

The Spatial Extent of Chemical Equilibrium in some High-Grade Metamorphic Rocks from the Grenville of Southeastern Ontario

W. H. BLACKBURN

Department of Geology, University of Kentucky, Lexington, Kentucky, U.S.A.

Received April 16, 1968

Abstract. Many of the recent studies of chemical equilibrium in metamorphic rocks may have been hampered by sampling which did not reflect single regions or domains of local equilibration. This paper records results of tests performed to determine the specific volume of rock in chemical equilibrium with respect to a certain phase, under a particular set of conditions. Two samples of high-grade metamorphic gneisses from the Grenville Series of southeastern Ontario were selected for intensive study. The garnets of one specimen, possessing a biotite-garnet-cordierite assemblage, underwent *in situ* laser microprobe spectrochemical determinations for Fe, Mg, Mn and Ca. Conclusions are thus possible as to the volumes over which free diffusion and chemical equilibrium took place. These volumes were found to be on the order of only a few cubic centimeters and their shapes are strongly controlled by rock structures such as foliation and lineation. A higher-grade pyroxene granulite was also investigated with respect to garnet and biotite equilibrium. Somewhat larger volumes of equilibration were noted in this rock.

Introduction

Attempts to define equilibrium relations in metamorphic rocks through the application of solid-state and chemical thermodynamics have become more popular in recent years with the advances in analytic apparatus and techniques (KRETZ, 1959, 1960, 1961; MUELLER, 1961, 1962; MOXHAM, 1965; MOORE, 1960; KRANK, 1961; PHINNEY, 1963; WYNNE-EDWARDS and HAY, 1963). The data of these studies and those obtained by the author during a preliminary study of equilibration in the Grenville gneisses of southeastern Ontario (BLACKBURN, 1967), commonly show considerable scatter when plotted on Roozeboom diagrams. In theory, this scatter should indicate non-equilibrium. However, ZEN (1963) has shown that from a textural and mineralogical standpoint, most metamorphic rocks are in equilibrium even at much lower grades than that of the rocks of this study. Irregularities in the elemental distributions between coexisting minerals might possibly be due to any of the following:

1. *Lack of Chemical Equilibrium in the Rock System.* In most cases this possibility may be eliminated; for both texture and mineralogy are consistent with thermodynamic equilibrium in metamorphic rocks as discussed by ESKOLA (1915), FYFE *et al.* (1958) and others. Further, WYNNE-EDWARDS and HAY (1963) have demonstrated equilibrium in the mineral assemblages of analogous cordierite-bearing gneisses of southeastern Ontario.
2. *Poor Precision and Accuracy of Chemical Determinations.* This is highly unlikely because many workers using different analytic techniques have encountered

the same difficulties with respect to the major and sometimes minor elements.

3. *Lack of Knowledge of All the Variables in the Chemical System.* This is indeed a serious problem in equilibration studies. Some of the parameters of metamorphism are cryptic and in order to decipher many of the variables, it is necessary to "plot everything against everything". Further, the distribution coefficient, $K_{\text{Mg}}^{\text{Bio/Gar}}$, for example, may vary with temperature and pressure according to the following relations after MCINTIRE (1963),

$$\left[\frac{\delta \ln K_{\text{Mg}}^{\text{Bio/Gar}}}{\delta T} \right]_P = \left[\frac{(-\Delta G^0/RT)}{\Delta T} \right]_P = \frac{\Delta \bar{H}}{RT^2} \quad (1)$$

$$\left[\frac{\delta \ln K_{\text{Mg}}^{\text{Bio/Gar}}}{\delta P} \right]_T = \left[\frac{(-\Delta G^0/RT)}{\Delta P} \right]_T = \frac{-\Delta \bar{V}}{RT} \quad (2)$$

Where $\Delta \bar{H}$ is the change in partial molar enthalpy and $\Delta \bar{V}$ is the change in partial molar volume. Under such circumstances the distribution coefficients could be altered by a change in temperature, T , and to a substantially less degree by change in pressure, P . Then the scattered distribution diagrams of equilibration studies could be caused by different P , T conditions among samples. However, PHINNEY (1963) studied samples less than 25 feet apart, and some of the author's samples were taken within 40 feet of one another; and these samples showed no less scatter.

4. *Samples Examined do not Reflect a Single Region or Domain of Chemical Communication and Equilibrium, or a Statistically Significant Number of these Domains if they are Small.* This indeed may be the fundamental problem, as the size of natural chemical systems in rocks is usually an unknown quantity. Local equilibrium is certainly established within a specific rock under the conditions imposed on it, but indication of this equilibrium may be lost by irregularities in the distribution functions due to small scale disequilibrium (PHINNEY, 1963). This disequilibrium could reasonably arise because of metamorphic equilibration throughout very small volumes caused by: (1) initial chemical inhomogeneities of the proto-rock; (2) slowness of diffusion to and from the sites of mineral growth; (3) low reaction rates; (4) zoning of some of the various metamorphic products.

Throughout the literature there has been vague and sketchy mention of the size of the domains of local equilibration (HARKER, 1932; KRETZ, 1960; MOXHAM, 1965; PHINNEY, 1963). Workers in the field of metamorphic equilibration have striven to collect and use small samples to insure local equilibrium conditions. However, the poor quality of the distributions and the unexplained indications of disequilibrium were still evident. PHINNEY (1963) found a correlation between the FeO/MgO ratios and the garnet/staurolite ratios in the rocks from St. Paul Island and Money Point, Nova Scotia. He attributed this to the regularity of the small scale diffusion of Fe and Mg during metamorphism. Checking his theory, he hand-picked biotite grains from several thin sections, noting the position of the grains picked. When analyzed spectrographically, these grains exhibited a distinctive Fe/Mg ratio and it was evident that the samples with a homogeneous texture showed similar compositions for all biotite grains. However, in the less homogeneous rocks, biotite grains showed similar compositions over a distance of only a few millimeters.

Similar observations have been made by HARKER (1893) in thermally metamorphosed limestones; by HAGNER *et al.* (1965) in mafic silicates of a single specimen of pyroxene amphibolite; by KRETZ (1966) in Australian biotite-muscovite-garnet gneisses; and by ALBEE *et al.* (1966) in kyanite-zone schists from Vermont.

Thus the problem remains of assigning a specific volume of equilibration to a particular phase with respect to a particular element under certain conditions of metamorphism. This paper gives the results and the conclusions drawn from tests on the assumption of local or mosaic equilibrium in some metamorphic rocks.

Method of Study

Geologic Setting

A regionally metamorphosed terrain of great age, which has most likely been affected by more than one regime of metamorphism, would seem to afford the most favorable conditions for the attainment of chemical equilibrium between coexisting minerals. With this end in view the author chose the Gananoque-Westport region of southeastern Ontario, situated on the "Frontenac Axis" — a belt joining the Adirondack Highlands to the main Grenville terrain (See Fig. 1).

