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GEOTHERMOBAROMETRY OF CORDIERITE-BEARING METAPELITES NEAR THE MORIN ANORTHOSITE COMPLEX, GRENVILLE PROVINCE, QUEBEC

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ABSTRACT

Six specimens of cordierite-bearing metapelite have been selected from an area of about 10,000 km^2 in the southern part of the Grenville province, north of Montreal, in order to evaluate temperature, pressure and water fugacity that prevailed during the 1 billion-year-old episode of high-grade metamorphism. Iron–magnesium distribution coefficients between biotite and garnet, as well as cordierite and garnet, were used for temperature determination. Pressure estimates were obtained through the magnesium content of cordierite using the calibration method of Martignole & Sisi (1981). Owing to the role of channel water in the stabilization of cordierite to higher P, knowledge of the water content of cordierite is a prerequisite in geobarometry. An approximate maximum hydration was obtained by subtraction from the sum of oxides and an empirical correction was introduced for the presence of other fluids such as CO_2. Pressures obtained by cordierite barometry closely correspond to those obtained using the plagioclase–garnet geobarometer. The highest temperatures, near 700°C with possible peaks around 800°C, are recorded close to the large Morin anorthosite complex. The lowest temperatures come from the northeastern part of the area which is a few km beyond the orthopyroxene isograd (550–600°C). The 600°C isotherm could thus be taken as the limit between amphibolite and granulite facies in the area. Pressure estimates from 4 to 7 kbar do not support nor explicitly refute the pressure gradient suggested by the restricted occurrence of high-pressure garnetiferous assemblages in charnockite around the Morin anorthosite. Estimates of water pressure are very crude owing to the imprecision in water determinations of cordierite. The presence of optically positive (CO_2-bearing) cordierite, in which the oxide sum is near one hundred, shows that water pressure may locally have been extremely low. In the cases where cordierite is hydrated, $P(H_2O)$ may have attained 0.3 P_{total}.

Keywords: cordierite, garnet, high-grade metapelites, geothermobarometry, Grenville province.

SOMMAIRE

La température, la pression et la pression d'eau durant le métamorphisme qui a affecté la Province de Grenville, il y a environ un milliard d'années, ont été évaluées au moyen de six échantillons de métapélite. Les estimations de température ont été obtenues à partir des coefficients de distribution du fer et du magnésium entre biotite et grenat ainsi que cordiérite et grenat, alors que le contenu en magnésium de la cordiérite a permis d'estimer la pression (Martignole & Sisi 1981). On doit connaître la quantité d'eau présente dans la cordiérite pour pouvoir utiliser ce géobaromètre, car l'eau favorise la stabilisation de la cordiérite vers des pressions plus élevées. En appliquant au reste obtenu dans la somme des oxydes une correction empirique pour tenir compte de la présence de CO_2 dans la cordiérite, on obtient des pressions comparables à celles que donne le baromètre plagioclase–grenat. Les températures les plus élevées vont de 700 à 800°C et se localisent au voisinage du complexe anorthositique de Morin. Les températures les plus basses, de 550 à 600°C, proviennent de la partie nord-est de la région, au delà de l'isograde de l'orthopyroxène. L'isotherme 600°C marquerait donc ici la limite entre les faciès amphibolite et granulite. Les estimations de pressions entre 4 et 7 kbar ne confirment ni n'infirment le gradient régional de pression que suggère la présence d'assemblages à grenat de haute pression dans les charnockites entourant le massif d'anorthosite de Morin. Les estimations de la pression d'eau sont encore très grossières, en partie à cause de l'imprécision sur la détermination de l'eau dans la cordiérite. La présence de cordiérite optiquement positive (contenant du CO_2), dans laquelle la somme des oxydes est proche de 100, montre que localement la pression d'eau a pu être très faible. Dans le cas de cordiérite hydratée, la pression d'eau a pu atteindre trois dixièmes de la pression totale.

Mots-clés: cordiérite, grenat, métapélites, faciès granulite, géothermobarométrie, province de Grenville.

INTRODUCTION

The southern part of the Grenville province

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in the Canadian Shield is underlain by high-grade metamorphic rocks intruded by large plutons of the anorthosite–farsundite suite (Martignole & Schrijver 1977). Whole-rock Rb/Sr data for the three main plutonic massifs, the Morin, Lac-Croche and St-Didace complexes (Fig. 1), have been published by Barton & Doig (1972, 1973, 1974, 1977) and indicate ages of 1030 ± 41, 1124 ± 27 and 1163 ± 51 Ma, respectively. Supracrustal rocks are mostly of the marble–quartzite–metapelite–granulite–amphibolite association known as the Grenville Supergroup. These rocks have given Rb/Sr ages of 1094 ± 43 Ma, whereas underlying granulites have ages ranging from 1600 ± 58 to 1576 ± 19 Ma (Barton & Doig 1973).

Detailed analytical work and thermodynamic calculations are in progress in order to unravel the physical conditions of both the peak of the 1.1 Ga "Grenville event" and the post-climax history of cooling and unloading. The present study will report some results concerning cordierite-bearing specimens of metapelite of the Grenville Supergroup.

REGIONAL METAMORPHIC SETTING

In the area north of the St. Lawrence Valley between Rivière Rouge and Rivière St-Maurice (Fig. 1), orthopyroxene is almost invariably present in oversaturated mafic or intermediate rocks. Sillimanite is the ubiquitous aluminum silicate in pelitic rocks, although kyanite has been reported from two localities (Martignole & Schrijver 1968). Isograds have been mapped around the Morin anorthosite complex (Martignole & Schrijver 1971) based on the appearance of garnet in saturated and oversaturated plutonites. Garnet growth is thought to be due to slow cooling under high pressure. Although garnet-forming reactions are controlled by rock composition (Martignole & Schrijver 1973), suitable rocks remote from the Morin anorthosite complex are not garnetiferous, thus suggesting a horizontal pressure gradient or a different cooling history. Moreover, for a distance of about 50 km around the Morin anorthosite, wollastonite is very common in impure marble. This mineral invariably is rimmed by quartz

