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THE REACTION FORMING CORDIERITE FROM GARNET, THE KHTADA LAKE METAMORPHIC COMPLEX, BRITISH COLUMBIA

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ABSTRACT

The compositions and zoning profiles of garnet which reacted to form cordierite in the bivariant assemblage cordierite-garnet-quartz-plagioclase-orthoclase-biotite-ilmenite-graphite are compared with the compositions of garnet from rocks of similar composition where cordierite did not form. The specimens come from the Khtada Lake metamorphic complex, 60 km east of Prince Rupert, British Columbia, an area of rocks of Tertiary granulite facies metamorphism.

The reaction forming cordierite around garnet, and in the matrix, is graphite+biotite+quartz+garnet+sillimanite= cordierite+orthoclase+Ca-plagioclase+ilmenite+CH_4+CO_2+H_2O. Only the garnet composition at the interface with cordierite can be considered to be, or have been, in equilibrium with the cordierite. As a result of the reaction, Mn and Fe are enriched, and Mg and Ca depleted, in the remaining garnet as it is consumed. No post-reaction exchange of Fe and Mg occurred between the cordierite and the garnet. The decrease of Ca in the garnet from variable (in the garnet center) to a uniform value at the boundary with cordierite, the inverse zoning of plagioclase in the matrix, and the apparent conservation of Mn in the residual garnet, are cited as the principal arguments in support of the conclusion. The data and interpretations are important to the use of cordierite and garnet compositions for the determination of pressure and temperature.

SOMMAIRE

On compare, au point de vue de leur composition des grenats zonés de deux types: l'un d'eux a réagi avec formation de cordiérite dans l'assemblage bivariant cordiérite-grenat-quartz-plagioclase-orthose-biotite-ilménite-graphite; l'autre provient de roches analogues en composition, mais dans lesquelles il ne s'est pas formé de cordiérite. Les spécimens proviennent du complexe métamorphique du lac Khtada, situé 60 Km à l'est de Prince Rupert en Colombie britannique, dans une région de métamorphisme de faciès granulitiques d'âge Tertiaire.

La réaction qui produit une couronne de cordiérite sur le grenat et dans la pâte s'écrit: graphite+biotite +quartz +grenat +sillimanite = cordiérite + orthose+plagioclase calcique+ilmenite +CH_4 +CO_2 + H_2O. Au cours de cette réaction, le grenat résiduel s'enrichit en Mn et Fe et s'appauvrit en Mg et Ca. Après la réaction, aucun échange de Fe et de Mg ne se produit entre la cordiérite et le grenat. Seule la composition du grenat au contact même de la cordiérite peut être considérée comme étant (ou ayant été) en équilibre avec la cordiérite. Pour étayer cette conclusion, on note: la diminution de la teneur en Ca qui passe d'une valeur variable au centre du grenat à une valeur uniforme au contact de la cordiérite; la zonation inverse du plagioclase dans la pâte et la préservation du manganèse dans le grenat résiduel. Les nouvelles données et interprétations sont importantes à l'emploi des compositions de cordiérites et de grenats pour la détermination de la pression et de la température.

(Traduit par la Rédaction)

INTRODUCTION

The composition of coexisting cordierite and garnet in bivariant assemblages has the potential of giving both pressure and temperature of formation of the two minerals. This statement may be made for any two solid-solution minerals in a bivariant assemblage. Attention has been directed recently to coexisting garnet and cordierite because the relatively large ΔV of most reactions involving formation of cordierite makes these reactions pressure sensitive. Further, the relatively large partitioning of Fe and Mg between garnet and cordierite should imply that the degree of partitioning will be sensitive to temperature and pressure, and therefore in bivariant assemblages the value of Mg/Fe in each mineral should also be sensitive to temperature and pressure. Experimental and observational work to date seems to support these expectations (Currie 1971; Hensen & Green 1973; Weisbrod 1973a; Dougan 1974; Henry 1974).

Several problems with the calibration of the garnet-cordierite geothermometer/geobarometer have been discussed in the literature. One is in the accurate determination and interpretation of the experimental results on the end-member systems. For a review of these problems, the reader is referred to Thompson (1976). Minor elements are known to affect the distribution of major elements between coexisting phases; the effect of Mn on the Fe-Mg distribution has been discussed by Weisbrod (1973b). The effect of Ca may also be important (Crawford 1977). The absence of structural water in garnet and cordierite, and the typically reduced state of Fe in both minerals, should rule out the effect of the activity of the volatile species as variables in the composition of coexisting garnet and cordierite; however, experimental and structural data on cordierite indicate that in some cases H_2O does play a role in the stability and structure of cordierite. Discussion of this role is in Newton (1972).

Analytical and observational data on garnet and cordierite in natural assemblages also suggest that there are special processes which occur in the formation of these minerals, and possibly later re-equilibration, which must be understood before an accurate application of the garnet-cordierite geobarometer can be made. Garnet, in moderate grades of metamorphism, is typically zoned (Hollister 1966) and at moderate grades of metamorphism also appears to be a very unreactive mineral (Hollister 1969). However, recent data (Woodsworth 1976; Anderson & Olimpio 1976) have confirmed the observation of Grant & Weiblen (1971) that, at high grades of metamorphism (upper amphibolite facies and higher), garnet loses these characteristics and homogeneous equilibrium is approached. Even where crystallization of garnet has occurred at high temperatures, however, little approach to homogeneous equilibria may occur if the garnet does not remain long at the temperature of final crystallization; this is the case for experimental runs, contact metamorphism, and perhaps those situations where rapid uplift and erosion have followed the peak of metamorphism. Cordierite is not considered a refractory mineral because its more open structure allows homogeneous equilibrium to be more easily attained, and/or because most cordierite occurs in metamorphic rocks which have formed at more elevated temperatures. Nevertheless, where cordierite forms as rims around garnet, compositional inhomogeneities have been reported (Richardson 1974).