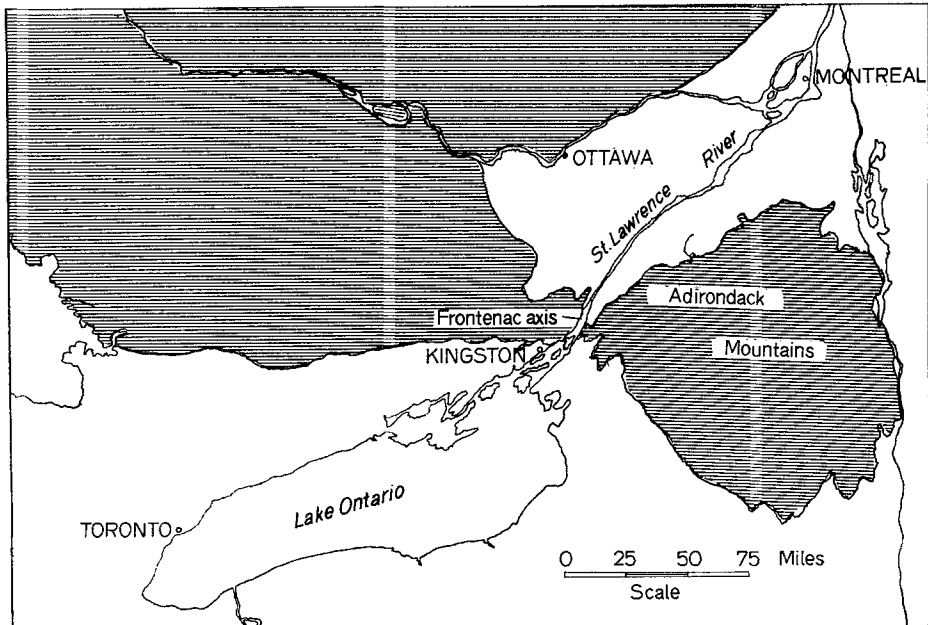


Fig. 1. Index map showing the location of the Frontenac Axis in relation to the Grenville Series rocks of Ontario and New York State. Grenville rocks are shown as hatch-marked areas

Approximately eighty percent of the exposed bedrock is Precambrian metamorphosed basic and acid volcanics, meta-sedimentary rocks (mainly marble, amphibolite, paragneiss and quartzite) and intrusions of basic and acid plutons (WYNNE-EDWARDS, 1959, 1962, 1967; HEWITT, 1964). The meta-sedimentary rocks of this area are for the most part quartz-biotite-feldspar gneisses and coarsely

crystalline marble. Garnet, garnet-cordierite and cordierite gneisses form units of varying thicknesses within the stratiform quartz-biotite-feldspar rocks. The gneisses are medium to coarse grained with lepidoblastic to granoblastic texture and pronounced foliation. The major minerals present are garnet, cordierite, biotite, sillimanite, magnetite, plagioclase, orthoclase or microcline and/or perthite. Corundum, spinel, zircon, apatite, dumortierite and tourmaline occur locally as trace constituents.

The assemblages associated with the garnet-cordierite gneisses of the Gananoque-Westport area, although biotitic, resemble granulite facies rocks. In the southwestern part of the Westport area, the rocks contain abundant hypersthene, only minor biotite and no cordierite (WYNNE-EDWARDS, 1959; WYNNE-EDWARDS and HAY, 1963). Metamorphism in this area thus has its upper *P* and *T* limit in true pyroxene-granulite facies. WYNNE-EDWARDS and HAY (1963) proposed that the garnet-cordierite assemblages represent a stage transitional between the upper amphibolite and granulite facies.

Description of the Samples

Two samples were selected for a study of the shape and size of equilibration domains. The selection was made on the basis of:

1. Sufficient garnet and biotite for analytical purposes.
 2. Lack of retrogression of garnet and biotite.
 3. Possession of typical assemblages for the gneisses of the Gananoque-Westport area.
 4. Rocks with two different grades of metamorphism were chosen to see the effect of grade on the size of the domains of chemical communication.
 5. Possession of distinct micro-structures, since it is possible that diffusion may be largely controlled by structural phenomena such as foliation and lineation.
- The samples selected for this intensive study included a biotite-garnet-cordierite gneiss (No. 17) and a pyroxene-garnet gneiss (No. 42) with a less distinct foliation. Modal analyses for these rocks are shown in Table 1.

Table 1. *Modal analyses^a of the gneisses used for the study of equilibration domains*

Sample number	17	42
Quartz	34.1	17.8
K-Feldspar	22.9	56.9
Plagioclase	2.9	9.7
Biotite	3.5	1.4
Garnet	11.1	5.2
Hypersthene	—	6.9
Cordierite	13.4	—
Sillimanite	9.9	—
Opagues ^b	2.2	1.7
Zircon	Tr	—
Sericite and chlorite	Tr	0.3

^a Modal values = volume percents.

^b Magnetite, ilmenite and pyrite.

Tr = 0.05 percent; — = Not present.

Sample 17 is a medium grained, strongly foliated gneiss with quartz, K-feldspar, garnet and biotite as major components observable in hand specimen. Microscopically, the gneiss exhibits an extremely well-developed foliation with foliation planes populated mainly with biotite, sillimanite, garnet and cordierite grains. A section, cut perpendicular to the foliation, shows greatly elongated garnets in the foliation plane. Some of these elongated garnets contain, besides local inclusions of quartz, K-feldspar and biotite, sillimanite needles which continue uninterrupted through the garnet. The biotite inclusions, like those of sillimanite, retain their orientation with

respect to foliation and lineation. The unequidimensional garnets, common in the gneisses collected, are described elsewhere (BLACKBURN and DENNEN, 1968).

Cordierite occurs as subhedral grains containing inclusions of quartz and sillimanite. It is usually altered to a waxy, yellow aggregate at grain boundaries and along fractures. The biotite is observed mainly as unaltered, ragged grains concentrated along the foliation surfaces but also scattered throughout the quartz-feldspar layers. The feldspars of specimen No. 17, orthoclase and a plagioclase of composition An_{40} , are unaltered.

Sample 42 exhibits a well developed layering in outcrop but foliation is not distinct due to the lack of platy minerals. The major phase constituents are quartz, K-feldspar, plagioclase, garnet and orthopyroxene. Garnet occurs as small- to medium-sized, unaltered, rounded grains with sparse inclusions of quartz. The orthopyroxene is hypersthene and occurs as scattered subhedral grains. Local chloritic alteration of the hypersthene is observed at grain boundaries. Biotite is a minor constituent of the rock and occurs as small ragged, unaltered grains scattered throughout the gneiss but concentrated in pyroxene-garnet-biotite layers. The K-feldspar present seems to be of the monoclinic variety and the plagioclase is An_{30} . Both K-feldspar and plagioclase are unaltered.

Spectrochemical Determinations of the Garnets of Sample 17

The original specimen of sample No. 17, measuring $9.0 \times 7.5 \times 7.3$ cm, was trimmed with a diamond saw to remove any weathered rind. Surfaces were then cut, parallel to (17II) and perpendicular to (17I) the foliation. These thick slices were in turn cut into slabs of roughly the dimensions of a petrographic slide. The slabs thus formed were cemented to petrographic glass slides and the exposed surface ground parallel to the glass base.

The selection of an analytic system for the investigation of the chemistry of many garnets distributed over a sizable area was of fundamental concern for this study. The electron micro-analyzer is, for many elements, a precise and accurate tool but handles only very small samples which would not be satisfactory in the present study where the garnets were examined with respect to size and distribution as well as chemistry (BLACKBURN, 1967). It was decided that the most practical tool for the job was the laser microprobe (BRECH, 1965, 1967). The technique for the laser-excited spectrochemical determinations in the garnets of sample 17 is described in detail elsewhere (BLACKBURN *et al.*, 1968).