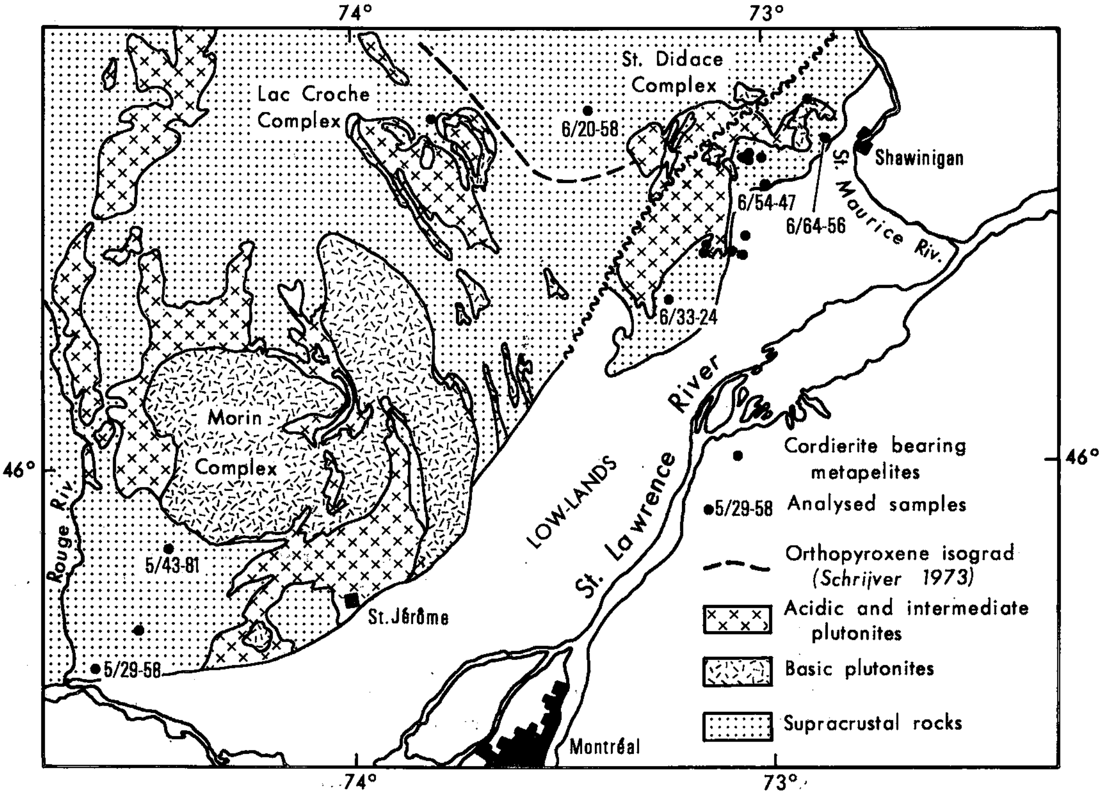

FIG. 1. Location map showing the Morin, Lac-Croche and St-Didace complexes and the sampling sites mentioned in the text.

where it occurs in a calcite matrix and by grossular and quartz where it occurs in a feldspar or scapolite matrix. The corresponding reactions could be due to pressure increase, but they are best interpreted as due to isobaric cooling under increasing activity of H_2O, as they are correlated with idocrase-forming reactions (Kerrick *et al.* 1973, Martignole & Schrijver 1977).

On the other hand, 150 km northeast of the Morin anorthosite, in the Shawinigan area, wollastonite occurs sporadically along the contacts of small noritic plutons, in contact with either quartz or calcite, whereas prograde grossular–quartz assemblages occur in the same area, suggesting either higher pressure and higher water activity than in the Morin area or lower temperature and higher water activity. The second possibility would be more in agreement with the absence of pressure-sensitive garnet-forming reactions in charnockitic rocks of the Shawinigan area. Finally, pressure estimates of 7 kbar have been derived from the concentration of the Ca-Tschermak's component in clinopyroxene in equilibrium with plagioclase from charnockitic rocks that have crystallized between 700 and 800°C (Martignole 1979), but this barometer is not sufficiently precise to reveal any pressure gradient.

In summary, impure marble and charnockitic rocks seem to bear the record of different metamorphic evolutions in two areas more than one hundred km apart: 1) isobaric cooling at a pressure of approximately 7 kbar from a temperature of about 800°C around the Morin anorthosite; 2) "frozen-in" conditions near the peak of metamorphism at significantly lower temperature and slightly lower pressure, but probably higher water fugacity, in the Shawinigan area.

In order to evaluate these trends more precisely, a search for cordierite-bearing assemblages was undertaken from more than two hundred metapelite samples throughout the area under discussion (Nantel 1977). Special attention was paid to the divariant assemblage Cd–Ga–Si–Qz because of its temperature-sensitive exchange reaction and its pressure-sensitive reactions involving end-members.

MINERAL ASSEMBLAGES IN METAPELITES

Among the two hundred specimens of metapelite, semipelite and aluminous quartzite observed, only seventeen contain cordierite; the most common assemblage is biotite–sillimanite–garnet. Cordierite-bearing assemblages are more common in the eastern part of the area, which could mean either lower pressure, or higher water fugacity, or Mg-rich bulk compositions. Around the Morin complex, corundum is widespread in metapelite and even in aluminous quartzite. Where it occurs in a quartz matrix, corundum is rimmed by sillimanite and garnet. Spinel is also common in aluminous metapelite around the Morin anorthosite, and a few occurrences of a spinel–magnetite intergrowth show that temperatures probably exceeded the spinel solvus. In the eastern part of the area, spinel and corundum occur only along the contact with small noritic masses, where garnet–sillimanite gneiss is converted to cordierite–orthopyroxene–spinel hornfels. These aluminous phases seem to record very high temperatures related to contact metamorphism superimposed on regional metamorphism. The same high-temperature event is probably responsible for the regional development of wollastonite around the Morin anorthosite and its limited development around minor intrusive bodies.