Because of the more refractory nature of garnet, a problem is posed for the interpretation of the compositions of cordierite and garnet in those situations where cordierite grows by a reaction which consumes garnet. Does the garnet dissolve to make cordierite, but without attainment of partition equilibrium between the two, as has been proposed for other high-grade reactions by Loomis (1974), or is partition equilibrium maintained by continuous diffusion through the garnet as it is being resorbed? Is the cordierite composition adjacent to the garnet in equilibrium only with the garnet, if with any mineral at all, or does it exchange continuously, as the reaction progresses, with other ferromagnesian minerals in the matrix? Is complete homogeneous equilibrium maintained in metamorphism followed by continuing ex-both cordierite and garnet up to the peak of change (not reaction) between the two minerals in response to decreasing temperature and/or pressure? In this case, proposed by Richardson (1974) and accepted by Thompson (1976), the compositions of the adjacent cordierite and garnet would not record maximum *P* and *T* conditions but rather some indeterminate *P* and *T* at which diffusion in the garnet and cordierite became negligible; the *P* and *T* at which this happened in the garnet may be different from those for the cordierite.

It is reasonable to presume that a likely situation leading to the growth of cordierite at the expense of garnet would be a decrease of pressure at high temperature, because the slope in *P-T* space of the major cordierite-producing reactions is small, due to the relatively large molar volume of cordierite. Such a situation would occur during rapid uplift of a metamorphic terrain, and would be enhanced by further increase of temperature with decrease of pressure if uplift were accompanied by crystallization of vapor-saturated partial melt. If equilibria involving reaction of garnet to form cordierite recorded uplift events of high-grade metamorphic terrains, it would be of importance in unravelling the history of orogenic belts.

The purpose of the present paper is to give a partial answer to some of the questions posed above. The approach is to interpret the compositional zoning of garnet, and the composition of rims of cordierite on the garnet, in the context of the geologic and metamorphic history of a Tertiary granulite facies metamorphic terrain. In the examples described in this paper, cordierite occurs as rims on garnet, or associated with mats of sillimanite, in the assemblage garnet-cordierite - sillimanite-plagioclase-ilmenite-quartz -orthoclase-biotite-graphite.

GEOLOGIC SETTING

The cordierite-bearing samples were collected from the Khtada Lake metamorphic complex in the central gneiss zone of the Coast Plutonic Complex, British Columbia (Fig. 1). The major aspects of the regional geology are reported in Hutchison (1970) based on the reconnaissance geologic map at a scale of 1:250,000 (Hutchison 1967). A brief note (Hollister 1975) points out

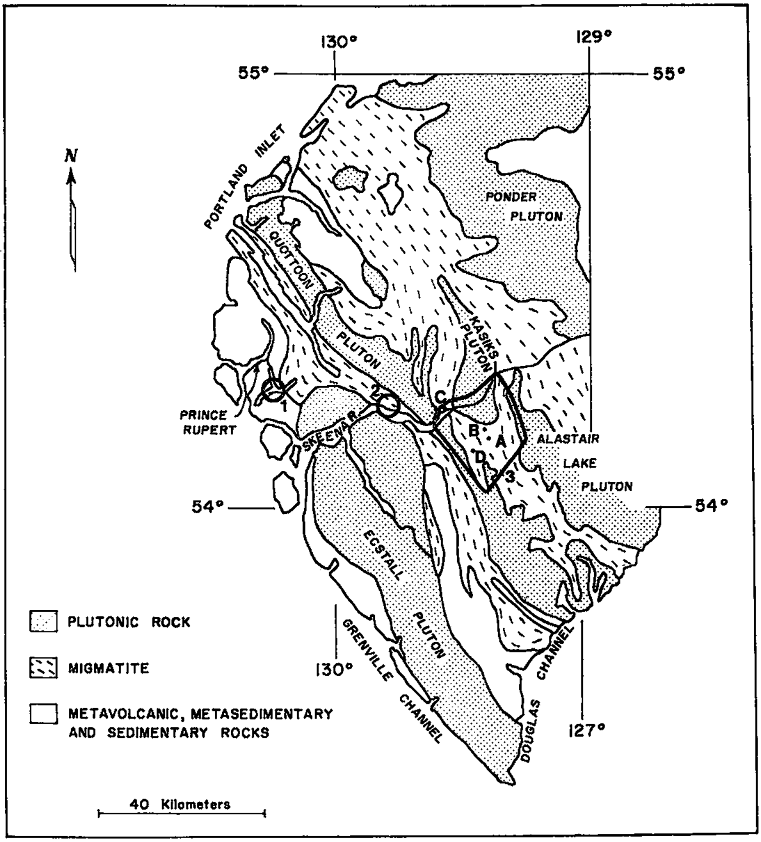


FIG. 1. Location of the three areas (1, 2, and 3) which have been studied in detail and are mentioned in text. Locales A, B, C, and D, within area 3, mark locations of analyzed specimens discussed in text. Regional geology adapted from Figure 5 of Hutchison (1970). Area 3, the Khtada Lake metamorphic complex, has been mapped at a scale of 1:50,000 by the author and students at Princeton University.

that the terrain contains Tertiary granulite facies rocks; Hollister & Burruss (1976) describe and interpret fluid inclusions found in quartz in several lithologies from the complex.

A nearly continuous metamorphic gradient exists (Hutchison 1970) between the islands west of Prince Rupert (Fig. 1), where chlorite-grade rocks occur, to the Khtada Lake metamorphic complex, which contains assemblages typical of the granulite facies (Hollister 1975). Besides the granulite facies localities, detailed petrographic studies have been completed at two other localities along the gradient. One of these is at locality 1, Figure 1, where a temperature of 650±50°C and pressure of 8±1 kbar (Hampson 1975; Hollister *et al.* 1975) have been estimated. This locality is just to the low-temperature side of the first appearance of migmatitic gneiss (Hutchison 1970). The second is well into the migmatitic gneiss (Point 2, Fig. 1) where Lappin (1976) has made a detailed study of the process of partial melting. Based on pelitic mineral assemblages and the compositions of the partial melts, Lappin estimates a pressure of 7±1 kbar and temperature of 775±50°C. Within the true granulite facies terrain, the pressure and temperature estimates are 6±1 kbar and 800±50°C (Hollister 1975; Hollister *et al.* 1975). This latter estimate is in part based on the garnet-cordierite equilibria discussed below, but is based primarily on other mineralogical and petrological data (Hollister 1975).