After grinding the slabs of sample 17 (17I and 17II) and measuring the apparent diameters of the garnets and the coordinates of their centers, a slab was placed on the microscope stage of the laser microprobe. Each garnet exposed on the slab was "shot" with the laser beam. When each garnet was determined in sections 17I (perpendicular to the foliation) and 17II (parallel to the foliation), the slabs were ground again to remove 0.25 mm, the garnet apparent diameters measured and the garnets probed again. Chemically analyzed standard glasses were "shot" on every plate. Following microphotometry of the analytic plates, line intensities were converted to intensity ratios for each element determined. Intensity ratio data, for both the garnets and standards, were converted to concentration data by means of a Fortran IV program of a least squares analysis adapted from SHAW and BANKLER (1954). The precision and accuracy of this

method was found to be entirely satisfactory for most petrologic investigations (BLACKBURN *et al.*, 1968).

Chemistry of the Garnets of Sample 17

Results

In total, 365 garnet grains were determined for Fe, Mg, Mn and Ca. It is desirable to present the data in the context of the rock, showing the concentration of an

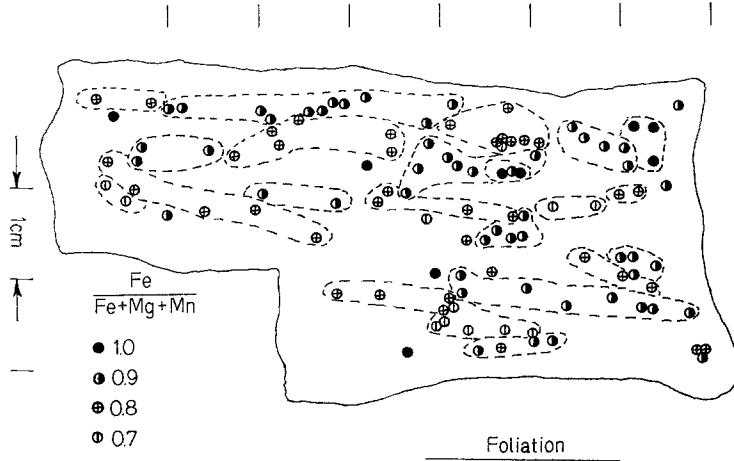


Fig. 2. Spatial distribution of iron in the garnets of Section 17I. Section 17I is cut perpendicular to the foliation

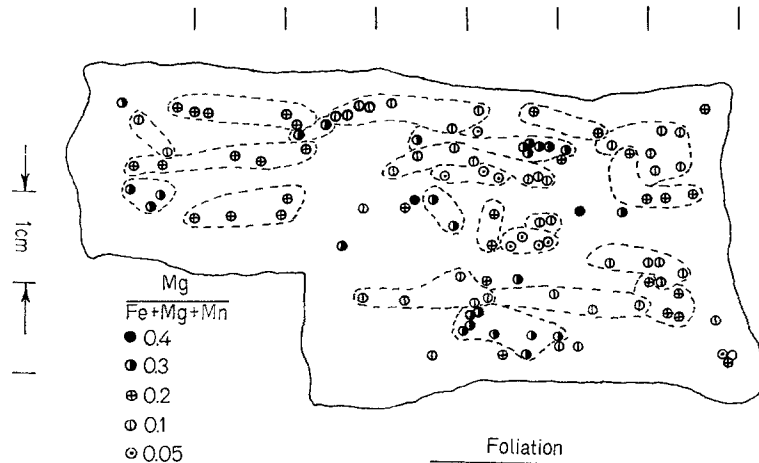


Fig. 3. Spatial distribution of magnesium in the garnets of Section 17I

element in a grain with respect to its position in the rock section. Since tabular notation is obviously useless, a diagrammatic presentation showing the position of each garnet grain along with the concentration of the element in question is employed.

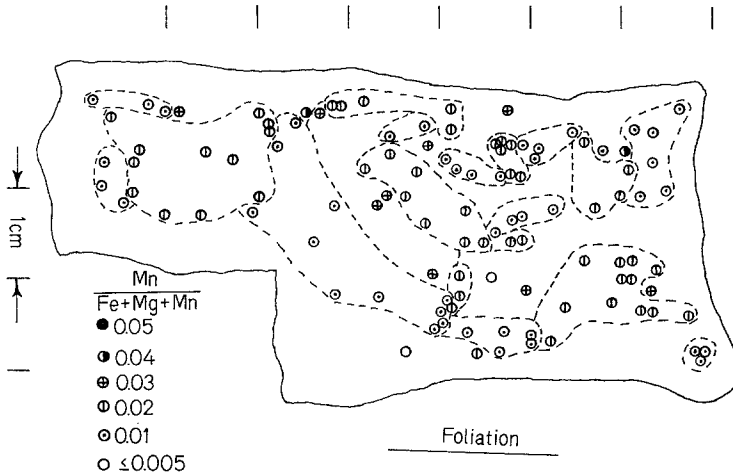


Fig. 4. Spatial distribution of manganese in the garnets of Section 17I

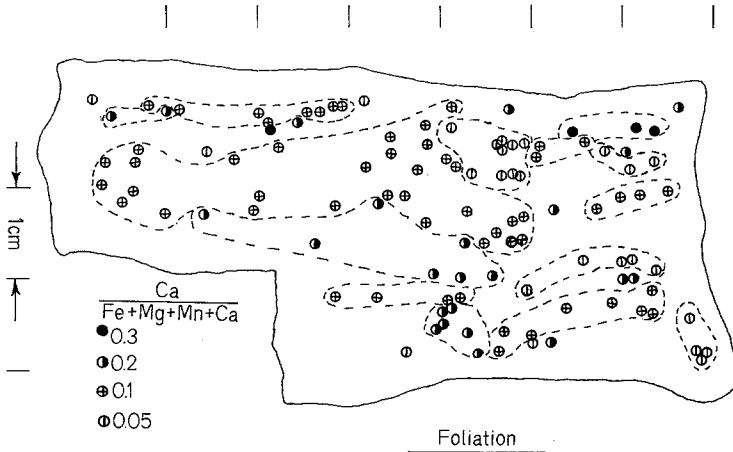


Fig. 5. Spatial distribution of calcium in the garnets of Section 17I

Fig. 2 to 5 show the spatial distribution of Fe, Mg, Mn and Ca in the garnets of section 17I, which is cut perpendicular to the foliation. A standard error of 10 percent is assumed for the analyses of all elements and various symbols are used to illustrate the concentration value of an element rounded off to the nearest significant decimal place. It is felt that this procedure gives a liberal estimate of the concentration since magnesium was the only element measured with a coefficient of variation above 10 percent (12.8%). Fig. 6, 7, 8 and 9 show the spatial distribution of Fe, Mg, Mn and Ca respectively, in section 17II.

