distributions were reported from marbles in contact aureoles and from schists in terrains of regional metamorphism. All of the size distributions were found to be unimodal and nearly normal, despite a variation in modal size, which ranged from 0.04 to 10 mm.

Galwey & Jones considered different models of nucleation and growth to account for their data, but from the outset they preferred the view that nucleation was not instantaneous, and that the crystal-size distribution is a reflection of the nucleation rate, a view that is now very much supported by the chemical data. Moreover, they concluded, from the bell-like form of the size distribution, that nucleation during the initial stages was acceleratory. The writer is in full agreement with this interpretation.

In one of the earlier papers (Galwey & Jones 1963), an attempt was made to account for the size distribution in terms of a growth rate of the form $dr/dt = k/t^{\alpha}$, where k and α are constants, and a rather complex expression for the nucleation rate. However, for the most part, the authors have been concerned with a comparison of size distributions in rocks of different origin, and the interpretation of the data in terms of different rates of increase of temperature. To this end they defined a function

$$K = kd_1$$

where d_1 is the modal diameter and k is inversely proportional to the deviation or 'spread' in the distribution. In fact, k is the slope of a straight line that is obtained when $\log [n/(100 - n)]$ is plotted against diameter, where n is the number of crystals in a size class plus the sum of all crystals in classes of *smaller* diameter; n is expressed as per cent.

Unfortunately, variations in K are not readily visualized in terms of variations in the histogram from which K is calculated. For, when the average size is small (d_1 small) k is large, and when the average size is large, k is small. Nevertheless, K does appear to correlate with the rate of heating as deduced on geologic grounds. For example at Garrison, adjacent to a dolerite sill, $K = 3.3$ to 3.7, and at Banberg, adjacent to a granodiorite pluton, $K = 1.8$ to 2.7 (Jones & Galwey 1966).

The Galwey-Jones plot applied to specimen 285 does not produce a straight line, and when applied to specimen 296 produces a line which

is approximately straight, with $K = 1.7$, in good agreement with the above data.

Nevertheless, the writer maintains that a crystal-size distribution, as expressed by a histogram contains more information that can adequately be expressed in terms of a single parameter. It is suggested therefore that comparisons may be carried out by use of the graph shown in Figure 16. This may, incidentally, be regarded as a cumulative-size-distribution curve that is upside down. It is drawn in this manner so that attention may be more readily focussed on the lower part of the curve, which represents the initial phase of crystallization, and because the curve may be thought of as an approximate nucleation-rate curve, with number of crystals plotted against time. It becomes an exact nucleation-rate curve only if the growth law, $dr/dt = k_1$, is obeyed.

Different size distributions may then be readily compared. In Figure 16, both the size distributions range from 0 to 0.8 mm and hence the beginning and end points of the curves coincide. When comparing distributions of different size range, the abscissa could be in units of time/ maximum time or radius/maximum radius, in order to cause the end points of the curves to coincide.

Notice (Fig. 16) that at low values of n, the slope of curve a (specimen 285) is greater than for curve b (specimen 296). Since the two specimens are not likely to have experienced significantly different rates of heating, the difference in slope may be due to a difference in reaction rate. The bimodal or trimodal nature of the distribution in 285 may be due to fluctuations in the reaction rate, possibly brought on by variations in the rate of strain or in the rate of release of water from the rock. The reaction rate can conceivably be affected by a large number of factors.

Exchange equilibrium involving zoned garnet crystals

It is only a few years ago that it became possible by use of the microprobe to examine detailed variations in composition within garnet crystals. Earlier, several investigations were made of the distribution of elements between garnet and other ferromagnesian minerals, using bulk analyses of garnet. We shall now briefly consider whether or not conclusions based on bulk analyses must be modified in view of the present information on compositional zoning.

The common bell-shaped curve that is obtained when Mn concentration is plotted against *distance* along a traverse passing through the centre of a crystal gives an exaggerated view of the amount of Mn in the crystal as a whole. It is very instructive to replot the curve, using *volume* on the abscissa, for such a plot will show that the central Mn-rich part of the crystal forms a very small fraction of the whole, and the average composition of the crystal is very nearly that given by its outer portions. For example, the MnO content in a crystal in specimen 285 begins at 3.5 per cent at the centre, decreases to 2.3 per cent and then rises to 2.5 per cent at the outer edge. The average content, that which would be obtained from a bulk analysis, is 2.5 per cent.

A zoned crystal does not of course represent an equilibrium situation, for the crystal ought to spontaneously become homogeneous, thereby arriving at a state of lower free energy. Thus, in a small volume of rock that has been thoroughly equilibrated, all the contained garnet crystals must be homogeneous and have the same chemical composition. The rock specimens of the present study were obviously not thoroughly equilibrated, but since the nature of the zoning in the garnet crystals can be understood in terms of equilibrium phase theory, a condition of equilibrium or near equilibrium evidently existed with reference to the outer margins of the growing garnet crystals, and the coexisting ferromagnesian minerals.

This equilibrium, a spatially restricted exchange equilibrium, is the one that was being investigated by bulk mineral analyses. The amount of 'contamination' of the bulk analyses by the high concentration of Mn and low concentration of Fe in the centres of only the relatively few largest crystals is apparently within or very near the limit of analytical error.

The compositional profiles have, however, raised many questions concerning the nearness of approach to equilibrium during metamorphism, and have helped to emphasize that numerous kinds of processes take place within rocks, each with its equilibrium characteristics.

SUMMARY

Although the present study was mainly concerned with methods whereby information on the kinetics of crystallization may be extracted from rocks, and with interpretations of a general nature, we shall conclude with a summary of our knowledge of the events that evidently produced garnet at the two localities near Yellowknife.

1. The rock initially contained chlorite, muscovite and quartz, and with rising temperature, these minerals reacted to produce biotite, cordierite, and garnet. The nature and proportion

of the products depended upon the initial composition of chlorite. The reaction progressed rapidly relative to the rate of diffusion in the silicate minerals, resulting in zoned garnet crystals.

2. Garnet crystals were constantly being created during the period of garnet crystallization. The nuclei formed at preferred sites in the rock, but potential nucleation sites were sufficiently abundant to give rise to an essentially random distribution of crystals. The nature of the crystal-size distribution indicates that the rate of appearance of new crystals (the nucleation rate) was acceleratory, and declined very late in the period of crystallization. Locally, the number of crystals increased in a pulsating manner, giving rise to a bimodal or trimodal size distribution.

3. The rate of growth of the garnet crystals, as indicated by compositional zoning in crystals of different size, was apparently such that the rate of increase of surface area per unit of time was approximately constant.

4. Hence the reaction rate (the rate of production of garnet in a given volume of rock) was highly acceleratory, and may be expressed approximately as a function of time raised to the power 5/2. A reaction rate of this kind could result from a steady rate of increase in temperature.

5. The physical and chemical characteristics of the garnet crystals in the two specimens from Yellowknife show numerous differences, and it seems likely that the rates of nucleation, crystal growth, and reaction varied considerably, from place to place, even when the rate of increase of temperature was the same. These variations may be due to a number of factors, such as the nature of the reactant crystals, the amount of strain experienced by the rock, and by variations in the ease of escape of water during metamorphism.

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