The locations of cordierite-bearing rocks described in this paper are, with the exception of one specimen at locale C, in the highest elevations within the area of the Khtada Lake metamorphic complex, area 3 in Figure 1. In most places within the complex, local relief exceeds


②
1mm
TPR-79D

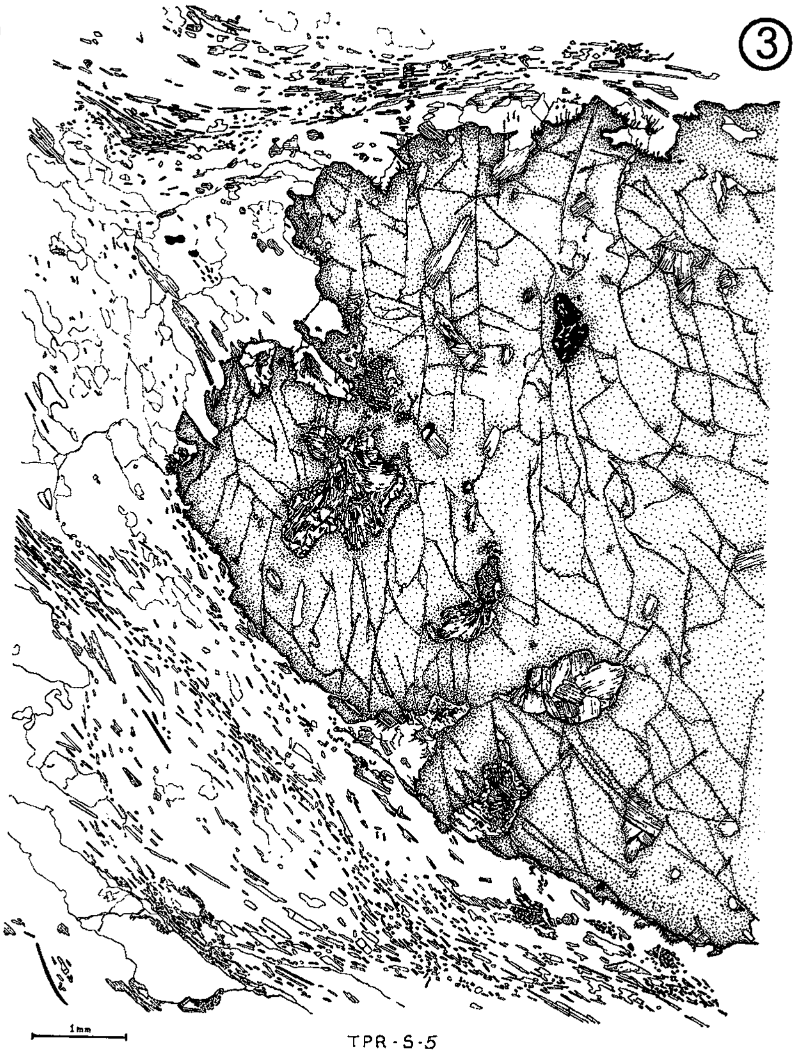

③
1mm
TPR-S-5

Fig. 2. Sketch of sample 79D, from locale D. Poikilitic garnets and mats of coarse sillimanite in matrix of quartz, plagioclase, and orthoclase. Biotite occurs adjacent to garnet and in sillimanite, top center of sketch. Opaque is ilmenite and graphite (right center).

Fig. 3. Sketch of sample S-5. Within garnet are inclusions of kyanite (top center), hercynite (lower right center, with sillimanite) as well as opaque grains and biotite. Sillimanite, biotite, quartz, plagioclase, orthoclase, and opaque grains are in matrix. Cordierite occurs between sillimanite and garnet both in apparent inclusions and in reentrants.

1500 meters. Rocks of the same composition, which are stratigraphically continuous with the cordierite-bearing occurrences, do occur at the lower elevations but, with the one exception discussed below, without cordierite. The tentative conclusion from these observations is that the nearly isobaric isograd between cordierite- and non-cordierite-bearing rocks of the same composition may intersect the topography of the region at a shallow angle.

Petrographic Description

Figures 2-4 illustrate typical textural features of the rocks under consideration. Figure 2 illustrates the assemblage sillimanite-garnet-plagioclase-quartz-orthoclase-biotite-ilmenite,

Fig. 4. Sketch of a portion of another thin section of sample S-5, showing in detail cordierite between sillimanite and garnet along border of garnet and in matrix associated with partly resorbed mats of sillimanite (center and lower right).

collected from the shore of Khtada Lake at an elevation of only 100 m; Figures 3 and 4 illustrate the typical texture of samples with the same assemblage plus cordierite, collected at an elevation of about 1500 m east of Khtada Lake. Except for the presence of cordierite, the rocks have similar mineralogy and texture. The reaction leading to the production of cordierite is deduced from the mineral associations and textures occurring across the isograd which marks the appearance of cordierite.

The obvious textural differences between Figure 2 and Figures 3 and 4 are the development of cordierite between sillimanite and garnet, at the obvious expense of both, and the association of cordierite with sillimanite in the matrix. The development of cordierite between sillimanite and garnet is clearly indicative of the reaction:

5 quartz+2 garnet+4 sillimanite=3 cordierite (1)

requiring migration of the Al_2SiO_5 component from the sillimanite to the garnet and the migration of FeO+MgO from the garnet to the sillimanite in the matrix.