An examination of the figures illustrating the spatial distribution of various elements in garnets of section 17I, shows small equilibration domains which, usually measure only a few mm across foliation but more extensive in the foliation

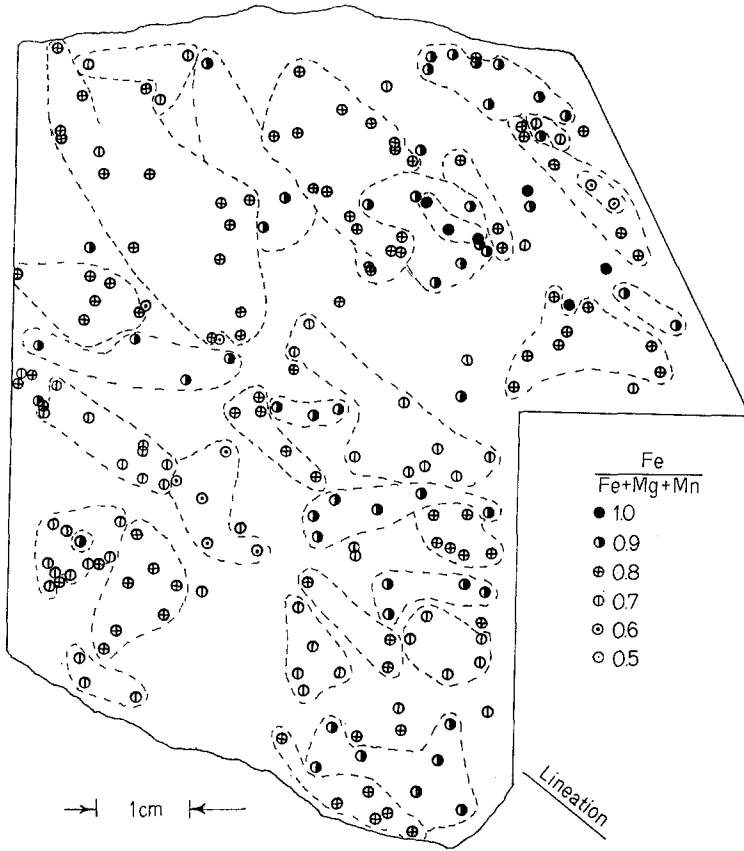


Fig. 6. Spatial distribution of iron in the garnets of Section 17II. Section 17II is cut parallel to the foliation

plane. Section 17II shows more extensive domains of equilibration, and these are usually elongated in the direction of lineation. The areas which contain garnets of the same composition with respect to a specific element have been outlined solely as a guide to the reader. These outlines are not intended to be composition contours.

Traverses, at $25\ \mu$ intervals across garnets from sections 17I and 17II showed no compositional zoning with respect to Mn, Mg, Fe or Ca (BLACKBURN, 1968). Thus it is concluded that compositional zoning in this rock is not prevalent and that the variations of garnet compositions within Sample 17 are real.

Discussion

The domains of garnet equilibration for Fe and Mg in Sample 17 are limited to less than 4 cm in the longest direction. In Section 17I, the areas over which garnets are of the same composition are elongated in the plane of the foliation to such an extent that in some cases chemical communication has been in effect over a

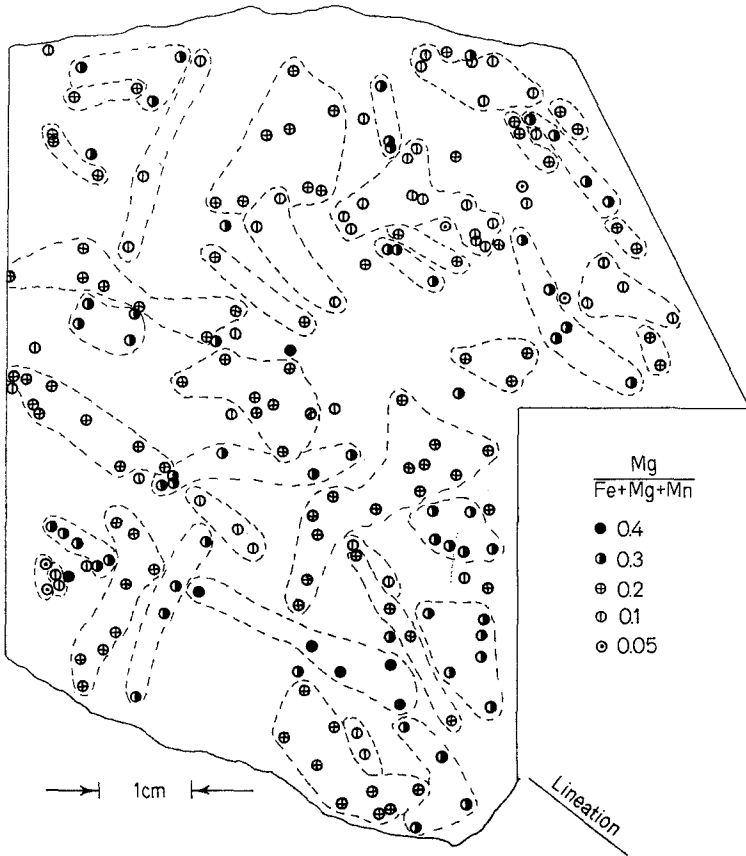


Fig. 7. Spatial distribution of magnesium in the garnets of Section 17II

distance of about 3 cm. However, garnets in the adjacent layer, a distance of about 1 cm, are of a different composition with respect to Fe and Mg. An examination of Fig. 6 and 7 gives the spatial relations of Fe and Mg in the garnets of section 17II, cut parallel to the foliation. Here the domains of equilibration are more extensive although elongated in the lineation direction.

In summary, the domains of spatial equilibration of Fe and Mg in garnets range from only a few millimeters to a few centimeters and tend to be elongated along foliation and lineation. Parallel to the foliation, chemical communication of garnets with respect to Fe and Mg took place over a maximum distance of 4 cm in the lineation direction and about 2 cm across it. Communication across foliation planes was usually limited to less than a centimeter suggesting equilibration volumes that are roughly ellipsoidal in shape with an axial ratio of close to 4:2:1. In section 17II, the spatial equilibration of Fe is more extensive than Mg. Iron shows less distinguishable domains but these are larger than the Mg domains. The domains of Mg equilibration are much more regular in their orientation in the lineation direction. This is possibly a reflection of the relative mobilities of Fe and Mg during metamorphism.

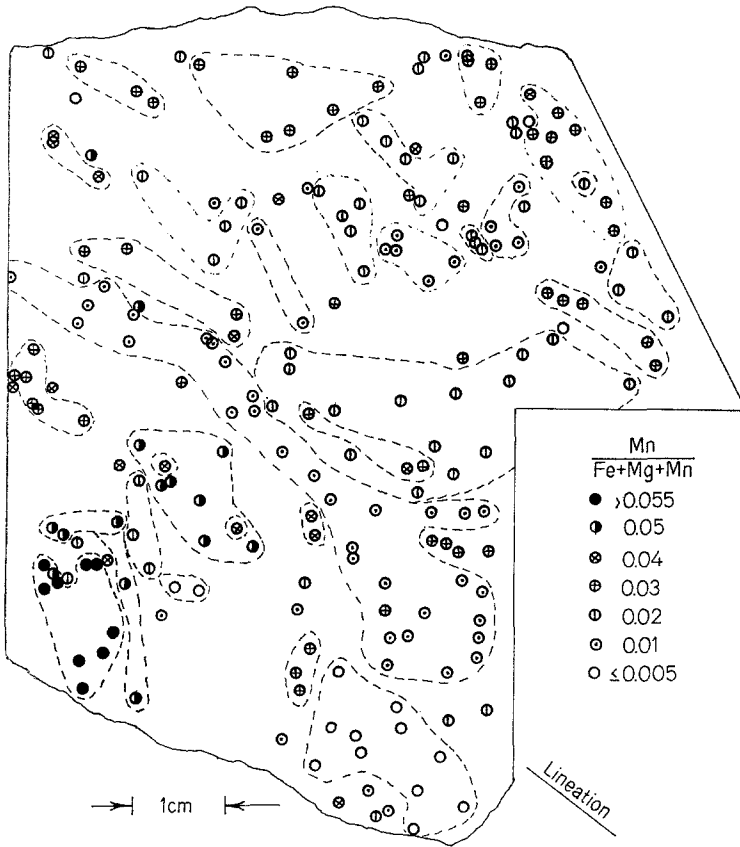


Fig. 8. Spatial distribution of manganese in the garnets of Section 17II

The spatial equilibration of Mn in garnets in sample 17 was found to be somewhat more extensive than that for Fe or Mg and the domains of identical garnet Mn concentration are more irregular in shape than their Fe and Mg counterparts. A distinct structural control is still evident, but equilibration across structural features is more extensive. For example, in section 17I (Fig. 4) equilibration domains measuring up to 1.5 cm across the foliation can be distinguished. The elongation in the foliation surface still persists, however. In section 17II (Fig. 8) the domains of Mn equilibration in garnets are at least as extensive as those for Fe, but they are regular in their orientation to the lineation direction.

