

CHEMICAL STUDY OF PHASE EQUILIBRIA IN
CHARNOCKITES, VARBERG, SWEDEN

S. K. SAXENA, *Institute of Mineralogy and Geology,
Uppsala, Sweden.*

ABSTRACT

The mineral assemblage in seven samples of charnockites is quartz, orthoclase, plagioclase, hypersthene, augite, biotite, hornblende, \pm garnet. . . . The distribution of several elements among coexisting minerals is mostly orderly. The distribution of Mg and Fe between any two coexisting ferromagnesian minerals can be explained by ion-exchange equilibrium. The distribution coefficients, however, vary with the concentration of Al in tetrahedral coordination in biotite or hornblende or with the concentration of Mn in garnet, wherever these minerals are involved.

A nearly uniform Ti content in biotite may be explained by an equilibrium: MgFe-biotite in MgFeTi-biotite + 3 quartz \rightleftharpoons orthoclase + 3 hypersthene + water. The difference in the equilibrium constant (Ca in plagioclase/Ca in garnet) for the reaction: diopside + anorthite in plagioclase \rightleftharpoons grossularite in garnet + hypersthene + quartz, in samples a few kilometers apart, may be due to the difference in pressure of formation of rocks.

An approach to chemical equilibrium through the reaction: MgFe-biotite in MgFeTi-biotite + hornblende + anorthite in plagioclase + 3 diopside + quartz \rightleftharpoons 2 grossularite in garnet + 10 hypersthene + orthoclase + 2 water, may finally be inferred. Besides chemical composition, the only significant variation was in pressure and this variation cannot be accounted for by simple lithostatic pressure.

INTRODUCTION

Samples of charnockites from Varberg district in Sweden (Quensel, 1950) contain nine to ten coexisting minerals excluding minor accessories such as zircon, apatite, pyrite etc. Of these minerals usually five to six are of variable composition. The distribution of elements among coexisting minerals and chemical equilibrium in the mineral assemblages are discussed in this paper.

GEOLOGICAL BACKGROUND

Varberg lies to the south of Gothenburg on the west coast of Sweden. Basic-to-acid members of the charnockite series are well exposed on the coast in and around Varberg. Charnockite massifs are surrounded by aplitic granite, which in turn is surrounded by the more widespread granitic gneisses.

According to Subramaniam (1960) 'the rocks of the "intermediate" division are hybrid rocks formed by reaction of charnockite magma with pyroxene granulites of the basement'. Quensel (1950) suggests that 'these probably attained their regenerated chemical and mineralogic composition in connection with reactions due to intergranular diffusion' and 'the hybridisation may represent either an initial, an intermediate or a ter-

minating stage in the metamorphic evolution of the charnockitic rocks, or most probably a consecutive process throughout the whole transformation period'. It is probable that the end process was a metamorphic recrystallization of a chemically inhomogeneous rock within a very small p - T field corresponding to some part of the granulite facies (hornblende granulite subfacies, Fyfe, Turner and Verhoogen, 1958). If chemical equilibrium was closely approached in the area at a certain p and T , it is reflected in the number and composition of the coexisting minerals.

This work is confined to a chemical study of coexisting minerals in eight samples of the charnockites (Fig. 1). Three samples are from Träslövsläge and four from Getterön. The mineral assemblage is quartz, orthoclase, plagioclase, biotite, hornblende, augite, hypersthene, garnet, magnetite and ilmenite. Two samples (4 and 5) do not contain garnet. The optic angle in orthoclase is around 50° . Untwinned plagioclase is in greater proportion than twinned ones. Garnets may vary in diameter up to a centimeter. Abbreviations and symbols used in the text and figures are listed in Table 2.

CHEMICAL COMPOSITION OF THE MINERALS

Chemical analysis was made on mineral grains in thin sections using a Geoscan (Cambridge) with operating conditions as: angle of incidence of electrons 90° , energy of electrons 15 kV, angle of emergence of X-rays 75° , specimen current $0.1 \mu\text{A}$ (for other details, see Saxena, 1968). Chemical analyses of minerals and the calculated formulae are not listed here.¹

Evans and Guidotti (1966) found distinct zoning in garnet crystals. Data on the variation in the composition of different grains of garnet found within a thin section are shown in Table 1. Important variations are in FeO (total Fe calculated as FeO) and CaO in samples 3 and 7. Garnet crystals are about a centimeter in diameter in sample 3. The difference in composition between the centre and the edge of crystal (a) in this sample is not large. Crystal (b), however, shows differences both within and from crystal (a). The size of garnet in other samples is small (less than 2 mm) and significant compositional differences in different grains in a thin section are noted only in sample 7. For the distribution diagrams the values of the crystals (a) are used.

The statistical errors, denoting the inhomogeneity within a mineral grain (Saxena, 1968), in most analyses were not significant. Some inhomogeneity was noted within the augite crystal in sample 4 and within the hornblende crystal in sample 6. Al_2O_3 varied significantly in the

¹ Tables are deposited with Mrs. M. Dahl, Geoscan Lab., Institute of Mineralogy and Geology, Uppsala, Sweden.

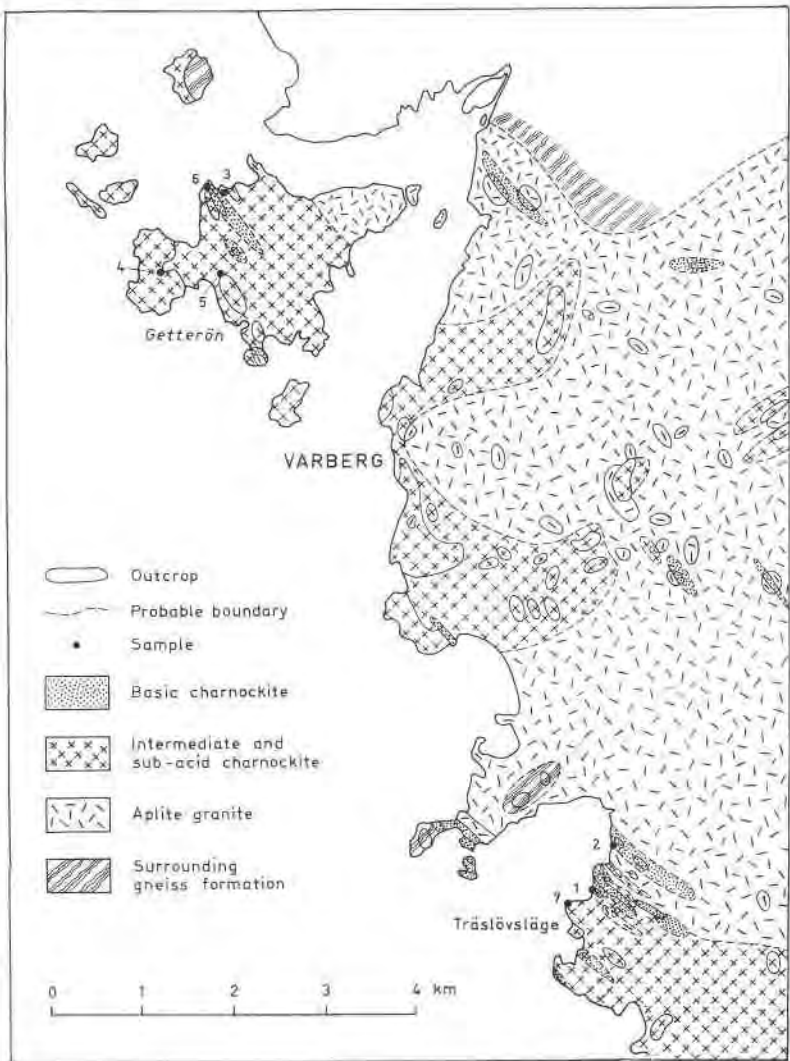


FIG. 1. Geological map of Varberg (after Quensel, 1950).