Primary muscovite is absent from the rocks in the Khtada Lake metamorphic complex. Biotite is present in only minor amounts in many of the pelitic rocks. However, the abundant garnet and sillimanite, and the presence of orthoclase, suggest that muscovite and biotite had a greater modal abundance at lower grades of metamorphism. The abundant, rather coarse clots of biotite included in the garnet in Figure 3, and virtual absence from the matrix, also suggest that biotite was present in greater modal abundance in the matrix but has nearly reacted out of the assemblages. In Figure 2, the biotite in the matrix only occurs between the garnet and sillimanite, not in contact with quartz, suggesting biotite+quartz had reacted in this rock until the two phases were no longer in contact.

Other pelitic rocks in the cordierite zone of the Khtada Lake metamorphic complex, which do not contain cordierite, instead contain a green spinel in the matrix. These rocks are either quartz-free or sillimanite-free.

These petrographic observations suggest that biotite was a reactant phase with sillimanite and quartz and that depending on the relative abundance of these three reactant minerals, the matrix assemblage, exclusive of orthoclase and garnet, would ideally have a combination of 3 of biotite+sillimanite+quartz+hercynite or 3 of biotite+sillimanite+quartz+cordierite. Emphasis in this paper is on the assemblages containing sillimanite+quartz+cordierite, but these other petrographic observations are mentioned in order to emphasize the role of biotite as a reactant phase and to bring out the petrogenetic fact that hercynite and cordierite do not occur as part of the same assemblage, although both may occur in the same thin section as they do in Figure 3. The simplified reaction consistent with these textural relations is:

biotite + sillimanite + 2 quartz =
garnet + orthoclase + H_2O (2)

Plagioclase must play a role in any reactions involving garnet because to make or resorb the grossular component in the garnet must require decrease or increase, respectively, of the anorthite component in the plagioclase according to the reaction 3 anorthite = grossularite + $2Al_2SiO_5$ + quartz. Reverse zoning of the plagioclase in the samples of Figures 3 and 4 (from An_{33} to An_{35} at the rim), where garnet is clearly a reactant phase with sillimanite (mole fraction grossular component = .04), confirms that a reaction involving anorthite is part of the total reaction in the rock.

Graphite and ilmenite are abundant phases in the matrix of the cordierite-bearing rocks. Interlayering of coarse graphite with biotite suggests a complementary role of these two minerals. In some obvious secondary occurrences, graphite is interlayered with muscovite. This latter case suggested to Hollister & Burruss (1976) that a retrograde reaction involving reaction of CH_4+CO_2 in the fluid phase with orthoclase+sillimanite resulted in growth of graphite+muscovite. Intergrowths of biotite and graphite may similarily owe their origin to a retrograde process. CH_4 and CO_2 were positively identified as constituents in fluid inclusions in these rocks. It is reasonable to presume that if graphite and muscovite were reactants in the progressive metamorphism of the Khtada Lake complex rocks, as concluded by Hollister & Burruss, then graphite and biotite were probably also reactants. As ilmenite is the only other important Ti-bearing mineral in these rocks, it too must be involved as a product of any reaction where biotite is a reactant. The reaction implied by these observations is:

graphite+biotite=$(CH_4+CO_2)_{fluid}$+orthoclase
+ilmenite+(Mg and Fe to reactions
producing cordierite and/or garnet) (4)

Based on petrography alone, the total reaction which includes cordierite as a product is the sum of reactions (1-4):

graphite+biotite+quartz+garnet+sillimanite
=cordierite+orthoclase+anorthite+
ilmenite+CH_4+CO_2+H_2O (5)

As there are no colinearities in composition among any three of the solid phases, determination of the variance of the system requires only that phases and elemental components be counted. Thus we have 10 phases (including fluid) and the 11 components: CaO, K_2O, Na_2O, MgO, FeO, C, H, O, TiO_2, Al_2O_3, SiO_2. Other components, including MnO, are trace constituents. If these components are all independent, the assemblage is trivariant; if the chemical potential of a volatile species (for example, H_2) is externally controlled, as is often assumed for metamorphic rocks, it is bivariant. If it is truly bivariant, the composition of any two phases with solid solution could in principle lead to the determination of pressure and temperature of crystallization of the rock, assuming, of course, complete equilibrium among all phases simultaneously.

The following solid solutions, which may be extensive enough within the phases of the assemblage to be useful, are:

(1) Na/K in the alkali feldspar
(2) Na/Ca in the plagioclase
(3) Mg/Fe in biotite
(4) Mg/Fe in ilmenite
(5) Mg/Fe in cordierite
(6) Ca/(Fe+Mg) in garnet
(7) Mg/(Fe+Ca) in garnet

The analytic data which follow concentrate on (5), (6), and (7), and to a lesser extent on (2).

Presentation of Data

Most of the data on which the conclusions of this paper are based were obtained from garnet and cordierite in rocks, with varible proportions of the 10-phase assemblage, which were collected from one small area, locale A, within area 3 of Figure 1. This locale is at an elevation of 1200 m. Other data are for garnet and cordierite which came from locale B (1400 m) and the one specimen from locale C (sea level). The data for garnet in the cordierite-free 9-phase assemblage came from locale C and locale D, at elevations below 100 m.

For garnet and cordierite in the rocks with 10 phases, all the data were taken from electron microprobe step scans at four-micron intervals across the contact between the garnet and cordierite and well into both phases. In most cases the cordierite was traversed entirely; the garnet was generally traversed from the cordierite inwards until compositional changes with distance were not readily detected. In the cordierite-free rocks, the data consist of "edge" compositions, made by averaging 5-10 microprobe spot analyses near the edges of the garnets, and "center" compositions, made by averaging 5-10 microprobe analyses from the central regions of the garnets. Fe, Mg, Ca, Al, Si, and Mn were the elements determined for all the analyses.