The spatial degree of equilibration in the garnets of sample 17 with respect to their Ca content is shown in Fig. 5 and 9. In Fig. 5, looking at the section perpendicular to the foliation, equilibration domains controlled by structure and those having no obvious structural control are both observed. The structurally controlled domains, for the most part, occur at one end of the section and it is proposed that variations in the whole rock Ca content were more prevalent here. This would probably be reflected in the mineral assemblage associated with each of these garnet equilibration domains. Calcium equilibration in the garnets of

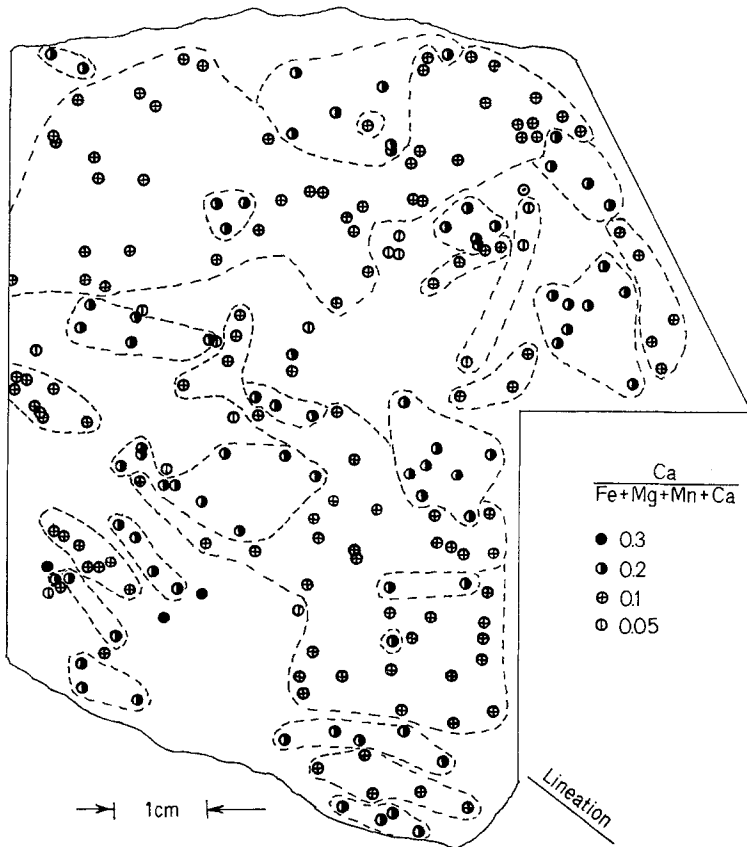


Fig. 9. Spatial distribution of calcium in the garnets of Section 17 II

section 17 II (Fig. 9) is more extensive than Fe, Mg or Mn. The domains are usually elongated in the lamination direction and extend up to 5 cm in their longest direction. There are also regions of garnets having the same Ca content which are distinctly elongated almost perpendicular to the trace of the lamination and some which show no preferred orientation.

Chemical Determinations of Biotite and Garnet from a Pyroxene Granulite Rock

As discussed above, it was decided to examine the spatial extent of chemical equilibration in a rock having a different mineral assemblage and possibly a different grade of metamorphism. The rock selected was a garnet-biotite-orthopyroxene gneiss, sample No. 42, which was described earlier. The relationship of biotite to hypersthene in this rock is unclear. From thin section analysis, no definite statement can be made as to whether the biotite is retrograde or the hypersthene prograde. The biotite occurs as small discrete grains only rarely in association with the pyroxene. It is suggested that the assemblage observed in Sample No. 42 is indicative of a pyroxene granulite and represents a higher temperature of metamorphism than Sample No. 17.

Method of Separation and Analysis

Sample 42 was trimmed with a diamond saw on those faces exhibiting weathering. A section, 1 cm thick, was then cut parallel to the foliation. This section, from here on referred to as 42II, was cut up into small cubes measuring roughly 1 cm on a side. Selected cubes of 42II were then crushed to $-20, +100$ mesh in a percussion mortar similar to that described by WAGER and BROWN (1960). The garnet and biotite were hand-picked under a binocular microscope and placed in electrodes or stored in gelatine capsules until analysis.

Determinations for Fe, Mg, Mn and Ca were made on the garnets separated; Fe, Mg and Mn were determined in the biotite. All analyses were performed by emission spectrography according to the parameters in Table 2. The samples of biotite and garnet were placed in preared electrodes and arced neat as the anode. Standards were neat samples of biotite and garnet whose Fe, Mg, Mn and Ca values had been determined by atomic absorption spectrophotometry (BLACKBURN, 1967). Relative line intensities of samples and standards for Fe, Mg and Mn were recalculated to the ratios $Fe/Fe + Mg + Mn$, $Mg/Fe + Mg + Mn$ and $Mn/Fe + Mg + Mn$. Working curves were made for the various elemental ratios by plotting these intensity ratios against the corresponding concentration ratios of the standards. The coefficient of variation of the method was close to 12 percent for all the elements determined.

Table 2. *Excitation parameters for the spectrochemical determination of Fe, Mg, Mn and Ca in garnet and biotite from Section 42II*

Spectrograph	3m Littrow-mounted quartz prism (Adam Hilger. Co., Ltd. No. E-478); source focused on masked collimator.
Excitation	9 amp. anode for 40 sec.; 25 Ω ; 7 mm analytic gap.
Electrodes	<i>Sample</i> -National Carbon Co. AGKSP Specpure graphite with a cavity measuring 0.5×3.0 mm. <i>Counter</i> -National Carbon Co. L1138F Specpure carbon, pointed.
Plates and development	Kodak Spectrum Analysis-1, developed for 4.5 minutes at 20°C in Kodak D-19 developer.
Plate calibration and photometry	Calibration by the preliminary curve method; photometry with a Hilger non-recording microphotometer.
Analytic lines	Fe 2912.2 Å, Mg 2779.8 Å, Mn 2794.8 Å, Ca 3158.9 Å

Results of the Determinations in Section 42II

Figs. 11 and 11A show the spatial distribution of Fe in garnet and biotite from Section 42II. Fig. 12, 12A, 13, 13A and 14 show the spatial distributions of Mg in garnet and biotite, Mn in garnet and biotite and Ca in garnet, respectively. In all the graphic representations the concentration ratios are rounded off to the nearest significant decimal place. A semi-quantitative modal analysis of the section was made while the garnet and biotite were being picked. The results of this are shown in Fig. 10. It should be noted that while biotite is ubiquitous in this sections, there is no garnet in the upper right hand corner. Traverses across garnets of Section 42II showed no compositional zoning (BLACKBURN, 1968).