latter. The value used in this case was that given by majority of spots analyzed. Two different crystals of augite were analysed in sample 7 for total iron and the difference between them was less than 4 weight percent. Zoning in plagioclase could be noted only in sample 7, where a plagioclase crystal contains 6.5 weight percent of CaO at the centre and 7.9 weight percent of CaO at the border. As noted before garnet crystals in this sample also vary in CaO. Three different crystals of plagioclase in sample

TABLE 1. PARTIAL CHEMICAL ANALYSES OF DIFFERENT GARNET CRYSTALS IN A ROCK THIN SECTION FOR SOME SAMPLES

Ref.	No.	'FeO'	MgO	CaO	Ref.	No.	'FeO'	MgO	CaO
1	(a)	22.6	8.9	6.4	3	(a) (centre)	19.0	1.5	17.1
	(b)	23.0	n.d.	6.4		(a) (edge)	18.4	n.d.	17.1
	(c)	22.9	n.d.	6.65		(b) (centre)	19.8	1.4	15.7
6	(a)	30.7	1.4	7.1	7	(b) (edge)	n.d.	n.d.	13.8
	(b)	31.0	n.d.	7.2		(a)	25.0	6.0	8.3
	(c)	31.6	n.d.	7.15		(b)	25.1	5.7	8.35
8	(a)	30.5	1.3	7.3		(c)	27.5	5.75	6.7
	(b)	n.d.	n.d.	7.5					
	(c)	n.d.	n.d.	7.35					

(a), (b), (c) are different crystals in a single specimen (thin section). In sample 3 the crystals are about a centimeter in diameter. In other samples they are less than 2 mm. 'FeO' is total Fe calculated as FeO.

8 (collected by Dr. S. Ghosh from somewhere in Getterön) do not differ in composition significantly.

THEORETICAL ASPECTS

Under chemical equilibrium, the chemical potential of a component in coexisting minerals are the same. Also the activity of the component is similar for a mineral phase in any part of the system. The similarity in the activity of such a component may be reflected in the mole fraction of that component in the solid solution.

At a particular p and T , the composition of a solid solution for the components, which are not uniform in their concentration in the different samples, should vary in a definite way. Equilibrium in such a case may be revealed by the pattern of distribution of a variable component between two or more coexisting minerals. Graphic representations as used by Kretz (1959) are particularly useful to show such relations.

TABLE 2. ABBREVIATIONS AND SYMBOLS

G	molar Gibbs free energy	K_D	distribution coefficient
f	activity coefficient	p	pressure
R	gas constant	T	absolute temperature
[]	phase	{ }	constituent of a solid solution
μ_A^α	chemical potential of a component A in phase α	X_A^α	mole fraction of a component A in phase α
Al ^{IV}	aluminium in tetrahedral coordination		
Al ^{VI}	aluminium in octahedral coordination		
F	orthoclase	Pl	plagioclase
Capx	augite	Opx	hypersthene
Gar	garnet	Horn	hornblende
		Bi	biotite

While applying the phase rule, water is considered a component and phase as done by Kretz (1964). Similarly Kretz's definition of variance and the idea of sub-systems are also used here. In the equation of a reaction only a particular constituent of a solid solution { } or a phase [] may be involved. In such cases μ and G stand for a constituent and a phase respectively. Thus μ_{Ca}^{Gar} stands for the chemical potential of Ca in the garnet mixture and G_{Ca}^{Gar} stands for the free energy of grossularite.

DISTRIBUTION OF ELEMENTS

In the graphical representations which follow, the concentration of an element in one mineral is plotted against the concentration of the same element in another coexisting mineral. For elements present in small amount, the weight percent of the oxides are used. In other cases either the number of ions in the formulae or the atomic ratios (Table 3) are used.

Titanium. It is present in significant concentration only in biotite and hornblende. Concentration of Ti in biotite is comparatively high and similar in five samples (Fig. 2). Substitutions of Al or Fe^{3+} for Ti and *vice versa* are common in these minerals (Saxena, 1966, 1967). In sample 6, the amount of Ti is somewhat less but the amount of octahedrally coordinated Al is high.

Aluminum. Except for sample 6, the distribution of Al between pairs of hornblende-biotite and hornblende-garnet seems to be orderly (Fig. 2).

TABLE 3. ATOMIC RATIOS AND DISTRIBUTION COEFFICIENTS OF SOME ELEMENTS

Ref. No.	X_{Ca}^{Gar}	X_{Ca}^{Capx}	X_{Ca}^{Pl}	X_{Fe}^{Bi}	X_{Fe}^{Horn}	X_{Fe}^{Capx}	X_{Fe}^{Opx}	X_{Fe}^{Gar}		
1	0.173	0.441	0.310	0.315	0.368	0.219	0.330	0.583		
2	0.293	0.431	0.320	0.407	0.428	0.324	0.394	0.726		
3	0.477	0.433	0.275	—	0.540	0.368	—	0.876		
4	—	0.416	0.193	0.560	0.577	0.490	0.620	—		
5	—	0.416	0.172	0.589	0.590	0.509	0.626	—		
6	0.207	0.423	0.166	0.731	0.758	0.648	0.751	0.922		
7	0.227	0.453	0.352	0.441	0.464	0.316	—	0.700		
	$K_{D(Fe)}^{Horn-Capx}$	$K_{D(Fe)}^{Horn-Opx}$	$K_{D(Fe)}^{Horn-Gar}$	$K_{D(Fe)}^{Capx-Opx}$	$K_{D(Fe)}^{Capx-Gar}$	$K_{D(Fe)}^{Opx-Gar}$	$K_{D(Fe)}^{Bi-Horn}$	$K_{D(Fe)}^{Bi-Capx}$	$K_{D(Fe)}^{Bi-Opx}$	$K_{D(Fe)}^{Bi-Gar}$
1	2.076	1.180	0.416	0.569	0.200	0.352	0.789	1.639	0.933	0.329
2	1.561	1.150	0.282	0.737	0.180	0.245	0.917	1.431	1.055	0.259
3	2.016	—	0.166	—	0.082	—	—	—	—	—
4	1.402	0.814	—	0.588	—	—	0.933	1.324	0.759	—
5	1.388	0.859	—	0.619	—	—	0.996	1.382	0.856	—
6	1.701	1.038	0.265	0.610	0.156	0.255	0.867	1.476	0.900	0.230
7	1.807	—	0.371	—	0.198	—	0.910	1.707	—	0.338

$X_{Ca}^{Gar} = Ca / (Ca + Fe + Mg + Mn)$, $X_{Ca}^{Capx} = Ca / \Sigma$ (octahedrally coordinated ions).

$X_{Ca}^{Pl} = Ca / (Ca + Na)$, $X_{Fe} = Fe / (Fe + Mg)$. Samples 4 and 5 do not contain garnet.

Biotite in sample 3 and orthopyroxene in samples 3 and 7 were not analysed.