Four rocks containing garnet and cordierite which were collected within locale A were absolutely fresh and these were chosen for the microprobe traverses. For each rock, traverses were made across at least two outer boundaries of garnets and also across re-entrants of cordierite, if present, at several locations, including the extreme interior portions of the re-entrants. One interior pair is illustrated in Figure 6. A maximum of 6 traverses was made on one specimen (S-3). Each total analysis was made by

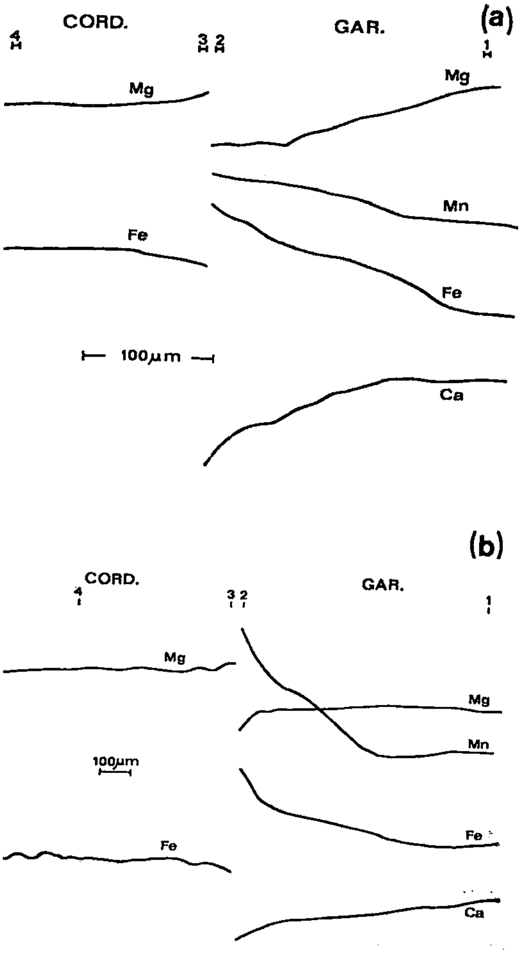


FIG. 5. Elemental profiles for the divalent cations of adjacent cordierite and garnet for traverse S-5 (Fig. 5a) and for S-6 (Fig. 5b). Cation proportions given in Table 1 for positions indicated. Vertical scale is relative concentration; horizontal scale is distance along traverses.

averaging 3 to 10 data points taken from the traverses which best represented the average composition of each mineral adjacent to their mutual contact and by averaging a group of points in each mineral near the extreme ends of the traverses. Figure 5 illustrates typical traverses and the region along the traverses for which complete reduced analyses were obtained. Table 1 gives tabulated results for representative samples, including the two of Figure 5. The average distribution function (computed from 16 garnet-cordierite pairs) at locale A [$Kd \equiv (Mg/Fe)\,cord/(Mg/Fe)\,gar$] is 9.1, with a range between 8.0 and 10.0.

Figure 6 illustrates graphically Mg/Mg+Fe for the adjacent analyses on the cordierite and garnet. There is a small but nevertheless distinct range of Mg/Mg+Fe for the cordierite and garnet between specimens and within single specimens for locale A. For each analysis pair, the tie-lines are nearly parallel, which is implied by the fact that K_D is almost the same (9.1±) for all the pairs. The two specimens from locale B, collected 200 m higher than locale A, are distinctly more Fe-rich. The one specimen with cordierite collected at locale C, 1200 m lower than locale A, has more magnesian cordierite and garnet. The parallel tie-line of the re-entrant pair illustrates that local equilibrium is maintained in the replacement process, although well-removed spatially from the other minerals of the assemblage.

As illustrated in Figure 5, Fe, Mg, Mn, and Ca are zoned in the garnet with approach to the contact with the cordierite; there is very little zoning of Fe and Mg in the cordierite, but what there is (Table 1) is towards lower Mg/Fe away from the garnet. It was also noticed that the cordierite associated with sillimanite in the matrix differed from the cordierite surrounding the garnet, by having slightly lower Mg/Fe. In the garnet, Fe and Mn rise with approach to the contact and Mg and Ca diminish.

DISCUSSION

The reaction

The compositional zoning data and the textures of the cordierite-bearing specimens give a consistent picture of the nature of the cordierite-producing reaction in the Khtada Lake metamorphic complex. Sillimanite and garnet,

TABLE 1. REPRESENTATIVE ANALYSES OF GARNET AND CORDIERITE

Sample	S5A				S5B				S6				296			
Analysis	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
MgO	5.25	3.97	8.64	8.58	5.03	3.65	7.58	7.48	5.63	3.89	8.40	7.98	3.44	3.01	7.32	6.95
Al_2O_3	21.67	21.90	34.72	34.34	21.40	21.27	32.99	33.14	22.15	21.32	32.89	32.86	22.01	21.94	34.20	34.45
SiO_2	37.42	37.64	47.70	49.58	39.04	38.86	49.84	49.08	37.58	37.64	48.53	48.58	37.88	37.83	49.39	49.67
CaO	1.99	1.52	.06	.03	2.34	1.72	.03	.02	3.55	1.46	.02	.03	2.50	1.64	.03	.02
MnO	.31	.35	.02	.03	.29	.40	.04	.04	.49	.87	.05	.08	.61	.62	.06	.07
FeO	34.30	36.13	8.49	8.90	33.88	36.19	9.34	9.57	31.24	35.66	8.44	8.88	35.18	36.05	10.08	10.52
Total	100.94	101.51	99.62	101.45	101.98	102.09	99.83	99.32	100.64	100.83	98.34	98.40	101.62	101.08	101.07	101.68
Cations on the basis of 12 oxygen for garnet and 18 for cordierite																
Ca	.17	.13	.01	.00	.20	.14	.00	.00	.30	.12	.00	.00	.21	.14	.00	.00
Mn	.02	.02	.00	.00	.02	.03	.00	.00	.03	.06	.01	.01	.04	.04	.01	.01
Mg	.62	.47	1.31	1.28	.58	.43	1.15	1.14	.66	.46	1.29	1.23	.40	.36	1.10	1.04
Fe	2.26	2.39	.72	.74	2.20	2.37	.79	.82	2.05	2.37	.73	.77	2.32	2.39	.85	.88
Al	2.02	2.04	4.17	4.04	1.96	1.96	3.95	4.00	2.05	2.00	3.99	3.99	2.04	2.05	4.06	4.07
Si	2.95	2.97	4.86	4.95	3.03	3.04	5.06	5.02	2.95	2.99	5.00	5.01	2.98	3.00	4.98	4.98