Discussion

The spatial distribution of Fe in the garnets of section 42II (Fig. 11) is more uniform than the same distribution in section 17II. The greater part of the section shows garnets with the ratio $Fe/Fe + Mg + Mn$ close to 0.6. Comparison of Figs. 10 and 11 shows that the areas with garnets of low Fe concentration are

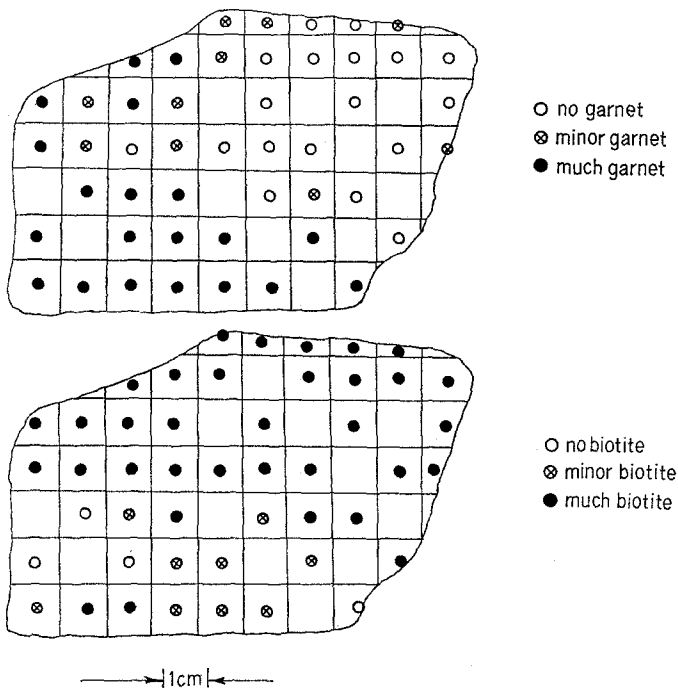


Fig. 10. Distribution of garnet and biotite in Section 42II. Section 42II is cut parallel to the foliation

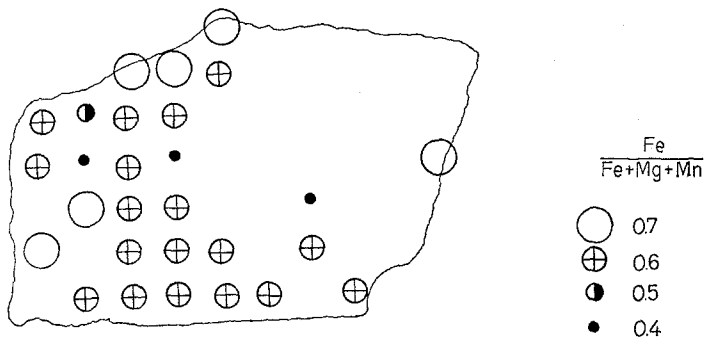


Fig. 11. Spatial distribution of iron in the garnets of Section 42II

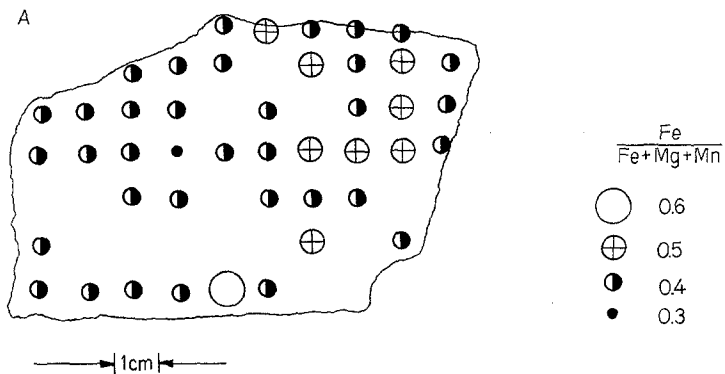


Fig. 11 A. Spatial distribution of iron in the biotite of Section 42II

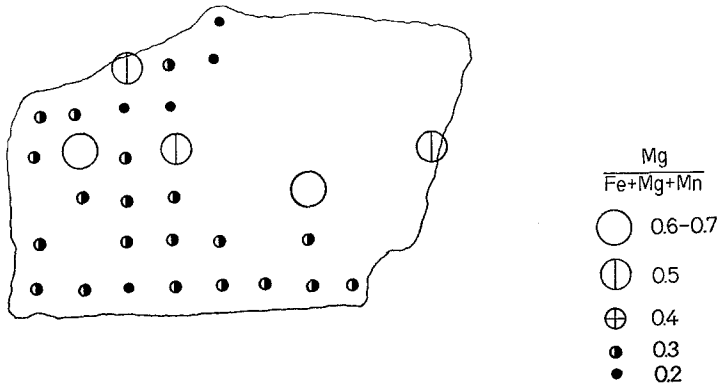


Fig. 12. Spatial distribution of magnesium in the garnets of Section 42II

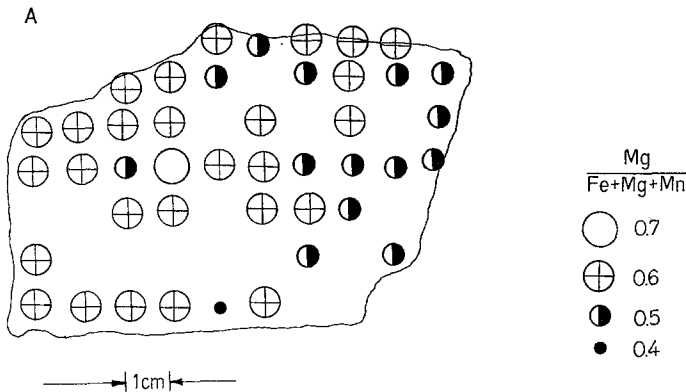


Fig. 12A. Spatial distribution of magnesium in the biotite of Section 42II

also areas of low garnet modal values and both the modal and compositional differences are probably due to a decrease in the whole-rock FeO/MgO ratio in the areas with little or no garnet. The spatial distribution of Fe in biotite (Fig. 11 A) shows a uniform distribution of Fe values over most of the section but the area containing little or no garnet exhibits somewhat higher biotite Fe values. However, this is expected as hypersthene is ubiquitous in the section and probably acts as an Fe-Mg buffer in the biotite-garnet-orthopyroxene system.

The distributions of magnesium in the garnet and biotite of section 42II are shown in Figs. 12 and 12A. Most of the garnets in the section have a Mg/Fe + Mg + Mn ratio of 0.4. Those garnets from cubes bordering on or in the garnet free area are higher in Mg, the ratio being 0.6 to 0.7. The magnesium content of biotite in this section is quite uniform throughout the section with lower values found in the garnet-deficient area.