Among the seventeen cordierite-bearing samples, six were selected for analysis, all showing the Cd–Ga–Si–Qz assemblage. In these sections, cordierite comes in globular grains locally altered to pinite. Subidiomorphic or elongate grains of garnet constitute up to 30% of the rock. Sillimanite is prismatic and commonly associated with a reddish brown biotite. Textural evidence for local equilibrium (linear grain contacts, subidiomorphic grains, absence of reaction rims) can be observed in large portions of each sample, but local disequilibrium also persists. In one sample, sapphirine is observed as a relict phase rimmed by cordierite, which in turn is rimmed by garnet. Except for this local reaction, the rest of the section shows textural equilibrium. In another section, sillimanite occurs not only in the groundmass, but also as small inclusions in cordierite. Another section shows local signs of textural disequilibrium and contains orthopyroxene as an additional phase. Garnet is in contact with cordierite except where it is filled with streaks of magnetite. Cordierite has broken down to aggregates of fine-grained sillimanite and orthopyroxene. In another part of the section, orthopyroxene phenocrysts are associated, but not in contact, with cordierite and sillimanite.

CHEMISTRY OF MINERALS

All analyses were performed with a MAC electron microprobe. For each sample the minerals were analyzed with a wavelength-dispersion system with LIF, PET and RAP crystal spectrometers.

Two sets of ten measurements were made on both cores and rims of mineral phases in order to check for zoning. Rim analyses were performed at a distance of 80 to 100 μm from crystal edges to avoid the effect of late exchange of cations at grain boundaries (*cf.*, Berg 1977). Counting time for each measurement was 100 seconds; data were processed according to the Bence & Albee (1968) correction program. Analytical results (Table 1) have been stored in the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Cordierite is practically unzoned, and its composition is almost constant throughout a thin section. The most magnesian cordierite (X_{Mg}^{Cd} 0.91) comes from south of the Morin complex (Fig. 1) and east of the Lac-Croche complex. The least magnesian cordierite comes from southeast of the St-Didace complex (X_{Mg}^{Cd} 0.78–0.80). Grain size does not allow analyses of channel-filling fluids by conventional techniques, but the sums of oxides for cordierite are significantly low and variable, even at the scale of a thin section. As Na has not been detected, these variations reflect changes in the amount of fluids filling cordierite channels (essentially CO_2 and H_2O). The proportion CO_2/H_2O has not been evaluated, but the presence of optically positive cordierite suggests that some grains contain CO_2 rather than H_2O (Armbruster & Bloss 1980).

Garnet, an almandine-rich solid solution, is usually zoned, in contrast with cordierite. The most conspicuous case of zoning is illustrated by the depletion in the grossular component at garnet rims in the Shawinigan area. The reverse pattern, though less pronounced, is observed in the Morin area. As the spessartine content is very low in both garnet cores and rims, the decrease in grossular content must be compensated by an increase in pyrope–almandine components. Fe–Mg zoning in garnet can only be estimated by comparing almandine–pyrope ratios of cores and rims. This ratio does not show systematic regional variations as in grossular: the garnet in two sections shows a marked increase in almandine towards the rim (6/20.58 and 6/64.56); one section shows the reverse zoning (6/33.24), with a slight increase in pyrope towards the rim. All other sections show minor and erratic zoning or none at all.

Plagioclase is in the range An_{26} to An_{88}, but is not noticeably zoned within a thin section. As oxide variations from grain to grain are usually of the same order of magnitude as the analytical error, average values have been calculated.

Biotite contains 4 to 5% TiO_2 with X_{Mg}^{Bi} ranging from 0.61 to 0.70. The sapphirine-bearing sample contains a TiO_2-poor, phlogopite-rich mica (TiO_2 1.30%) with a X_{Mg}^{Bi} of 0.80.

Sapphirine included in cordierite (X_{Mg}^{Sa} 0.80) has a composition that plots in the triangle defined by associated cordierite, garnet and sillimanite, suggesting the possible reaction sapphirine + quartz = cordierite + garnet + sillimanite.

EQUILIBRIUM AND DISEQUILIBRIUM CRITERIA IN FE–MG EXCHANGE REACTIONS

Mineral zoning and compositional variations for a given mineral at the scale of a thin section show that chemical equilibrium may not necessarily have been attained, even where textural equilibrium has been established. Therefore, a set of criteria has to be elaborated in order to either identify local conditions of chemical equilibrium or to unravel the trends in the physical conditions responsible for the observed disequilibrium. Although disequilibrium assemblages are not unconditionally suitable for quantitative thermodynamic calculations, they might provide a better understanding of metamorphic gradients than do equilibrium assemblages. Equilibrium criteria will thus be used to give quantitative estimates of intensive parameters, whereas qualitative estimates of the variations of these parameters will be obtained through the analysis of disequilibrium processes.

The simplest and most widely used criterion of local equilibrium between two mineral species concerns composition at grain contacts. As this condition is not always realized, we shall admit that grains less than a few tenths of millimetres apart and separated by a quartzose matrix or an unzoned Fe–Mg mineral of a third species are probably close to chemical equilibrium. Fe–Mg distribution coefficients obtained by applying these criteria will be called "equilibrium K_D" values.

In order to estimate the conditions of earlier stages of metamorphism, zoned minerals were considered. In the case where a zoned and a homogeneous mineral are in contact, if the outer rim of the zoned mineral is sufficiently narrow and if the element participating in the zoning is a major constituent of the unzoned mineral, the unzoned mineral can be considered as an infinite reservoir for the element participating in the zoning pattern (*cf.*, Tracy *et al.*

1976). The distribution coefficient obtained from the core composition of the unzoned mineral will thus be close to an "early equilibrium K_D" value.

Moreover, in order to obtain information in terms of intensive parameters about the magnitude of disequilibrium, all possible distribution coefficients were calculated according to the procedure followed by Deb & Saxena (1976). It is clear that this procedure yields some extreme values of artifact K_D, but the comparison between temperatures obtained from extreme K_D, average K_D and "equilibrium K_D" values might be informative.