Sample	330B				30N				30P	79D		89G	
Analysis	1	2	3	4	1	2	3	4	1	1	2	1	2
MgO	3.80	2.97	7.64	7.36	7.07	4.34	8.75	8.33	6.03	4.52	4.51	5.80	5.31
Al_2O_3	21.31	20.94	33.36	33.10	21.90	21.54	33.16	33.24	21.78	21.59	21.59	21.70	21.56
SiO_2	37.67	36.39	50.33	48.30	38.07	37.88	48.32	48.25	37.60	38.33	38.33	38.39	38.39
CaO	1.84	1.54	.03	.03	1.97	1.30	.02	.01	1.60	1.79	1.74	1.39	1.45
MnO	.80	.88	.07	.09	.61	.95	.06	.07	.45	.63	.66	.58	.64
FeO	35.66	36.62	9.89	10.36	31.54	36.03	7.65	8.21	32.96	34.37	34.24	33.84	34.26
Total	101.07	99.34	101.32	99.24	101.17	102.03	98.05	98.09	100.41	101.35	101.06	101.70	101.61
Cations on the basis of 12 oxygen for garnet and 18 for cordierite													
Ca	.16	.13	.00	.00	.16	.11	.00	.00	.14	.15	.15	.12	.12
Mn	.05	.06	.01	.01	.04	.06	.01	.01	.03	.04	.04	.04	.04
Mg	.45	.36	1.14	1.13	.82	.51	1.34	1.28	.71	.53	.53	.67	.62
Fe	2.37	2.50	.83	.89	2.05	2.37	.66	.71	2.17	2.26	2.25	2.20	2.24
Al	1.99	2.01	3.95	4.02	2.01	2.00	4.02	4.04	2.02	2.00	2.00	1.99	1.99
Si	2.99	2.97	5.05	4.97	2.96	2.98	4.97	4.97	2.96	3.01	3.01	2.99	3.00

Samples S5A, S5B, and S6 are from locale A (Fig.1); 296 and 330B, locale B; 30N and 30P, locale C; 79D and 89G, locale D. Analysis numbers indicate relative position of garnet and cordierite analyses as shown for two examples in Figure 5.

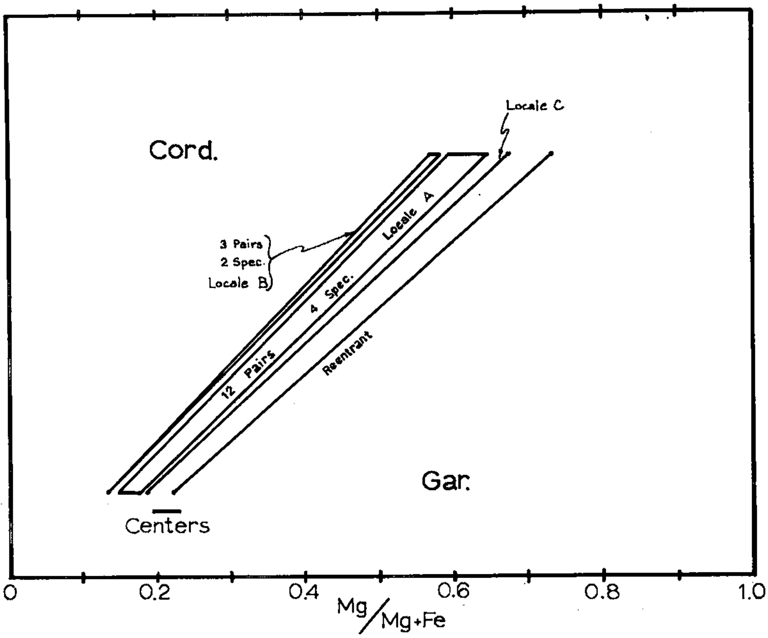


FIG. 6. Illustration of Mg/Mg+Fe in coexisting cordierite and garnet from 3 locales within the Khtada Lake metamorphic complex. Illustrated also is the range of compositions of the centers of the garnets rimmed by cordierite. Both edge and rim compositions of garnets in assemblages without cordierite (Table 1) fall within the "centers" range.

adjacent to each other in the pre-cordierite assemblages (Fig. 2), react to form a rim of cordierite on the garnet (Figs. 3 and 4), thus separating the garnet from the sillimanite.

Mn, not readily accommodated in the cordierite structure, is enriched in the borders of most garnets rimmed by cordierite. Generally, the wider the cordierite rim, and therefore the more garnet presumably consumed in the cordierite-producing reaction, the more Mn enrichment in the garnet (compare Figs. 5A and 5B). Garnets with no cordierite rims, or very thin cordierite rims (Fig. 5A), have only slight Mn enrichment (Table 1).

The Ca content of garnet decreases to the contact with cordierite (Fig. 5). Garnet without rims of cordierite shows negligible Ca-zoning. If Ca were conserved by the garnet, as is the case for Mn, it too should increase to the contact. The fact that it does not, and that it is not contained in the cordierite, implies that the plagioclase in the matrix must be involved in the total reaction. The zoning of Ca in the garnet, from somewhat variable initial values to almost the same value in each example (Fig. 7), suggests that it has changed from an unbuffered value in the 9-phase, cordierite-free assemblage to a buffered value in the 10-phase cordierite-bearing assemblage. This Ca compositional response to a change in variance of the assemblage is consistent with the analysis of the variance of the assemblage given above.