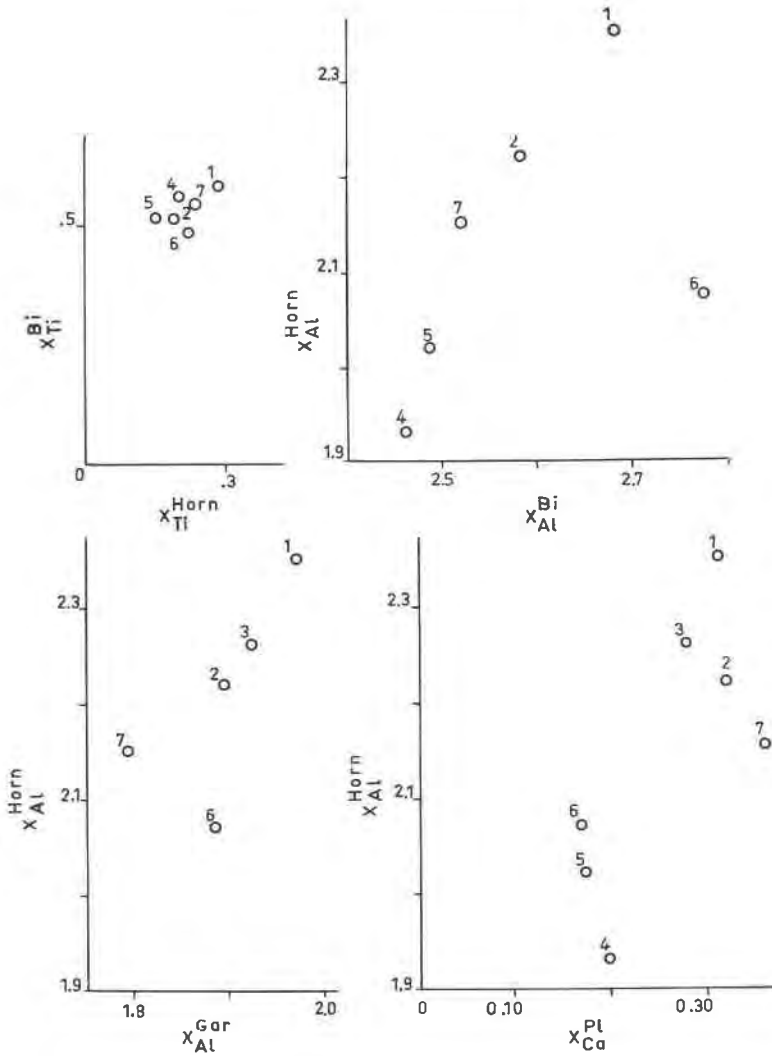


FIG. 2. Distribution of Ti and total Al among coexisting minerals. X represents number of ion in minerals. Concentration of Ti does not vary significantly. Distribution of Al in sample 6 is particularly disorderly due to inhomogeneity in the hornblende crystal.

The distribution between plagioclase (where X_{Ca}^{Pl} is taken to represent the concentration of Al) and hornblende indicates that samples with high anorthite in plagioclase in general also contain high total Al in hornblende. In garnets (samples 1, 2, 3 and 7) Al varies between 1.79 to 1.97 (ion on the 12 O basis). From the calculated chemical formulae of

garnets, it is noted that the total of 8 coordinated positions vary from 3.17 to 3.01 in these samples in the opposite direction. This is probably due to the variable concentration of Fe^{3+} in the total Fe.

Manganese. Figure 3 shows a very orderly distribution of MnO between pairs of coexisting minerals. Although the distribution is shown only between hornblende and another mineral, the orderliness in the distribution between other pairs of minerals, such as orthopyroxene-clino-

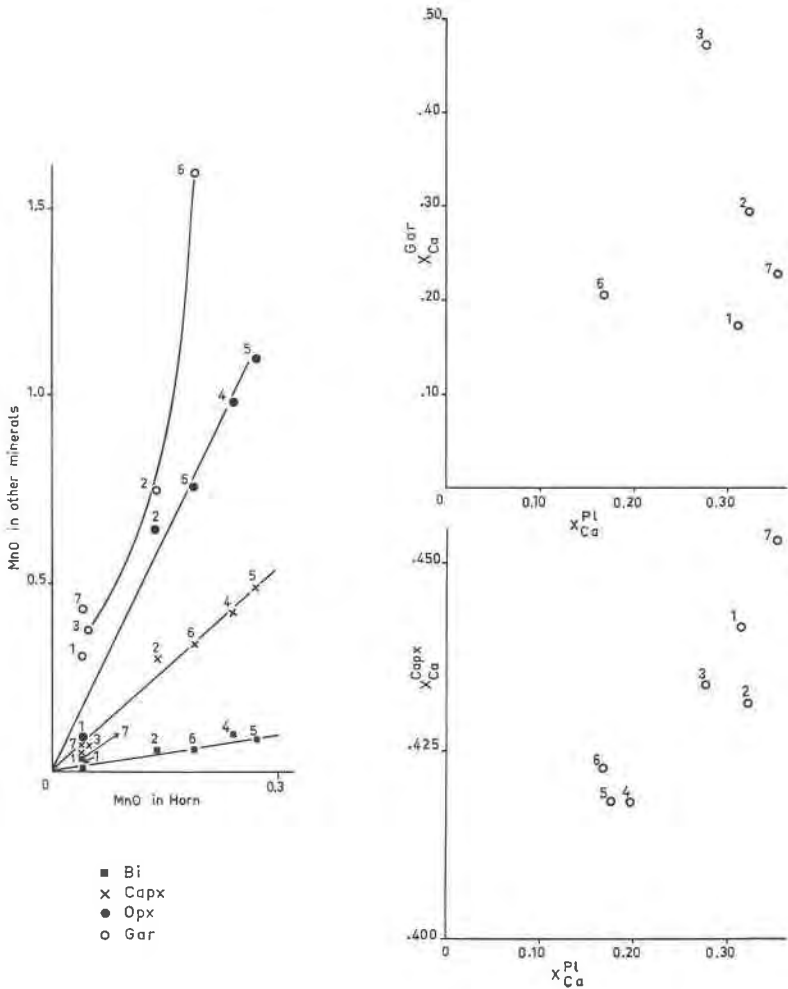
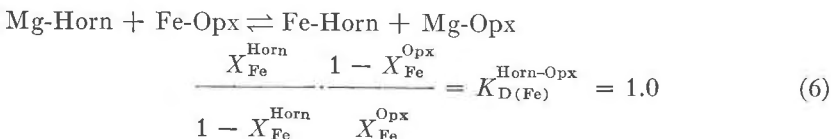
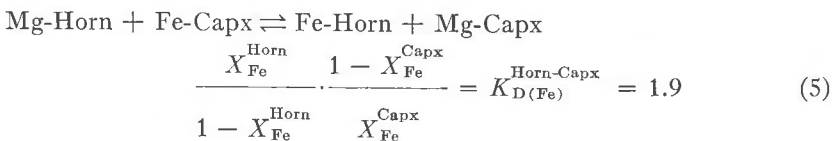
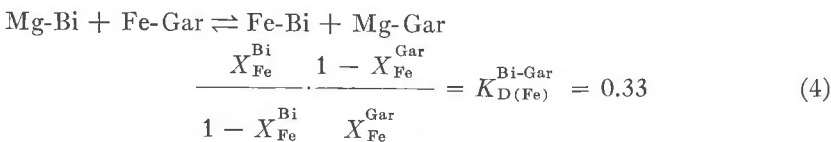
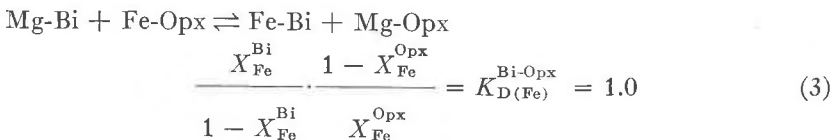
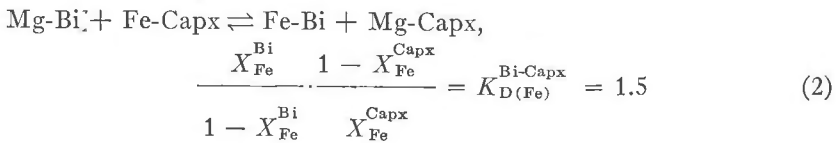
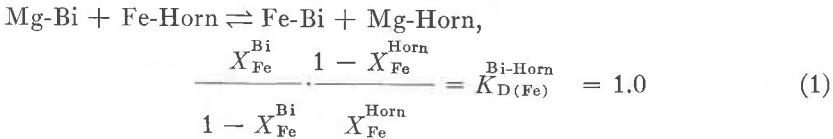