The spatial distribution of the value X_{Mn}^{Gar} in the section 42II is quite uniform. Out of the 28 cubes in which manganese was determined in the garnet, only 6 had garnets in which the ratio Mn/Fe + Mg + Mn was outside of the range 0.03 to 0.04. These irregular values were scattered and no correlation between the modal ratio, garnet/biotite, is apparent. The accuracy of these irregular results might be

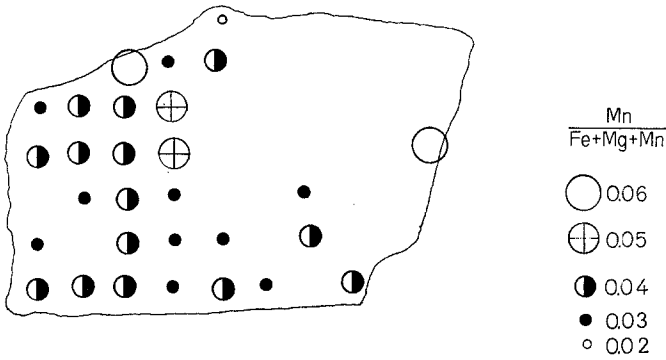


Fig. 13. Spatial distribution of manganese in the garnets of Section 42II

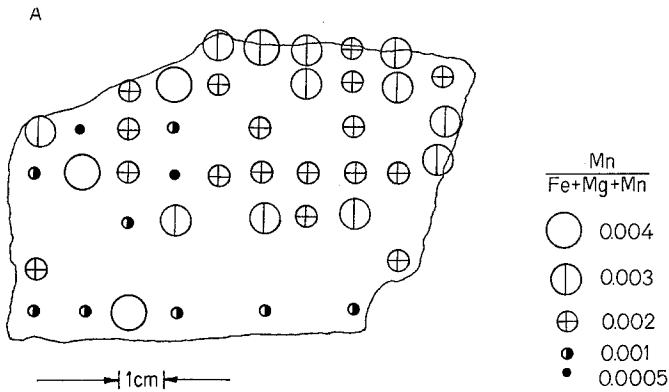


Fig. 13A. Spatial distribution of manganese in the biotite of Section 42II

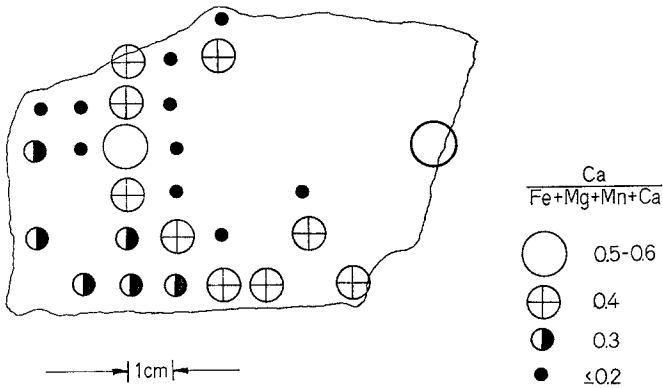


Fig. 14. Spatial distribution of calcium in the garnets of Section 42II

questioned although there is no justification in discarding these values for analytic reasons. It is obvious from Fig. 13 that the equilibration domain with respect to Mn in garnet is much larger than those observed in sample 17 and it may be said that the garnets of this specimen have close to the same Mn content

throughout the section and possibly beyond. The spatial distribution of Mn/Fe + Mg + Mn in the biotite of specimen 42II is less regular than distributions of Fe and Mg (see Fig. 13A). There seems to be an increase in the Mn content of the biotite going from the lower left hand corner to the upper right hand corner or towards the garnet deficient zone possibly due to an increase in MnO content of the rock in this area.

The calcium content of the garnets in this section varies from 0.02 to 0.06 as the ratio Ca/Fe + Mg + Mn + Ca (Fig. 14). Quite definite relationships to the zone of garnet deficiency and to the Ca content of the garnet surrounding this zone may be seen. The garnet closest to this zone has a very low Ca content ranging from $X_{Ca}^{Gar} = 0.02$ down to undetectable Ca. The next zone outwards contains garnets in which X_{Ca}^{Gar} groups around the value 0.04. Moving farther outwards, i.e. to the lower left hand corner, the atomic ratio for Ca drops again to 0.03. The relationship here is unclear and the Ca contents of the gneiss and of the orthopyroxene would have to be taken into consideration before a meaningful evaluation could be made. WYNNE-EDWARDS and HAY (1963) point out that in the biotite-cordierite-garnet gneisses discussed above, a low CaO content prohibits the growth of garnet and biotite-cordierite gneisses are formed. If the pyroxene-garnet gneiss under question here is a prograde product of a biotite-garnet cordierite gneiss, it is possible that the hypersthene displaced cordierite and part of the biotite in the changing ferromagnesian assemblage, and the area now deficient in garnet was originally a biotite-cordierite assemblage deficient in CaO.

In summary, it may be said that for Fe, Mg and Mn in garnet, the spatial degree of equilibration was measurably larger in this pyroxene garnet gneiss. Variations within a hand specimen may still be seen, however, and these variations are probably due to variations in whole rock chemistry as reflected in the mineralogical variations. The spatial equilibration of Ca in garnets was found to be no more extensive than in the biotite-cordierite-garnet assemblages. Again the calcium content of the garnet seems to be related to their modal abundance which may in turn be dependent on the CaO content of the rock.

Fig. 15 shows the distribution coefficient $K_{Fe}^{Gar/Bio}$ for each cube in the section 42II where garnet and biotite were both measured. A distinct elongated area within the section exhibits a distribution coefficient $K_{Fe}^{Gar/Bio} = 1.0$, while the surrounding garnet-biotite pairs show $K_{Fe}^{Gar/Bio} = 2.0$. The elongation of this zone of $K_{Fe}^{Gar/Bio} = 1.0$ is reminiscent of the structural control on the equilibration domains exhibited in specimen 17. However, there is no obvious macroscopic reason for the elongation of the equilibration domain as shown in Fig. 15. The zone measures above 4 cm across at its widest point and has an apparent length of close to 8 cm although it probably extends past the edge of the section.

The spatial distribution of the coefficient $K_{Mg}^{Gar/Bio}$ is not nearly so regular as that for Fe. Four distinct groups of values for $K_{Mg}^{Gar/Bio}$ appear, these being 0.4, 0.6, 0.7 and 1.0. These values are shown diagrammatically in Fig. 15A. Comparison of Fig. 10 and 15A shows that the value $K_{Mg}^{Gar/Bio} = 1.0$ in all but one case is correspondent with a low garnet/biotite ratio. Areas over which the values $K_{Mg}^{Gar/Bio}$ are equal are much smaller than the equivalent distribution for Fe. It is possible that this irregularity is due to the dependence of the atomic ratio Mg/Fe + Mg +

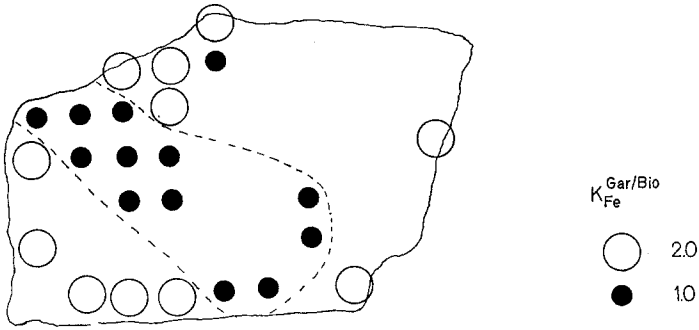


Fig. 15. Spatial distribution of the distribution coefficient $K_{Fe}^{Gar/Bio}$ in Section 42II