In the garnet, Mg/Fe clearly decreases towards the contact with the cordierite (Fig. 5); there is a slight increase of Mg/Fe in the cordierite towards the contact with garnet (Fig. 5). This is consistent with an interpretation of cordierite growing primarily at the expense of garnet. Because cordierite has a higher Mg/Fe than coexisting garnet, the remaining garnet must increase in Fe in exchange for Mg, if other ferromagnesian phases are not involved, or are involved in only minor amounts, in the reaction.

The chemical system involving only the cordierite envelopes around garnet is not closed, however, because cordierite also occurs around sillimanite in the matrix, away from garnet (Fig. 4). This requires migration of Mg and Fe from the reacting garnet to the sillimanite.

Therefore, the total general picture of the reaction must be destruction of garnet, with Mn diffusing back into the remaining garnet because of the lack of suitable sites in the new minerals (mainly cordierite) forming by the reaction. Mg

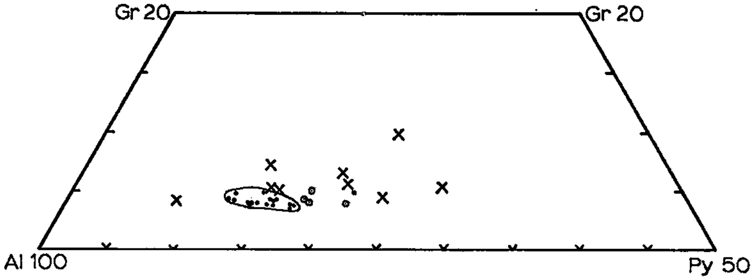


FIG. 7. Garnet compositions in terms of relative content of grossular, almandine, and pyrope contents. (O), specimens from the cordierite-free rocks of locales C and D. (X) center compositions of garnets in cordierite-bearing assemblages. (•) garnet compositions adjacent to replacement cordierite. The tight cluster of these edge compositions is circled. The one re-entrant point is also shown.

and Fe from the reacting garnet go to the newly forming cordierite, both at its contacts with the garnet and in the matrix, with the Mg/Fe ratio appropriate for equilibrium at the prevailing pressure and temperature. The excess Fe diffuses back into the garnet along with the Mn.

Ca also moves from the garnet to form more calcic plagioclase outside the cordierite, in the matrix. The more calcic plagioclase can result from the reaction grossular+quartz+sillimanite =anorthite. If there were no phases which could be formed in the matrix at the prevailing pressure and temperature to accommodate the Ca, it too probably would have been conserved in the garnet as was Mn.

Excluding Mn, there are no compositional degrees of freedom at a given *P* and *T*, as discussed above. Hence, Ca, which prior to the reaction could occur in variable quantity in the garnets of the 9-phase assemblage, is restricted to a specific quantity in each Ca-bearing phase in the 10-phase assemblage. This effect is illustrated in Figure 7. Mn, on the other hand, may vary in quantity in the garnets of the 10-phase assemblage; Mn does vary from .02 to .09 atoms per garnet formula unit.

From the composition of the cordierite enveloping the garnet, and from the compositions of the garnet adjacent to the cordierite and that taken inside of the change in slope of the zoning profiles, an approximate reaction may be written which takes into account the molecular proportions of reactants and products. The reaction may be written differently according to different assumptions. I have chosen a constant-oxygen assumption for the replacement of garnet by cordierite. Thus only diffusion of cations in a matrix of oxygen atoms to and from the migrating interface between cordierite and garnet is considered in the model. The constant-oxygen assumption approximates a constant-volume assumption at the reaction interfaces. A reaction based on assumption of constant Al and consistent with both the chemical and textural data could not be written.

In arriving at coefficients for the following reactions, approximate Ca and Mn-free formulas for garnet and cordierite were used, and decimal points were avoided. For the reacting garnet, per 300 Fe+Mg+Ca+Mn, the analyses (Table 1) for Mg range between 36 and 82 and those for Fe between 205 and 250. Normalizing to 300 Fe+Mg, the convenient values of 255 Fe and 45 Mg were chosen for the reacting garnet. Likewise, for cordierite, the values 120 Mg-cordierite and 80 Fe-cordierite were selected.

Reaction (6) is that part of reaction (1) which is assignable to the boundary between garnet and cordierite, assuming no loss or gain of oxygen at the site of reaction, and balanced for the cations:

$$\begin{aligned}&255\ \text{almandine} + 45\ \text{pyrope} + 200\ \text{Al} + 100\\ &\quad \text{Si} + 105\ \text{Mg} = 80\ \text{Fe-cordierite} + 120\\ &\quad \text{Mg-cordierite} + 605\ \text{Fe} \qquad (6)\end{aligned}$$

In this form of the reaction, the proportion of Al and Si needed to form cordierite at the boundary with garnet is exactly that proportion in sillimanite. The 105 Mg required for the reaction must come out of the remaining garnet; the Mg thus lost can be conveniently replaced by 105 of 605 Fe atoms released by the reaction. However, both Mg and Fe must be released from the boundary in the approximate proportion 80 Fe to 120 Mg in order to form cordierite at the expense of sillimanite in the matrix. For atomic balance, (Fe+Mg) leaving the cordierite-garnet interface must equal 500 (605-105). Thus, the reactant side of reaction (1) must be (200 Fe + 300 Mg). Adding this to both sides of reaction (6) and subtracting 605 Fe from both sides, gives the correct reaction:

$$255\ \mathrm{Fe_3Al_2Si_3O_{12}} + 45\ \mathrm{Mg_3Al_2Si_3O_{12}} + 200\ \mathrm{Al} + 100\ \mathrm{Si} + (405\mathrm{Mg}–405\mathrm{Fe}) = 80\ \mathrm{Fe_2Al_4Si_5O_{18}} + 120\ \mathrm{Mg_2Al_4Si_5O_{18}} + 200\ \mathrm{Fe} + 300\ \mathrm{Mg} \qquad (7)$$

The term on the reactant side, (405 Mg–405 Fe), represents the approximate exchange of Fe for Mg which must occur in the remaining garnet reservoir in order to liberate Mg and Fe in the correct proportions to make cordierite in the matrix.