TABLE 2 : TEMPERATURE ESTIMATES FROM DISTRIBUTION COEFFICIENTS*

Sample	Type of K_D	Cd-Ga		Bi-Ga	
		Grain	T(°C)±30	Grain	T(°C±30
5/29.58	aver		671		765
	min		823		878
	max		509		624
	Equi	N-N$_1$	676		
	Equi	N-N$_2$	659		
	Equi	G$_1$-G$_2$	646		
	Equi	G$_2$-G$_1$	627		
5/43.81	aver		696		702
	min		772		872
	max		651		602
	Equi	I-C	735	D-C	673
	Equi	I$_2$-A$_1$	683		
6/20.58	aver		577		621
	min		655		693
	max		523		557
	Equi	D$_2$C(r)	591	I-I	631
	Equi	A$_1$-A$_1$	558		
		A$_2$-A$_2$	542		
	early	D$_2$-C (c)	595		
6/33.24	aver		641		722
	min		679		
	max		619		
	Equi	C$_1$-F$_2$(r)	672		
	Equi	B-G	636	G-G	633
	early	C$_1$-F$_2$(c)	662		
6/54.47	aver		688		678
	min		755		728
	max		576		576
	Equi	D$_2$-D(r)	704	A-A	701
	Equi	D$_1$-D(r)	697	D-D(r)	686
	Equi	E$_2$-F(r)	672		
	early	D$_2$-D(c)	714	D-D(c)	693
	early	E$_2$-F(c)	647		
6/64.56	aver		643		640
	min		712		728
	max		590		580
	Equi	D$_1$-C	624	C-C	628
	Equi	A-A(r)	616	A-A(r)	604
	Equi	B$_1$-F	605		
	Equi	D$_1$-D(r)	597	D-D(r)	608
	early	A-A(c)	678	A-A(c)	660
	early	D$_1$-D(c)	690	D-D(c)	697

* The letters (r) and (c) refer to rim and core compositions, respectively; aver average, min minimum, max maximum, equi equilibrium Cd-Ga and Bi-Ga calibrations (Thompson 1976).

CORDIERITE-GARNET THERMOMETRY

The marked Fe–Mg partitioning between cordierite and garnet observed both in natural assemblages (Thompson 1976) and experimental runs (Hensen & Green 1973, Holdaway & Lee 1977) has been used for thermometric calibration (Table 2). The equilibrium constant of the exchange reaction:

$$\mathrm{MgCd} + \mathrm{FeGa} \rightleftarrows \mathrm{FeCd} + \mathrm{MgGa} \ldots\ldots\ldots (.1)$$

is represented by the distribution coefficient

$$K_{D_1}{}^{Cd-Ga} = \frac{X_{Mg}{}^{Cd}}{X_{Fe}{}^{Cd}} \cdot \frac{X_{Fe}{}^{Ga}}{X_{Mg}{}^{Ga}}$$

This coefficient is an exponential function of T. Among the various published equations relating the two variables, we have used the one of Thompson (1976) because it had already been selected as one of the functions in the calibration of the cordierite–garnet–H_2O fields by Martignole & Sisi (1981). This was necessary in order to preserve the consistency of results.

Temperatures obtained from "equilibrium K_D" values

Temperatures calculated from equilibrium K_D values range from 542°C northwest of the St-Didace complex to 735°C a few km south of the Morin anorthosite. The number of samples is too small to discuss the regional variation between these two extremes, but one may notice that the lowest temperatures tend to be recorded remote from plutonic complexes. The two-hundred-degree difference between the extreme values shows that there is not a single blocking temperature in high-grade metapelites; thus differences between estimated temperatures should be significant. At the scale of the thin section, temperatures derived from equilibrium K_D values show a significant variation (50 ± 30°C) near the Morin anorthosite, whereas in the eastern part of the area variations are within the error limit. This might correspond to re-adjustment upon cooling *versus* "frozen-in" equilibria. The possibility of re-adjustment does not seem to be related to any special temperature, as it is conspicuous from samples recording the lowest as well as the highest temperatures. The highest T obtained from equilibrium K_D values can thus be considered to represent the closest approach to the peak of the last thermal event.

Temperatures obtained from "early equilibrium K_D" values

In all but two samples, Fe–Mg zoning of garnet is not sufficiently pronounced to allow derivation of significantly different temperatures from core and rim compositions. These two samples are from NW and SE of the St-Didace complex and do show reliable temperature differences. Temperatures derived from core and rim compositions in sample 6/20.58 define roughly the same interval as the one recorded by the equilibrium K_D values. In sample 6/64.56, the temperature obtained using garnet core is more than 70°C higher than the one given by garnet rims and, as such, probably records a stage of higher temperature.

Temperature obtained from average and extreme K_D values

The temperatures derived from average K_D values generally fall in the range defined by temperatures determined from adjacent cordierite and garnet. In cases where garnet is not zoned, average K_D values give an average blocking temperature. Where garnet is zoned, the average temperature does not correspond to any specific event. Temperatures obtained from extreme K_D values show that equilibrium was attained where they are equivalent to maximum and minimum T obtained from equilibrium K_D (sample 6/33.24). In this case there is no artifact K_D. Where their range is much larger than the range defined by the equilibrium K_D values, they provide a scale for estimating the magnitude of disequilibrium. However, disequilibrium cannot be described only in terms of Mg/(Mg + Fe) variations. It is also influenced by the fluid content of cordierite, which in turn controls the stabilization pressure of this mineral, and thus its Mg/(Mg + Fe), as will be seen in the section dealing with cordierite barometry.

BIOTITE–GARNET THERMOMETRY

The Fe–Mg exchange reaction between biotite and garnet is represented by the distribution coefficient:

$$K_{D2\text{Fe-Mg}}{}^{\text{Bi-Ga}} = \frac{X_{\text{Mg}}{}^{\text{Bi}}}{X_{\text{Fe}}{}^{\text{Bi}}} \cdot \frac{X_{\text{Fe}}{}^{\text{Ga}}}{X_{\text{Mg}}{}^{\text{Ga}}}$$

Temperatures have been calculated from Thompson's (1976) calibration from K_D values obtained following the criteria defined above. Owing to the fact that the partition of iron and magnesium between biotite and garnet is less pronounced than that between cordierite and garnet, the effect of chemical disequilibrium in terms of Mg/(Mg + Fe) will be more pronounced in terms of temperature determinations than it was in the case of cordierite–garnet thermometry. This might be the reason why, in several cases, average temperatures derived from $K_D{}^{\text{Bi-Ga}}$ are significantly different from those derived from $K_D{}^{\text{Cd-Ga}}$. We have no explanation, though, as to why they are usually higher. On the other hand, wherever biotite is in contact with the same garnet as cordierite, temperatures obtained from the two thermometers are identical. When equilibrium criteria defined above are applied, Bi–Ga thermometry gives temperatures in the range 604–710°C, both extremes being from the vicinity of the St-Didace complex.