FIG. 3. Distribution of Mn (MnO weight percent) and Ca. $X_{\text{Ca}}^{\text{Pl}} = \text{Ca}/(\text{Ca} + \text{Na})$, $X_{\text{Ca}}^{\text{Gar}} = \text{Ca}/(\text{Ca} + \text{Fe} + \text{Mg} + \text{Mn})$ and $X_{\text{Ca}}^{\text{Cpx}} = \text{Ca}/\Sigma$ (octahedrally coordinated ions). Scattering of the distribution points for Ca is discussed in the text.

pyroxene is obvious. Among coexisting minerals, the concentration of Mn increases in the order biotite→hornblende→clinopyroxene→orthopyroxene→garnet in approximate ratios as 1:3:6:12: <20 respectively.

Calcium. In hornblende Ca does not vary significantly. Figure 3 shows rather a scattered distribution of Ca between plagioclase and garnet. The distribution between plagioclase and clinopyroxene is more orderly, although the variation in the latter mineral is small.

Iron and magnesium. In Figures 4 to 8 simple ion-exchange equilibria between pairs of minerals are represented. The symmetric curves are drawn with distribution coefficients for each pair averaged from Table 3. They represent hypothetical ideal solutions (see Mueller, 1960). The ion-exchange reactions and the distribution coefficients are:



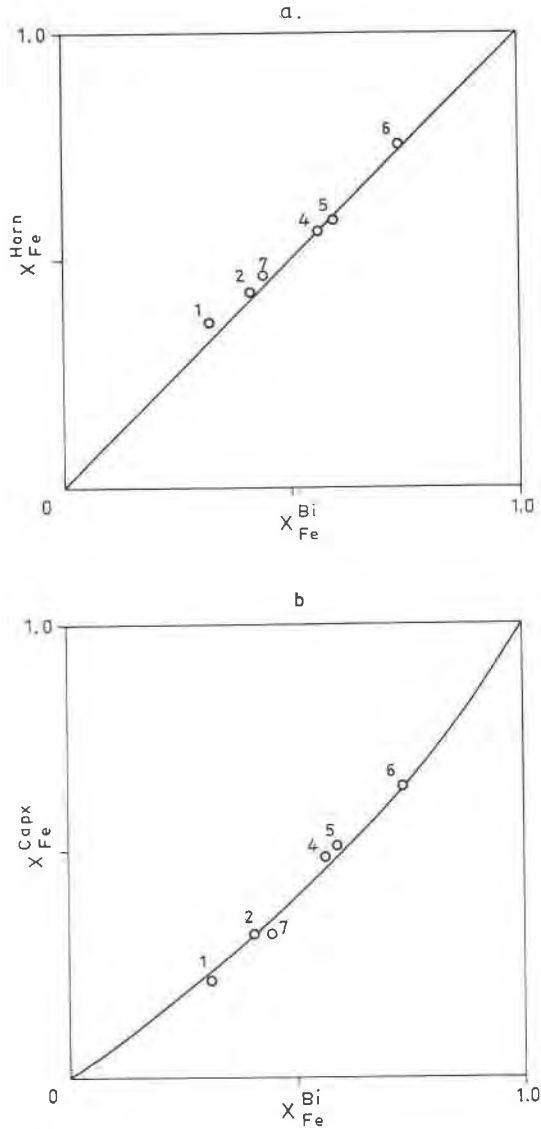


FIG. 4. Distribution of Fe between biotite and hornblende and between biotite and clinopyroxene. $X = Fe/(Fe+Mg)$. The curves are drawn to follow the equations (1) and (2) in (a) and (b) respectively.

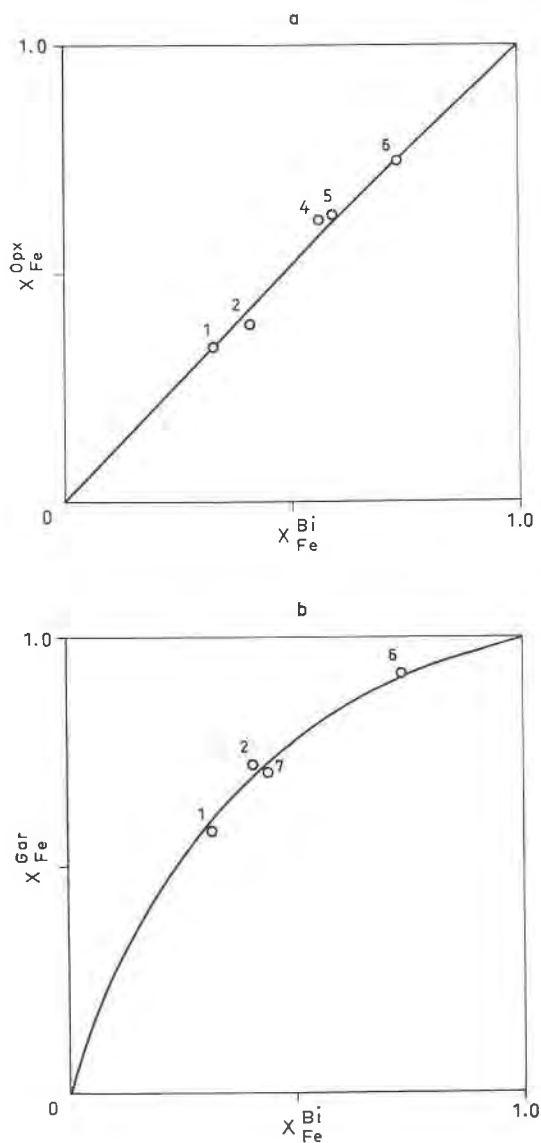
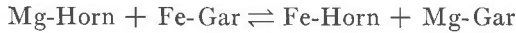
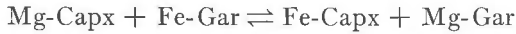


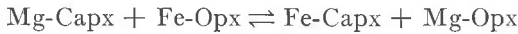
FIG. 5. Distribution of Fe between biotite and orthopyroxene and between biotite and garnet. $X = \text{Fe}/(\text{Fe} + \text{Mg})$. The curves are drawn to follow the equations (3) and (4) in (a) and (b) respectively.