In the matrix, cordierite is made by the reaction:

$$300\ \mathrm{Mg} + 200\ \mathrm{Fe} + 600\ \mathrm{Al_2SiO_5} + 750\ \mathrm{SiO_2} = 100\ \mathrm{Fe_2Al_4Si_5O_{18}} + 150\ \mathrm{Mg_2Al_4Si_5O_{18}} + 200\ \mathrm{Al} + 100\ \mathrm{Si} \qquad (8)$$

Reaction (8), which also conserves oxygen at the site of formation of the cordierite, releases the Al and Si required to form cordierite by reaction (7). The net reaction is illustrated in Figure 8. It is reaction (1) balanced for cations, and illustrates that exchange of Fe for Mg in the remaining garnet is required by the model.

Compared to the Mg and Fe components of the garnet, the molecular proportion of the grossular component in the reaction is relatively small; it involves approximately 12 moles of grossular (Fig. 8) relative to 300 moles of the combined almandine and pyrope components. The net subreaction involving the grossular component is then approximately:

$$12\ \mathrm{Ca_3Al_2Si_3O_{12}} + 24\ \mathrm{Al_2SiO_5} + 12\ \mathrm{SiO_2} = 36\ \mathrm{CaAl_2Si_2O_8} \qquad (9)$$

The details of the reaction, however, are probably analogous to those involving production of cordierite with

$$12\ \mathrm{Ca_3Al_2Si_3O_{12}} + 18\ \mathrm{Si} = 36\ \mathrm{Ca} + 12\ \mathrm{Al_2SiO_5} + 42\ \mathrm{SiO_2} \qquad (10)$$

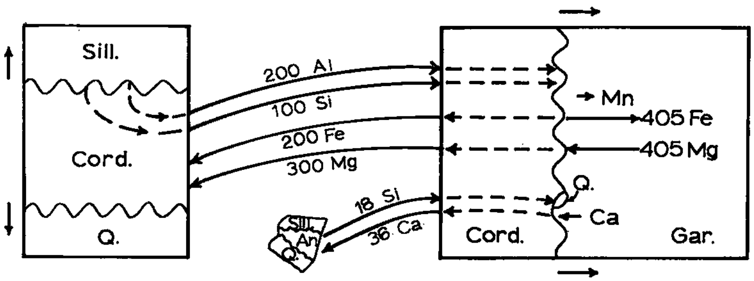
occurring at the garnet-cordierite interface, and,

$$36\ \mathrm{Ca} + 54\ \mathrm{SiO_2} + 36\ \mathrm{Al_2SiO_5} = 18\ \mathrm{Si} + \mathrm{CaAl_2Si_2O_8} \qquad (11)$$

occurring in the matrix. Again, these reactions are written assuming constant oxygen at the reaction interfaces. The 42 $\mathrm{SiO_2}$ on the product side of (10) may be represented by the tiny blebs of quartz which occur scattered along the garnet-cordierite interface and are schematically illustrated in Figure 8.

CONCLUSIONS

The data presented in this paper strongly suggest that the composition of garnet in equilibrium with cordierite forming from the garnet, in a bivariant assemblage, is that at the interface between the cordierite and garnet. Once formed, there is no evidence, in the specimens studied



$$300\ \mathrm{Fe_{255}Mg_{45}Al_2Si_3O_{12}} + 600\ \mathrm{Al_2SiO_5} + 750\ \mathrm{SiO_2} + 405\ \mathrm{Mg}$$

$$= 450\ \mathrm{Fe_{.8}Mg_{1.2}Al_4Si_5O_{18}} + 405\ \mathrm{Fe}$$

$$12\ \mathrm{Ca_3Al_2Si_3O_{12}} + 24\ \mathrm{Al_2SiO_5} + 12\ \mathrm{SiO_2} = 36\ \mathrm{CaAl_2Si_2O_8}$$

FIG. 8. Cartoon illustrating reaction to produce cordierite. Arrows indicate relative growth (or resorbtion) of the minerals and the direction of migration of the cations. Coefficients for the minerals involved in the subreactions are relative. The composition of the equilibrium plagioclase is $\mathrm{An_{35}}$.

from the Khtada Lake metamorphic complex, that exchange without reaction occurs between the cordierite and the garnet. The data suggest that compositional zoning near the borders of garnet rimmed by cordierite is the result of diffusion of Mn and Fe into the garnet as it is replaced on a constant-oxygen basis by cordierite.

It is clear that, at the temperature involved (near 800°C), diffusion does occur in garnet (Woodsworth 1976). For the Khtada Lake specimens, however, the equilibrium compositions of cordierite and garnet were probably preserved by rapid uplift at the peak of metamorphism (Hollister 1975). It therefore appears that the study of zoning profiles of garnets which have reacted to form cordierite, in bivariant assemblages, should ultimately prove useful for determining uplift rates of metamorphic terrains.

The data are important for the absolute determination of P and T from the composition of coexisting cordierite and garnet. The composition of the cordierite, if Hensen & Green's (1973) data are used, gives a reasonable pressure; however, if the garnet composition is also used, the temperature is too low (in the kyanite stability field) to be consistent with the other petrological and geological data available for the Khtada Lake metamorphic complex. A reasonable P (or T) is obtained, consistent with Currie's (1971) experimental data, based on the K_D ($\sim$9.1) between the cordierite and garnet (Dougan 1974).

The interpretation of the zoning profiles of the garnets rimmed by cordierite is consistent with the conclusion of Loomis (1975) that garnet, when it is being resorbed in a reaction, does not maintain partition equilibrium with the reaction products, except at its extreme edge. This conclusion is contrary to that of Richardson (1974) and which was accepted by Thompson (1976). These authors interpret features, apparently similar to those given in the present papers, as resulting from retrograde exchange between garnet and cordierite. It is difficult to reconcile their interpretation with Mn and Ca zoning in garnet as described in the present paper.

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