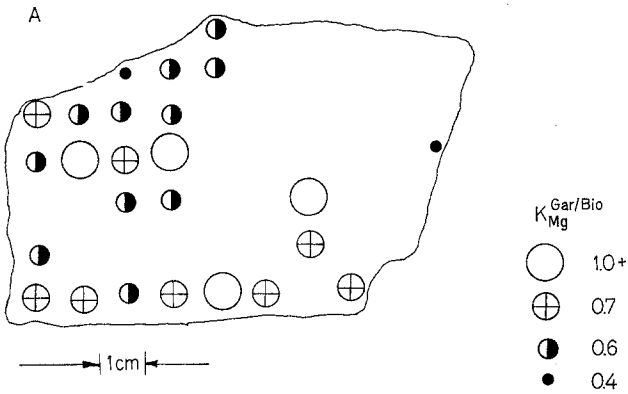


Fig. 15 A. Spatial distribution of the distribution coefficient $K_{Mg}^{Gar/Bio}$ in Section 42II

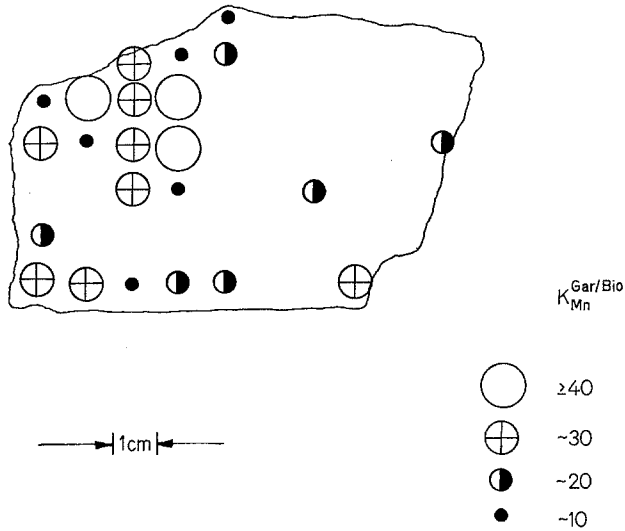


Fig. 16. Spatial distribution of the distribution coefficient $K_{Mn}^{Gar/Bio}$ in Section 42II

Mn in garnet on whole-rock chemistry and/or the composition of the coexisting hypersthene and its modal concentration in the rock.

The values of the distribution coefficient $K_{Mn}^{Gar/Bio}$ are shown in Fig. 16. It is obvious from this diagram that the value of $K_{Mn}^{Gar/Bio}$ is constant over very small intervals. The variability lies in the irregular distribution of the Mn content of the biotites as the ratio Mn/Fe + Mg + Mn in the garnets is nearly constant over the section.

Summary and Conclusions

The spatial extent of chemical equilibration in the garnets of specimens 17 and 42, as described above for Fe, Mg, Mn and Ca is in good agreement with the results of other workers. PHINNEY (1963) found that the Fe/Mg ratios of the biotites picked from some thin sections showed significant change over a few millimeters. However, biotites from sections which exhibited the same assemblage throughout and were essentially mineralogically and texturally homogeneous gave nearly identical Fe/Mg ratios. BROWNLOW (1961) described a similar phenomenon where the compositions of coexisting biotite-actinolite pairs from a contact zone show significant differences within a few inches. ZEN (1961) has discussed the petrology of pyrophyllite deposits in North Carolina and finds that the coexisting minerals are in equilibrium, but only on a small scale and within a particular assemblage which is controlled by the relative concentrations of Al_2O_3 , SiO_2 and H_2O . HARKER (1932, p. 19) described metasediments in which bands of different composition, and only a few millimeters thick, are preserved into high grades of metamorphism. Finally ALBEE *et al.* (1966) have shown that although the schists of the Mt. Grant area of Vermont have reached widespread equilibrium with respect to the O^{18}/O^{16} ratio, the presence of different mineral assemblages in adjacent bands of the schist point to equilibration of cations on a very small scale.

The data of this study coupled with the examples above give persuasive evidence to the concept of "local" equilibration (THOMPSON, 1959) or the analogous situation of "mosaic" equilibrium discussed by KORZHINSKII (1959, p. 19). In each case, the rock system as a whole may not be in equilibrium but in each of the small regions thermodynamic equilibrium is attained if definite relationships occur between all the parameters. In other words, the chemical potential of an element must be equal in each phase of the assemblage. The spatial extent of local equilibration of the assemblage is thus the volume over which all minerals have equal chemical potentials for each component element. The definition of the extent of local chemical equilibrium for one of the phases of an assemblage thus defines the maximum extent of the equilibration domain of the assemblage. For example, the garnet bearing assemblages of specimen 17 are as follows:

cordierite + garnet + biotite
 cordierite + garnet
 garnet + biotite.

If the spatial extent of local equilibration is defined for garnet, then this places an upper limit on the volume of local equilibration with respect to a specific

element in the particular assemblage. In this case, the assemblage is possibly controlled by the whole rock chemistry (WYNNE-EDWARDS and HAY, 1963). It may be concluded that, in agreement with PHINNEY (1963), the author finds that the chemically analyzed minerals from a normal hand specimen really represent average compositions, different parts of which are in equilibrium with different assemblages. It is germane to note that often the domains of equilibration for the particular elements, as described earlier in this chapter, do not coincide in shape or size, thus causing the volumes in which the garnets are of the same concentration for all elements determined to be very small. The hypothesis that the domain of chemical equilibrium will increase in size with increased grade of metamorphism seems to hold true. PHINNEY (1963) found Fe/Mg equilibration in biotites from staurolite bearing schists on the order of only a few millimetres. Specimen 17 of this study showed equilibration of Fe and Mg over distances of about 4 cm in the longest direction. A pyroxene granulite, Sample No. 42II, showed equilibration, parallel to foliation, over areas of almost hand specimen dimensions.

The examination of equilibration domains in specimen 17 showed the distinct structural control on their sizes and shapes. The longest axis is almost always parallel to the foliation and lineation, the intermediate axis being parallel to the foliation and perpendicular to the lineation. It is interesting to note here that the axial ratio for the shape of the equilibrium volumes very often corresponds with the axial ratio of the flattened, elongated garnets positioned on the foliation surfaces. It is possible that during metamorphism the structural features largely control the rate and extent of diffusion and thus the rate of garnet growth (BLACKBURN and DENNEN, 1968). In this light, the size of the volume of chemical equilibrium with respect to a certain element is a direct measure of the volume of free diffusivity and chemical communication. The small volumes encountered in this study indicate that diffusion in metamorphic rocks of high grade is very limited and the origin of seemingly homogeneous granites without the intervention of a liquid phase is deemed virtually impossible.

Further, the results given here add complications to the sampling of metamorphic rocks for chemical analysis. An analysis, if used to define the chemical system to which the rock belongs, should be representative of the assemblage present in thermodynamic equilibrium. The common practice of assuming a closed system over the size of a hand specimen for rocks of medium grain size (or a thousand grains) is not sufficient. The specimen taken should, strictly speaking, be the size of one domain of equilibration or, better still, a volume sufficiently large to include 1,000 domains.

Acknowledgements. The author wishes to thank Prof. W. H. DENNEN for his encouragement and supervision during this study; Mr. R. E. BRUNEAU, who did the machine computations; Profs. W. H. DENNEN, I. S. FISHER, and L. J. CAMPBELL for critically reading the manuscript. This work was supported by Grant GP-4235 from the National Science Foundation.

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Dr. W. H. BLACKBURN
Dept. of Geology, University of Kentucky
Lexington, Kentucky, U.S.A.