CORDIERITE–GARNET BAROMETRY

The reaction through which cordierite is converted to garnet, sillimanite and quartz is pressure-sensitive; the Mg content of cordierite should thus be a good geobarometer. Unfortunately H_2O, like Mg, stabilizes cordierite towards higher pressure; also water cannot be directly determined by electron-microprobe analysis. Moreover, CO_2, as well as other gases, enter the cordierite channels, which means that, neglecting the analytical error, the amount obtained by subtraction from the total of oxides in a microprobe analysis represents all gaseous species entering the cordierite structure. Pressures estimates have been performed according to the cordierite–garnet–H_2O calibration of Martignole & Sisi (1981), for which H_2O in cordierite should be known. Accordingly, a semiquantitative estimate of H_2O was obtained by combining several types of information. These are based on the possible significance of the oxide sums and on optical data of analyzed samples of cordierite.

By subtraction, a very crude estimate of the

TABLE 3. ESTIMATES OF FLUID CONTENT IN CORDIERITE

Sample	$\Delta\Sigma$	$\overline{X}\Sigma$	Average fluid	n H_2O Max
5/29.58	2.76	98.90 ± 0.98	1.1 ± 0.98	0.4
5/43.81	2.10	97.75 ± 0.84	2.25 ± 0.84	0.8
6/20.58	2.08	99.85 ± 0.83	0.15 ± 0.83	0
6/33.24	1.62	97.78 ± 0.65	2.22 ± 0.65	0.7
6/54.47	0.83	97.91 ± 0.33	2.09 ± 0.33	0.7
6/64.56	1.45	99.29 ± 0.54	0.71 ± 0.54	0.2

$\Delta\Sigma$: range in remainder between sum of oxides and 100.
$\overline{X}\Sigma$: average sum of oxides for all analyzed grains in a section.

fluid content of cordierite can be obtained. Cordierite totals are usually lower than 100, whereas totals for garnet crystals analyzed under the same conditions tend to be close to 100 and even higher (Table 3). At this stage, there are two possibilities for estimating the fluid content. An average fluid content can be calculated from the average oxide sum in a section. In most sections, the number obtained is higher than the error of oxide sums ($\simeq$ 1%). This method does not give any information on the nature of the fluid; if it is taken as pure H_2O, the degree of hydration of cordierite will usually be overestimated. If the range of fluid content is calculated for a single section, it appears to be usually higher than the error in the oxide sum, and variations in fluid content can thus be estimated (Table 3). If combined with optical information, a semiquantitative estimate of H_2O and CO_2 content of cordierite can be obtained. Recent experiments by Armbruster & Bloss (1980) have demonstrated that there is a relationship among $2V_x$, mean index of refraction and the nature of the channel-filling fluids in Mg-cordierite. CO_2-rich cordierite is optically positive, whereas water-rich cordierite is negative, with a relatively small $2V$ ($\simeq$ 50°). Fluid-free cordierite has a $2V$ very close to 90°. Combining optical observations (wherever possible) with estimated fluid contents, three cases of fluid variations have been found (Fig. 2).

In the first case, a decrease in totals of microprobe data is correlated with a decrease in the magnesium content at the scale of the thin section. If the variation in microprobe totals is related to fluid content, this shows that the availability of fluid may not be uniform, even at a very small scale, and that, for a given pressure, equilibrium could be attained by increasing the magnesium content of cordierite where water was not available. It is interesting to point out that according to the cordierite–garnet calibration of Martignole & Sisi (1981), for a given T, the same reduction of chemical potential, resulting in the same ΔP of stabilization, is achieved by either introducing 1% (wt.) H_2O in a dry cordierite or by increasing X_{Mg}^{Cd} by 0.07. This could be applied to sample 5/29.58 to show that water could compensate for the decrease in X_{Mg}^{Cd}.

In the second case, the fluid content varies from 0 to about 2%, without any correlation with the Mg content (samples 6/20.58, 6/64.56). Keeping in mind the imprecision attached to these numbers, there is a possibility that the corresponding cordierite grains only contain CO_2, a fluid much heavier than H_2O, which probably does not interact significantly with the stability pressure of cordierite (see Martignole & Sisi 1981). Optically positive cordierite has been identified in the corresponding sections, showing that CO_2 is the main channel-filling fluid (sample 6/20.58). In the pressure calculations, these cordierite compositions will be considered as anhydrous (nH_2O = 0).

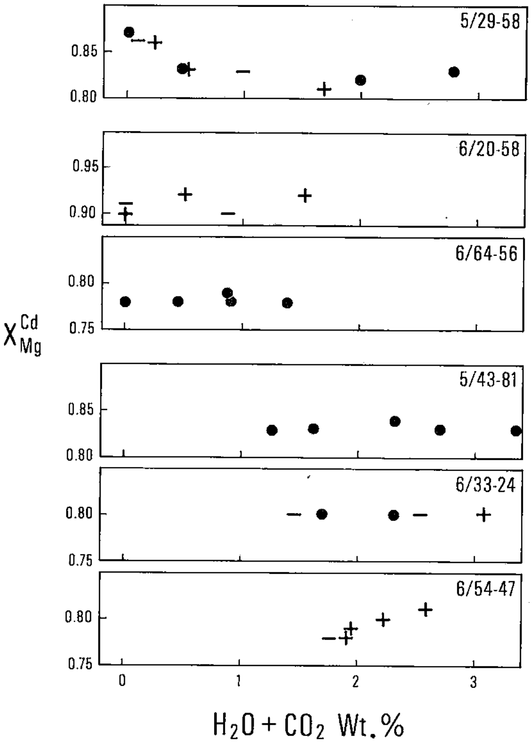

FIG. 2. Fluid content of cordierite *versus* X_{Mg}^{Cd}. Optically positive cordierite +, negative –. Dots: unidentified optical sign. Cases 1 (5/29.58) 2 (6/20.58, 6/64.56) and 3 (5/43.81, 6/33.24, 6/54.47) are described in the text.