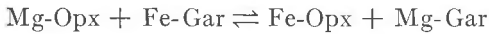
$$\frac{X_{\text{Fe}}^{\text{Horn}}}{1 - X_{\text{Fe}}^{\text{Horn}}} \cdot \frac{1 - X_{\text{Fe}}^{\text{Gar}}}{X_{\text{Fe}}^{\text{Gar}}} = K_{\text{D}(\text{Fe})}^{\text{Horn-Gar}} = 0.33 \quad (7)$$



$$\frac{X_{\text{Fe}}^{\text{Capx}}}{1 - X_{\text{Fe}}^{\text{Capx}}} \cdot \frac{1 - X_{\text{Fe}}^{\text{Gar}}}{X_{\text{Fe}}^{\text{Gar}}} = K_{\text{D}(\text{Fe})}^{\text{Capx-Gar}} = 0.16 \quad (8)$$



$$\frac{X_{\text{Fe}}^{\text{Capx}}}{1 - X_{\text{Fe}}^{\text{Capx}}} \cdot \frac{1 - X_{\text{Fe}}^{\text{Opx}}}{X_{\text{Fe}}^{\text{Opx}}} = K_{\text{D}(\text{Fe})}^{\text{Capx-Opx}} = 0.60 \quad (9)$$



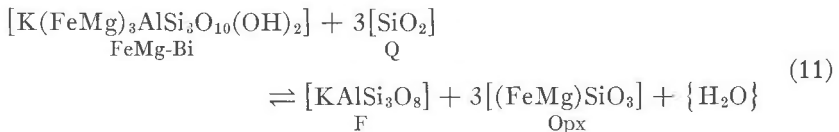
$$\frac{X_{\text{Fe}}^{\text{Opx}}}{1 - X_{\text{Fe}}^{\text{Opx}}} \cdot \frac{1 - X_{\text{Fe}}^{\text{Gar}}}{X_{\text{Fe}}^{\text{Gar}}} = K_{\text{D}(\text{Fe})}^{\text{Opx-Gar}} = 0.25 \quad (10)$$

These distribution relationships are discussed later.

ANALYSIS OF EQUILIBRIUM

The distribution of manganese is orderly and consistent with Nernst's law for the distribution of a dilute component among coexisting phases. This is an expression of a close approach to chemical equilibrium with respect to this component in the rocks. As the elements Si, Al, Ti and Fe^{3+} replace each other in various amounts, the distribution of Al (except in sample 6) may also be regarded as regular. The distribution of other elements needs further discussion.

Titanium. Let us consider a hypothetical system:



As there are five components— $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ (K:Al remains unchanged in the equation), FeO, MgO, SiO_2 and five phases (including the intergranular phase with water), the system is bivariant and at a specified

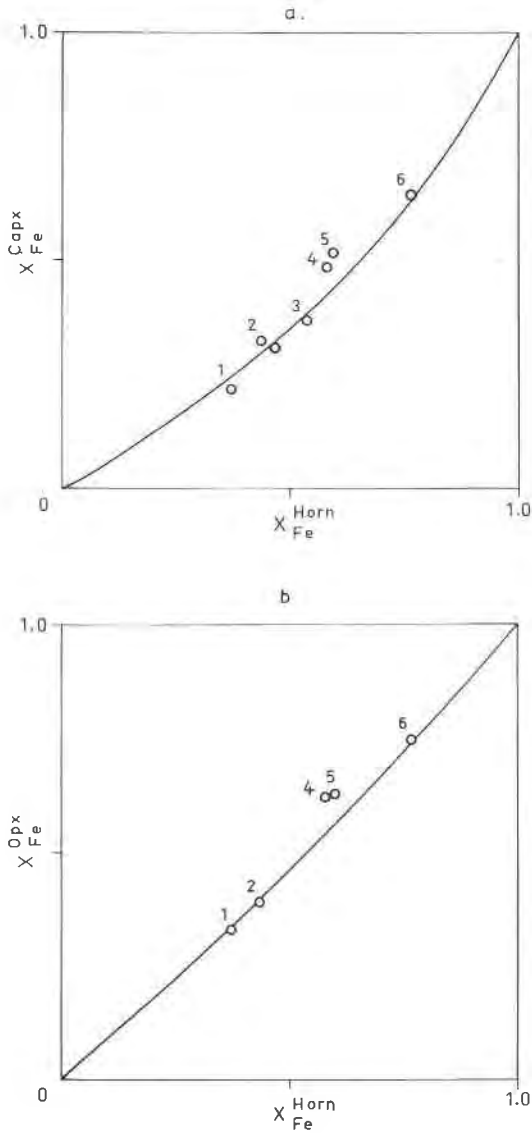


FIG. 6. Distribution of Fe between hornblende and clinopyroxene and between hornblende and orthopyroxene. $X = Fe/(Fe+Mg)$. The curves are drawn to follow the equations (5) and (6) in (a) and (b) respectively.

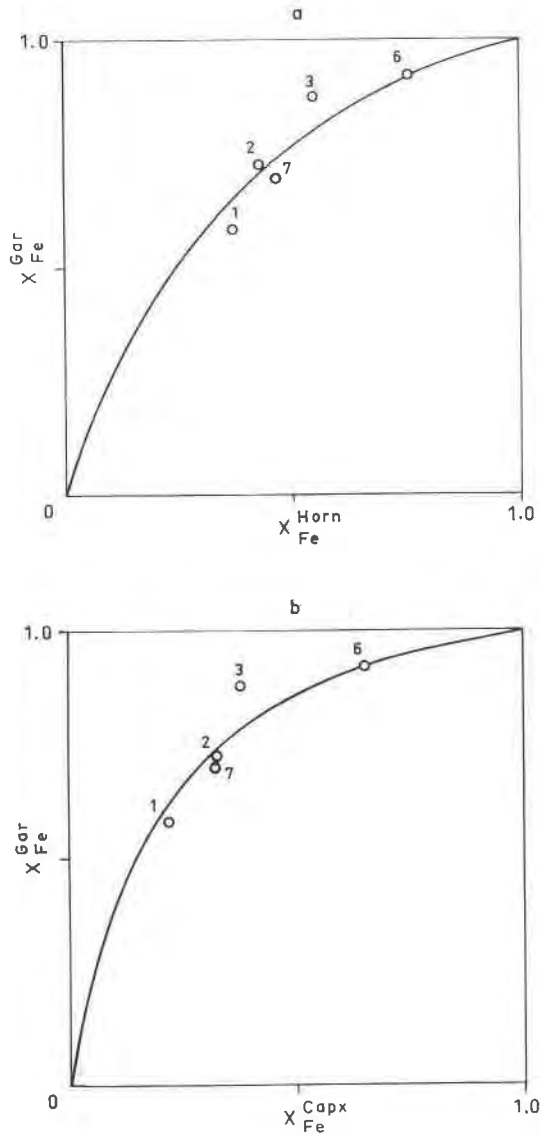


FIG. 7. Distribution of Fe between hornblende and garnet and between clinopyroxene and garnet. $X = \text{Fe}/(\text{Fe} + \text{Mg})$. The curves are drawn to follow the equations (7) and (8) in (a) and (b) respectively.

chemical potential of water and total pressure, the phases could coexist in equilibrium over a range of temperature. The variance in the natural system is probably higher than that of the hypothetical system (11) and this difference may be attributed to the presence of certain other components. These could be Al, Fe³⁺ or Ti. They may vary significantly in biotite. Kretz (1964) attributed the increase in variance in the system biotite-sillimanite-quartz-garnet-orthoclase-water to Ti in biotite. If p , T and chemical potential of water did not vary significantly in the area and provided the mixture of the particular component with FeMg-biotite is close to ideal, the mole fraction of this component might be uniform in the six samples. The variation in Fe³⁺ in biotite cannot be verified here but Ti content of biotite is similarly high and lies in the range of ± 10 percent. If the low value of $X_{\text{Ti}}^{\text{Bi}}$ in sample 6 is due to Al^{IV} in the mineral, the rest of the values could be considered as within the range of analytical error.

The high concentration of Ti in biotite relative to other coexisting minerals is remarkable. Ramberg (1949) mentioned that biotite in high grade metamorphic rocks requires a higher concentration of Ti for stability. Biotites from the rocks of upper amphibolite facies (Kretz, 1964) contain TiO₂ varying between 4.2 to 5.6 percent by weight and a biotite from Madras charnockite (Howie, 1955) contains 4.43 percent. Biotites from low grade metamorphic rocks usually contain less than 3 percent TiO₂ by weight.