The third case is the one where cordierite always contains a significant amount of fluid, the variation of which does not show any correlation with magnesium content. Two possibilities can account for this situation: 1) the fluid is essentially CO_2 and does not affect the Mg content of cordierite, or 2) the fluid is a mixture of CO_2 and H_2O, but H_2O has a roughly constant value in all cordierite grains, corresponding to the minimum fluid content. As optically positive cordierite seems to occur preferentially among those grains that have the highest fluid content, we favor the second possibility. In consequence, the minimum fluid content will be taken as a maximum H_2O value for all the grains of the section (*e.g.*, 6/33.24, 6/54.47).

Turning now to the error resulting from the subtraction method of estimating H_2O, if an error of 1% on the oxide sum is retained, a maximum error of 0.3 on estimated nH_2O would be obtained. According to the Cd–Ga–H_2O calibration (Martignole & Sisi 1981), this error results at 700 ± 100°C in a 500 to 1500 bars uncertainty in estimated pressure, depending on the absolute value of nH_2O. Pressures obtained after application of those criteria are presented in Table 4.

ESTIMATION OF P(H_2O)

Cordierite hydration is a function of T and P when $P_{fluid} = P(H_2O)$ (Schreyer & Yoder 1964), but it depends on $X(H_2O)$ if the fluid phase is a CO_2–H_2O mixture (Johannes & Schreyer 1981). In the first case, water is the unique fluid filling cordierite cavities; its fugacity should be obtained through experimental hydration data, given the hydration number of a cordierite and the equilibrium P. In the second case, water pressure in the mixed fluid in equilibrium with cordierite cannot be estimated directly from hydration data. Experiments by Johannes & Schreyer (1981) have shown that CO_2 does not behave as an inert gas; the strong partition of water in favor of cordierite implies that the hydration theory of Martignole & Sisi (1981) should be reformulated with new Henry's constants for various values of $X(CO_2)$ as soon as more experimental data become available.

TABLE 4. PRESSURE ESTIMATES FROM CORDIERITE BAROMETRY

Sample	Grain	nH_2O		X_{Mg}^{CD}	T(oC) Cd-Ga	P(Kbar)	P_{H_2O}(bars)
		Min	Max				
5/29.58	G_2	0.0	0.4	0.87	627	5.0-5.8	0- 500
	G_1^2	0.0		0.86	646	5.1-5.9	
	N^1	0.0		0.86	676	5.1-5.9	
5/43.81	J_2	0.4	0.8	0.84	683	5.8-7.4	700-3500
	J_1^2	0.4		0.84	735	6.0-7.5	
6/20.58	A_1	0.0	0.0	0.91	558	4.8 -	0
	A_2^1	0.0		0.91	542	4.8 -	
	D_2^2	0.0		0.90	591	5.0 -	
6/33.24	B	0.5	0.7	0.80	636	5.6-6.9	1000-2000
	C_1	0.5		0.80	672	5.8-7.1	
6/54.47	D_1	0.6	0.7	0.79	697	6.5-7.3	2000-2500
	D_2^1	0.6		0.78	704	6.5-7.3	
	E_2^2	0.6		0.81	672	6.3-7.1	
	D_2	0.6		0.78	714	6.6-7.6	
	E_2^2	0.6		0.81	647	6.1-6.9	
6/64.56	D_1	0.0	0.2	0.79	624	4.3-4.5	0.200
	B_1	0.0		0.78	605	4.1-4.3	
	A^1	0.0		0.78	616	4.2-4.4	
	D_1	0.0		0.79	597	4.1-4.3	
	D_1	0.0		0.79	690	5.0-5.3	
	A^1	0.0		0.78	678	4.7-5.0	

In the meantime, a semiquantitative estimate of P(H_2O) can be obtained by using nH_2O from the criteria defined above. If all the fluid in cordierite is taken as H_2O, the nH_2O value will be overestimated in most cases. But it can be seen from the experimental data of Johannes & Schreyer (1981) that Henry's constant for the adsorption of a CO_2–H_2O mixture is increased compared to that for H_2O adsorption. For a given T and nH_2O, $P(H_2O)$ obtained from hydration isotherms (Martignole & Sisi 1981) will lead to an underestimate in the case of mixed fluids. This effect will partly counteract the error introduced by considering all the fluid as H_2O. Considering the enormous imprecision attached to the method of estimating the hydration number and the absence of calibration for H_2O–CO_2 mixtures, water pressures estimated following these procedures can only be considered as very crude (Table 4). The only conclusion that can be retained is that in the metapelites described here, P(H_2O) was considerably lower than the lithostatic pressure and, in some cases, the fluid phase was extremely rich in CO_2. A problem remains concerning 1) fluid-absent cordierite (Berg 1977, this study) and 2) possible variations in the fluid content of cordierite grains throughout a single section. These cases suggest that late hydration is not inevitable, and that quenching from a situation with steep gradients in fluid concentration and composition is not impossible. If such is the case, estimations of regional H_2O and CO_2 pressures will become very doubtful.

PLAGIOCLASE–GARNET BAROMETRY

Where garnet is associated with plagioclase, sillimanite and quartz, its grossular content is related to the anorthite content of the plagioclase. The equilibrium constant of the corresponding reaction can be derived from the high-pressure breakdown of anorthite:

$$3\ \text{an} \rightleftarrows \text{gross} + 2\ \text{sill} + \text{qz} \quad \ldots\ldots\ldots\ldots (3)$$

$$K_3 = \frac{a_{gr}{}^{ga}}{a_{an}{}^{pl\ 3}}$$

Since the first application of this reaction in geobarometry (Ghent 1976), activity models for garnet solutions have been considerably improved (Newton & Haselton 1981); equilibrium curves for K_3 can be drawn with a reasonable precision. As these curves have a gentle positive slope in a P–T diagram, derivation of an accurate pressure is dependent on a temperature estimate that represents the same metamorphic event as the garnet–plagioclase equilibrium. Pressure estimates in turn are influenced by intragranular and intergranular chemical inhomogeneities. Garnet zoning, already discussed in terms of almandine–pyrope ratios, is often very pronounced in terms of grossular content. Both increase and decrease in grossular content *versus* almandine + pyrope are found towards garnet rims. On the contrary, plagioclase is not zoned; as it constitutes a large reservoir of Ca compared to the Ca variations of garnet rims, we can assume that the plagioclase in equilibrum with garnet, at the time when the garnet had the composition of its core, was not significantly different from the actual plagioclase. Equilibrium constants can thus be calculated for garnet cores and rims using the same matrix plagioclase. Moreover, as chemical equilibrium has not been attained at the scale of a thin section in terms of grossular content, disequilibrium in Ca of garnets will be used, following the same general procedure as for Fe–Mg disequilibrium, to give qualitative estimates of metamorphic trends.

Estimation of metamorphic pressures

Estimation of metamorphic pressures have been performed according to the most recent calibration of the garnet–plagioclase geobarometer (Newton & Haselton 1981), which considers the latest refinements on the calculation of the activities of anorthite (Newton & Wood 1980) and grossular as well as a correction to account for the nonregularity of garnet solutions, especially for low concentrations of the grossular component (Cressey *et al.* 1978).

Newton & Haselton (1981) based their calculations on Goldsmith's (1980) end-member curve for anorthite breakdown. This is thought to carry less uncertainty in pressure calibration than previously published experimental data. In addition, we have done the same calculations using the curve of Hariya & Kennedy (1968), which is closest to an average value of all published experiments at temperatures corresponding to the granulite facies (*cf.*, Newton &

TABLE 5. PRESSURE ESTIMATES FROM GROSSULAR-ANORTHITE BAROMETRY*

Sample		T(°C) (Cd-Ga)	Plagioclase		Garnet		ΔV_3(cm^3)	Pressure (Kbar)		
Rock	Ga		X_{an}	a_{an}	X_{gr}	$a_{gr}(10^{-3})$		Goldsmith	H & K	Cd-Ga (minimum)
5/29.58	N_2	659	0.883	0.845	0.0265	0.0671	58.5	1.9	2.5	5.1
	G_1	627		0.847	0.0354	0.165	58.1	2.8	3.3	5.0
5/43.81	C	735	0.546	0.682	0.0262	0.0588	58.5	3.3	3.9	6.0
	A_1(r)	683		0.710	0.0368	0.115	57.8	2.7	3.3	5.8
	A_1(c)	683		0.710	0.0260	0.0535	58.8	2.5	3.1	5.8
6/20.58	A_1	558	0.272	0.482	0.0269	0.0985	58.0	3.4	4.0	4.8
	A_2	542		0.496	0.0253	0.0774	58.4	2.9	3.4	4.8
	C(r)	591		0.456	0.0269	0.0885	58.5	3.9	4.5	5.0
	C(c)	595		0.453	0.0366	0.2394	57.4	5.3	5.9	5.0
6/33.24	C_1	636	0.235	0.355	0.0275	0.0554	58.5	4.8	5.4	5.6
	F_2(c)	662		0.343	0.0259	0.0490	58.5	5.1	5.7	5.8
6/54.47	D(r)	704	0.362	0.526	0.0368	0.125	57.4	5.2	5.8	6.5
	F(r)	672		0.547	0.0342	0.112	57.8	4.5	5.1	6.3
	D(c)	714		0.520	0.0664	0.688	55.5	8.1	8.7	6.8
	F(c)	647		0.565	0.0676	0.802	55.3	7.0	7.6	6.1
6/64.56	C	624	0.419	0.655	0.0365	0.122	57.2	3.4	4.0	5.0
	F	605		0.679	0.0375	0.123	57.3	3.2	3.8	4.1
	A(r)	616		0.662	0.0381	0.135	57.3	3.4	4.0	4.2
	D(r)	597		0.679	0.0385	0.138	57.3	3.1	3.7	4.3
	A(c)	678		0.614	0.0389	0.145	57.3	4.5	5.1	4.7
	D(c)	690		0.606	0.0568	0.440	55.2	6.5	7.1	5.0

* Newton & Haselton (1981) calibration; letters (r) and (c) refer to rim and core compositions, respectively.

Haselton 1981). Given the high P–T experiments of Hariya & Kennedy, provided the extrapolation to lower T is valid, and after correction for the kyanite–sillimanite inversion using Holdaway's (1971) values for ΔS and ΔH, the following equation can be derived for the end-member reaction used when sillimanite is the stable aluminum silicate: P (bars) = 113 + 23.8 T (°C). Calculated pressures are reported in Table 5. Pressures obtained from cordierite barometry are given for comparison. Note that calculations performed with the end-member curve of Hariya & Kennedy (1968) more closely approach pressures given by cordierite.

Estimation of metamorphic trends through chemical disequilibrium

Grossular zoning in garnet, which is mainly pressure-dependent if developed in the presence of aluminum silicate–plagioclase–quartz, can be correlated with almandine–pyrope zoning, which is essentially temperature-dependent. Variations in chemical composition between several garnet grains throughout a single section can be studied in the same way. The correlation between Fe–Mg variations and Ca variations is best visualized (Fig. 3) by plotting 100Mg/(Mg + Fe + Ca + Mn) *versus* 100Ca/(Ca + Mg + Fe + Mn). In this type of diagram, a vertical trend [decrease in Mg/(Mg + Fe + Ca + Mn) at constant Ca/(Ca + Mg + Fe + Mn)] corresponds to a decrease in temperature at constant grossular content (K constant), namely a temperature decrease along a slope of about 1°C per 24 bars. A horizontal line in the diagram corresponds to a pressure variation at constant temperature; the polarity of this variation is given by the position of the points corresponding to garnet cores and rims. A line with a negative slope corresponds to a decrease in temperature correlated with an increase in grossular content, and thus an increase of K_3, suggesting an isobaric path of cooling. These three types of trends are represented in metapelites from the area under discussion (Fig. 4). Samples coming from the vicinity of the Morin anorthosite (5/29.58, 5/43.81) have garnet