Distribution of Ca between plagioclase and garnet. The scattered distribution of Ca between garnet and plagioclase, but a rather orderly distribution between clinopyroxene and plagioclase, suggests that the scattering in the former case may be due to some variable other than composition. Composition of garnets varies significantly in the different grains in sample 3 and 7. However, an approach to chemical equilibrium is apparent. In samples 1, 6 and 8 the compositional differences in the crystals are small. In sample 8, a plagioclase inclusion in garnet and the plagioclase in the rock did not show a variation in the CaO weight percent by more than ± 2 . In sample 7, crystals (a) and (b) (Table 1) do not differ much. Crystal (a) in sample 3 is about a centimeter in diameter but the difference in composition between the centre and the edge is small. It is, therefore, reasonable to consider equilibrium reactions, particularly if it involves the distribution of Ca among the coexisting phases.

Kretz (1964) suggested the importance of pressure in influencing the distribution of Ca between plagioclase and garnet. DeWaard (1965) suggested that increasing pressure gives rise to the garnet-clinopyroxene subfacies, according to the reaction:

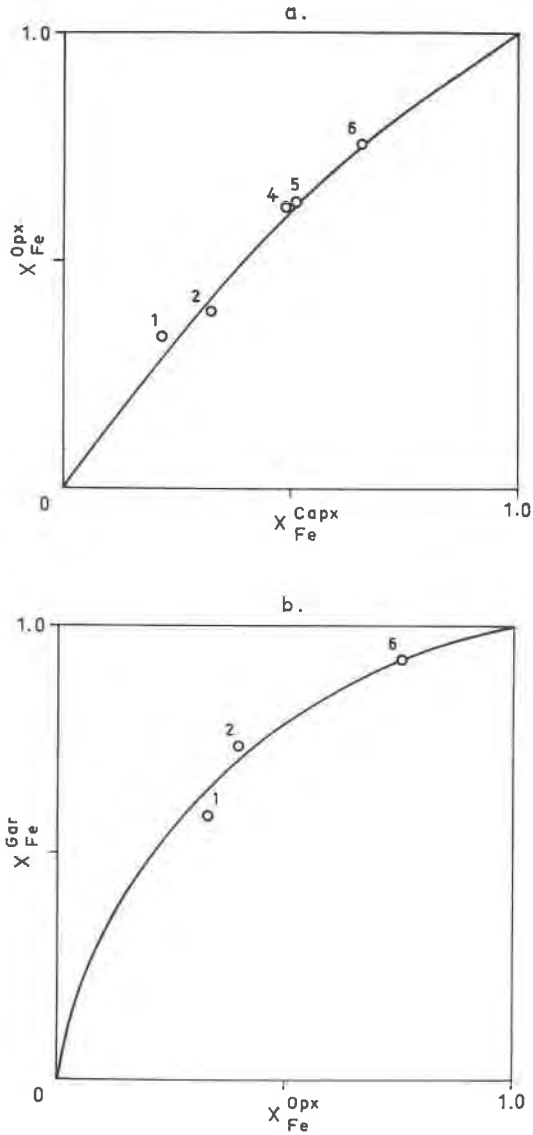
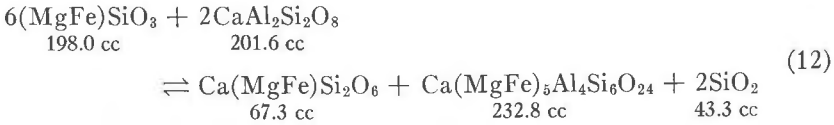
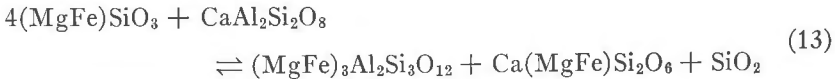


FIG. 8. Distribution of Fe between orthopyroxene and clinopyroxene and between orthopyroxene and garnet. $X = Fe/(Fe+Mg)$. The curves are drawn to follow the equations (9) and (10) in (a) and (b) respectively.

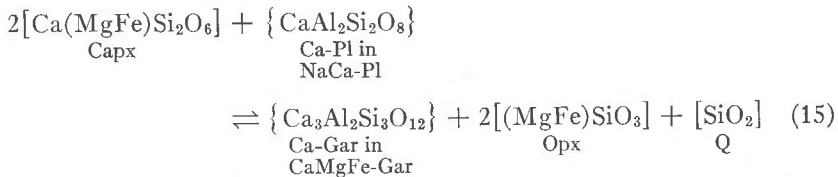


Green and Ringwood (1967) find that with increasing pressure garnet becomes richer in pyrope and suggest the growth of garnet by the following reactions:



These equations are inadequate to show the distribution of Ca between garnet and plagioclase since they either do not contain grossularite or show it as an invariable component in garnet. Plagioclase is the only Ca-bearing phase on the left hand side. This imposes a restriction on the Ca content of garnet on the right hand side in (12) for one Ca atom must go to diopside, which leaves Ca:Al as 1:4 in garnet. Therefore we cannot have more than one Ca per five atoms of (MgFe) in garnet.

One possible reaction representing equilibrium among these phases may be written as:



Quensel (1950) described "large garnets with reaction rims of plagioclase and diopside denoting an incipient charnockitization." In sample 3 such reaction rims may be clearly observed. Quensel also described 'diopside particles' encircled by hypersthene from such rocks.

To discuss equilibrium in (15) thermodynamically, the following simplifications are used: (i) mixing of Mg and Fe in the minerals is not taken into account, (ii) it is assumed that all mixtures are closely ideal (using the ideal molecular model) and (iii) concentration of Ca in clinopyroxene is regarded as more or less invariable. The thermodynamic condition of equilibrium in (15) is

$$\Delta G = 0 = 2G^{\text{Opx}} + G^{\text{Q}} + \mu_{\text{Ca}}^{\text{Gar}} - 2G^{\text{Capx}} - \mu_{\text{Ca}}^{\text{Pl}} \quad (16)$$

Substituting

$$\text{Substituting } \mu_{\text{Ca}}^{\text{Pl}} = G_{\text{Ca}}^{\text{Pl}} + RT \ln X_{\text{Ca}}^{\text{Pl}}$$

and

$$\mu_{\text{Ca}}^{\text{Gar}} = G_{\text{Ca}}^{\text{Gar}} + RT \ln X_{\text{Ca}}^{\text{Gar}}$$

in (16) and transferring, we obtain

$$\frac{X_{\text{Ca}}^{\text{Pl}}}{X_{\text{Ca}}^{\text{Gar}}} = \exp \left[\frac{\Delta G_{(15)}}{RT} \right] \quad (17)$$

Kretz (1964) obtained a similar expression for the distribution of Ca between garnet and plagioclase. The effect of increasing temperature on reaction (15) is not known but by estimate ΔV is negative (-20.27 cc) indicating that with increasing pressure the ratio $X_{\text{Ca}}^{\text{Pl}}/X_{\text{Ca}}^{\text{Gar}}$ must decrease. The ratios of $X_{\text{Ca}}^{\text{Pl}}/X_{\text{Ca}}^{\text{Gar}}$ (Table 4) for the samples of Getterön (0.61–0.82) are distinctly different from those of Träslövsläge (1.10–1.80). This may indicate a higher p for the assemblage from Getterön.