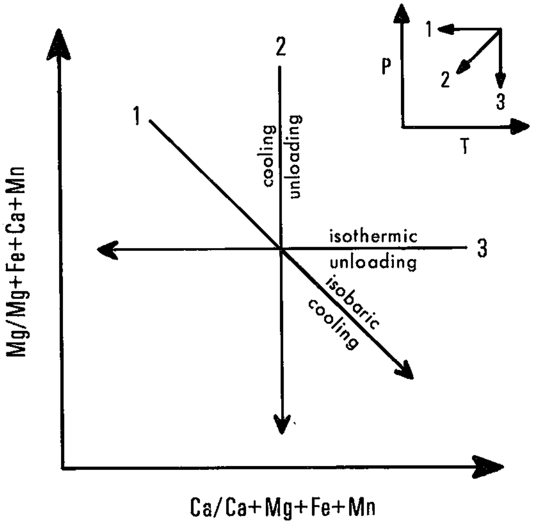

FIG. 3. Mg/(Mg + Fe + Ca + Mn) *versus* Ca/(Ca + Mg + Fe + Mn) diagram showing the different trends responsible for chemical disequilibrium in garnet compositions.

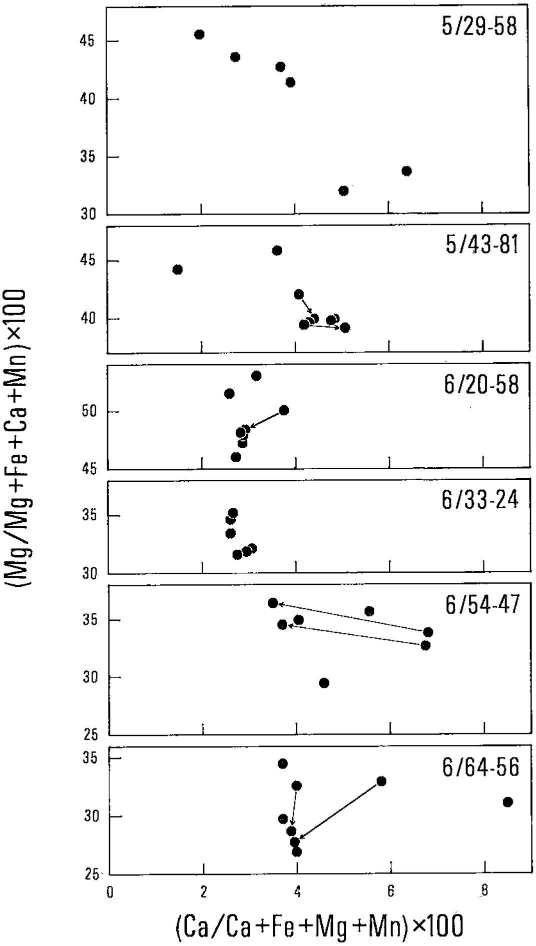

FIG. 4. Application of Fig. 3 to analyzed grains of garnet (for interpretation see text). The arrows go from core to rims.

composition trends indicative of isobaric cooling (trend 1), whereas cooling accompanied by unloading (trend 2) is exemplified by samples coming from south and west of the St-Didace complex (6/20.58, 6/33.24); an almost isothermal unloading (trend 3) is suggested by samples coming from the eastern margin of the St-Didace complex (6/54.47, 6/64.56). It appears, therefore, that two regions about 200 km apart have suffered different cooling–unloading histories: rapid cooling after the temperature climax in the Shawinigan area and slow cooling without significant unloading around the Morin anorthosite. Simultaneous cooling and unloading between these two regions suggest that variations in late metamorphic evolution are progressive from west to east.

CONCLUSIONS

Results of careful microprobe analyses of high-grade metapelites have shown that equilibrium between iron–magnesium solid solutions is far from being attained (or, perhaps, is rarely preserved if ever attained) at the scale of a thin section (Nantel 1977). This situation appears to be fairly common in granulite-facies rocks (see Lonker 1981) and is probably largely due to re-equilibration upon cooling. Keeping in mind the difficulties resulting from these readjustments, both cordierite–garnet- and biotite-garnet-derived temperatures show that metamorphic temperatures were higher around the Morin anorthosite complex (over 700°C) than in the Shawinigan area. The coincidence of the highest temperatures with regional development of wollastonite in impure marble is probably due to a vast contact aureole superimposed on granulite-facies regional metamorphism.

The minimum temperature (around 550°C) was recorded in a locality immediately north of the orthopyroxene isograd (Schrijver 1973) in the hornblende zone. The isograd would thus correspond here to a temperature around 600°C. Finally, near Shawinigan, a sample (6/64.56) containing relics of kyanite and andalusite gives temperatures from 597 to 628°C, a reasonable range for the aluminum silicate triple point.

The interpretation of pressure estimates from cordierite barometry and plagioclase–garnet barometry is not as clear, as it does not confirm the pressure gradient suggested near the Morin anorthosite by the development of garnet in charnockitic rocks. Pressures obtained using the garnet–cordierite barometer range from 4 to nearly 7 kbar, whereas the plagioclase–garnet barometer gives slightly lower values, especially if Goldsmith's (1980) end-member curve for anorthite breakdown is adopted. According to both barometers, the highest pressures were not attained near the Morin anorthosite but near the St-Didace complex. In this complex, charnockitic rocks of suitable composition are not garnetiferous. Kinetic constraints may be responsible for this anomaly in the formation of late metamorphic assemblages, together with the variation in cooling–unloading paths.

All specimens of metapelite analyzed have sillimanite as the stable aluminum silicate; all the pressures obtained, when combined with computed temperatures, plot in the sillimanite stability field, near the kyanite–sillimanite inversion curve. The sample from which relics of andalusite and kyanite have been recorded gives pressures in the range of 4.1 to 5.0 kbar (Cd–Ga barometry), showing that kyanite and sillimanite were probably metastable during andalusite growth.

Finally, the very crude estimate of P(H_2O) obtained by means of the subtraction method and hydration data on cordierite does not reveal any systematic variation in water pressure throughout the area. The method is not yet sufficiently precise to be used as a reliable indicator of water fugacity but a correction for water is necessary in order to obtain better results in cordierite geobarometry.

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