It was assumed that all the mixtures are ideal. It may be that grossularite does not mix ideally with pyrope and almandine in garnet but the mixture of anorthite and albite is close to ideal. An increasing concentration of Ca in the rock may therefore be accompanied by an increasing concentration of anorthite in plagioclase but not of grossularite in garnet. This could be the case in samples 1, 2 and 7, where anorthite is high but not grossularite. In samples 6 and 8 both anorthite and grossularite are low. However, in sample 3 both anorthite and grossularite are high, which supports the inferences in the previous sections. In order to be certain that the composition of garnet as determined by Geoscan is correct, parts of garnet crystals taken out from sample 3 were mixed and

TABLE 4. DISTRIBUTION OF CALCIUM BETWEEN GARNET AND PLAGIOCLASE

Ref. No.	$X_{\text{Ca}}^{\text{Pl}}/X_{\text{Ca}}^{\text{Gar}}$	Locality
1	1.80	Träslövsläge
2	1.10	Träslövsläge
7	1.50	Träslövsläge
3	0.61	Getterön
6	0.82	Getterön
8	0.78	Getterön

Sample 8: $X_{\text{Ca}}^{\text{Pl}}=0.171$, $X_{\text{Ca}}^{\text{Gar}}=0.217$. For sample 3 an average value of Ca in garnet (Table 1) is used.

the cell constant was determined on such a powder. The cell constant is 11.66 Å. In figure 1 (Winchell, 1958) a straight line drawn with 11.66 Å cuts the 'Alm-Gro' base of the triangle at about Alm₆₀Gro₄₀ and if this is to be modified by 10 percent pyrope, we have a minimum of about 36 percent grossularite in garnet. If chemical equilibrium was closely approached with respect to (15) in some rocks (samples 1 and 6) the probable difference in pressure between the two localities may be estimated approximately with the help of the equation:

$$\frac{\partial \ln K}{\partial P} = \frac{\Delta V}{RT}$$

In the present case for K we may use X_{Ca}^{Pl}/X_{Ca}^{Gar} with ΔV for the equation (15). It is estimated that a difference of about 4 kilobars reduces X_{Ca}^{Pl}/X_{Ca}^{Gar} from 1.8 to 0.85. These values are comparable to the values found for the two localities.

This estimate of pressure difference is based on the equilibrium constants obtained through certain simplification and therefore the estimated value may be significantly different from a real value. A large difference of pressure in the formation of the rocks in the two localities separated by less than ten kilometers cannot possibly be accounted for by simple lithostatic pressure. To explain similar discrepancy elsewhere, Clark (1961) and Rutland (1965) discussed tectonic overpressures. Much more work is required to understand this aspect of metamorphism and the question, whether tectonic overpressures are possible or there is some other chemical explanation, must be left open.

The absence of garnet in samples 4 and 5 is probably due to a lower concentration of both Al and Ca as reflected in the compositions of hornblende and plagioclase. In this respect the activity of these elements in sample 6 appears to be the critical lower limit where garnet could form at such p - T .

Iron and magnesium. Saxena (1968) discussed the distribution among biotite, hornblende and garnet. Calculation of mole fraction of Fe in biotite or hornblende as Fe/Σ (octahedrally coordinated ions) was suggested to facilitate the recognition of irregularities in K_D due to the variation of Ca or Mn in the coexisting garnet. As the pyroxenes may be nearly quasi-binary ideal solutions, the mole fraction of Fe is calculated here as $Fe/(Fe+Mg)$. A similar mole fraction is also used for other coexisting minerals. The variations in the concentration of other octahedral or tetrahedral elements influencing the binary mixing in hornblende or biotite could be correlated with K_D values.

The approach to ideal mixing for Fe and Mg in the minerals is shown

by the disposition of the distribution points along the symmetric curves (Figs. 4 to 8). $K_{D(\text{Fe})}$ values in Table 3 are not so uniform as they should be for ideal mixtures. For the maximum possible error ($\pm 5\%$) in the present data, $K_{D(\text{Fe})}^{\text{Bi-Horn}}$ for sample 1 may vary from 0.7 to 1.0. However, for comparison of these analyses with each other, the analytical error would be much smaller and the irregularities in $K_{D(\text{Fe})}$ might be due to one or more of the causes discussed below.

Some irregularities could be due to the variations in Fe^{3+} influencing the value of total Fe in the analysis. The inverse variation of the number of 8-coordinated ions with the number of Al^{3+} ion in garnet formulae indicates that there may be a variable amount of Fe^{3+} . Similarly variations in the concentration of Fe^{3+} are probable in hornblende, biotite and clinopyroxene.

Figure 9 shows various possible correlations of $K_{D(\text{Fe})}$ with the concentration of a third element in one or both of the minerals (see Kretz, 1959, 1960). The correlation of Al^{IV} in biotite or in hornblende with $K_{D(\text{Fe})}$ can be noted in some cases. As Al^{IV} varies significantly both in biotite and hornblende, it is more useful to investigate the correlation of $K_{D(\text{Al})}^{\text{Bi-Horn}}$ ($= X_{\text{Al}^{\text{IV}}}^{\text{Bi}}/X_{\text{Al}^{\text{VI}}}^{\text{Horn}}$) with $K_{D(\text{Fe})}^{\text{Bi-Horn}}$. This relation is quite regular. These correlations are significant as they indicate a relation between the concentration of Al^{IV} and Fe/Mg ratio in a silicate (Ramberg, 1952).

Concentration of Mn varies somewhat in these garnets. Concentration of Mg is small and, therefore, even small variations of Mn may affect $K_{D(\text{Fe})}$ involving garnets significantly (Saxena, 1968). In Figure 9 the correlation between $K_{D(\text{Fe})}^{\text{Capx-Gar}}$ and $X_{\text{Mn}}^{\text{Gar}}$ (number of Mn ion in the formula) is regular. Such correlations between $X_{\text{Mn}}^{\text{Gar}}$ and $K_{D(\text{Fe})}^{\text{Bi-Gar}}$ or $K_{D(\text{Fe})}^{\text{Horn-Gar}}$ are more complex due to other compositional variations in biotite and hornblende. However the relation of $K_{D(\text{Fe})}^{\text{Horn-Gar}}$ with $X_{\text{Mn}}^{\text{Gar}}$ is orderly (Fig. 9).

The values of ΔV for the ion-exchange reactions (not involving garnet) are small and the pressure differences as suggested by the differences of $X_{\text{Ca}}^{\text{Pl}}/X_{\text{Ca}}^{\text{Gar}}$ may not affect $K_{D(\text{Fe})}$ significantly. The values of $K_{D(\text{Fe})}$ for the ion-exchange reactions (4, 7 8 and 10) where garnet end members are involved might be affected particularly if the difference in pressure was as large as 4 kilobars. $K_{D(\text{Fe})}$ for Bi-Gar, Horn-Gar, Capx-Gar and Opx-Gar are consistently high in sample 1 (Träslövsläge) and low in sample 6 (Getterön). These differences, however, could well be due to other compositional variations in one or both the minerals as shown in Figure 9.

Some irregularities in $K_{D(\text{Fe})}$ may be due to lack of complete equilibrium for the exchange reactions considered before. In sample 2 clinopyroxene is partly altered to amphibole. This sample shows a signifi-

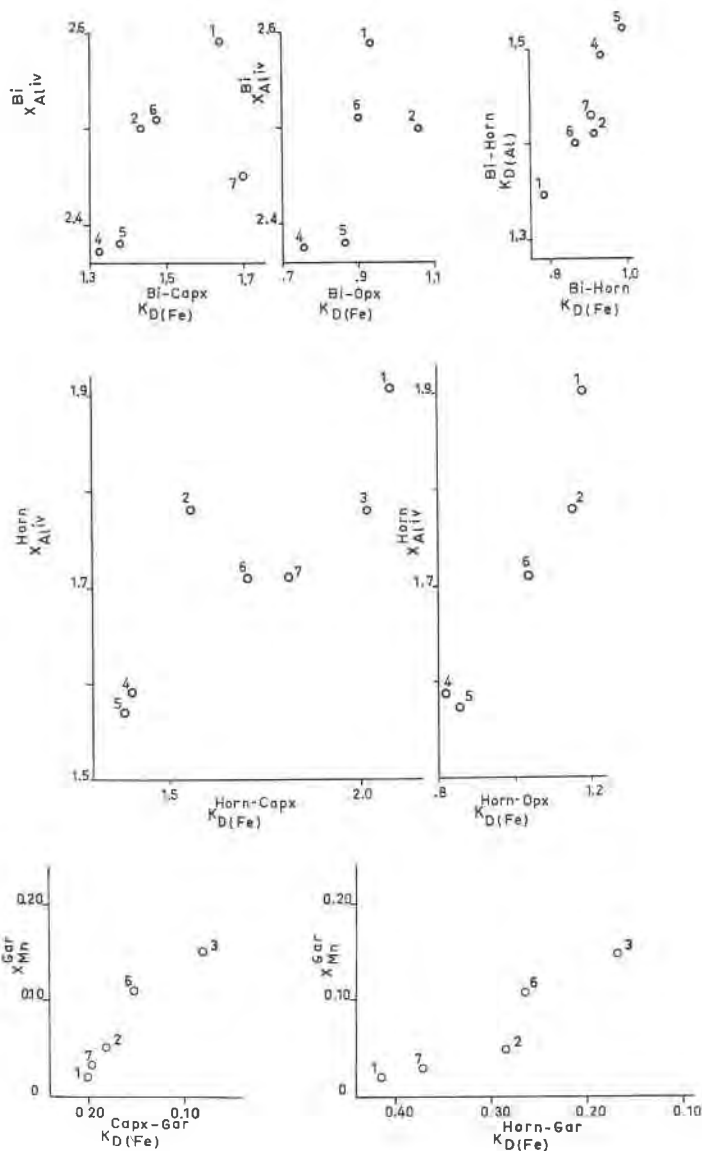
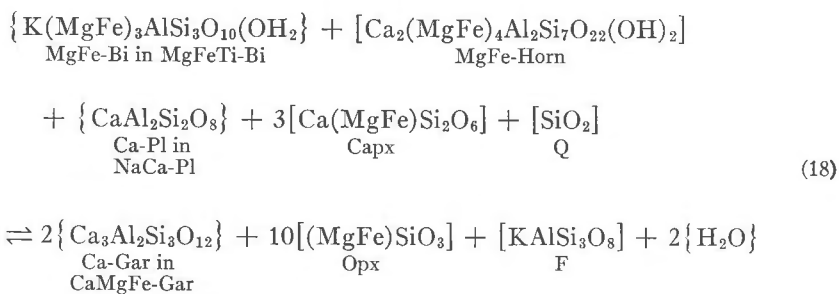


FIG. 9. Variation of $K_{D(Fe)}$ with the variations in the concentration of a third ion in one or both the minerals. X represents number of ion in the mineral. $K_{D(Al)}^{Bi-Horn} = X_{Aliv}^{Bi} / X_{Aliv}^{Horn}$. Some correlations are distinct e.g. between X_{Mn}^{Gar} and $K_{D(Fe)}^{Capx-Gar}$ and between $K_{D(Fe)}^{Bi-Horn}$ and $K_{D(Al)}^{Bi-Horn}$. Others are less distinct probably due to more complex solid solutions in hornblende and biotite.

cantly different $K_{D(\text{Fe})}^{\text{Capx-Opx}}$ which is otherwise reasonably similar in the remaining samples. The variation in the concentration of a third component does not significantly change $K_{D(\text{Fe})}^{\text{Capx-Opx}}$. The similarities in these values demonstrate a close approach to chemical equilibrium (except sample 2) with respect to the distribution of Fe and Mg.

SUMMARY AND CONCLUSIONS

It is possible to combine equations (11) and (15) and rewrite the "charnockitization" reaction by introducing hornblende on the left hand side as below:



The system (18) contains 9 components (including TiO_2 and Na_2O) and 9 phases. It is, therefore, bivariant. It appears that the encountered variations in the concentration of components other than that of Ca in garnet and in plagioclase do not influence equilibrium in (18) significantly. Temperature and chemical potential of water were probably uniform in the area and $X_{\text{Ca}}^{\text{Pl}}/X_{\text{Ca}}^{\text{Gar}}$ was related exponentially to total pressure.

The distribution relationships and the correlations of various distribution coefficients with either pressure or compositional variations are consistent with the possibility of a close approach to chemical equilibrium in these rocks. However the degree to which this equilibrium was approached might be somewhat different in different places. For example the variation in the concentration of Ca in garnet crystals within sample 3 indicate a lack of chemical equilibrium which is not the case with other samples (6 and 8) from the same locality.

It is probable that other intensive variables including temperature were more or less similar in the two localities—Getterön and Träslövsläge but pressure was higher in Getterön. The difference in pressure as indicated by chemical considerations cannot be due to simple lithostatic pressure and whether tectonic overpressures are possible or there is some other chemical explanation remains to be understood.

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REFERENCES

- CLARK, S. P. JR. (1961) A redetermination of equilibrium relations between kyanite and sillimanite. *Amer. J. Sci.*, **259**, 641-650.
- EVANS, B. W., AND C. V. GUIDOTTI (1966) The sillimanite-potash feldspar isograd in western Maine, U.S.A. *Contr. Mineral. Petrology*, **12**, 25-62.
- FYFE, W. S., F. J. TURNER AND J. VERHOOGEN (1958) Metamorphic reactions and metamorphic facies. *Geol. Soc. Amer. Mem.* **73**.
- GREEN, D. H., AND A. E. RINGWOOD (1967) An experimental investigation of the gabbro to eclogite transformation and its petrologic applications. *Geochim. Cosmochim. Acta*, **31**, 767-834.
- HOWIE, R. A. (1955) The geochemistry of the charnockite series of Madras, India. *Trans. Roy. Soc. Edinburgh*, **62**, 725-768.
- KRETZ, R. (1959) Chemical study of garnet, biotite and hornblende from gneisses of south-western Quebec, with emphasis on distribution of elements in coexisting minerals. *J. Geol.*, **67**, 371-402.
- (1960) The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles, and biotites in skarns. *Geochim. Cosmochim. Acta*, **20**, 161-191.
- (1964) Analysis of equilibrium in garnet-biotite-sillimanite gneisses from Quebec. *J. Petrology*, **5**, 1-20.
- MUELLER, R. F. (1960) Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron formation. *Amer. J. Sci.*, **258**, 449-493.
- QUENSEL, P. (1950) The Charnockite series of Varberg district on the south-western coast of Sweden. *Arkiv Mineral. Geol.*, **1**, 227-332.
- RAMBERG, H. (1948) Titanic iron ore formed by dissociation of silicates in granulite facies. *Econ. Geol.*, **43**, 553-570.
- (1952) Chemical bonds and the distribution of cations in silicates. *J. Geol.*, **60**, 331-355.
- RUTLAND, R. W. R. (1965) Tectonic overpressures. In *Controls of metamorphism*. (Ed. Pitcher, W. S. and Flinn, G. W.), Edinburgh (Oliver & Boyd), 119-39.
- SAXENA, S. K. (1966) Distribution of elements between coexisting muscovite and biotite and crystal chemical role of titanium in micas. *Neues Jahrb. Mineral. Abhand.*, **105**, 1-17.
- (1967) Intracrystalline chemical variations in certain calcic pyroxenes and biotites. *Neues Jahrb. Mineral. Abhand.*, **107**, 299-316.
- (1968) Distribution of elements between coexisting minerals and nature of solid solution in garnet. *Amer. Mineral.*, **53**, 994-1014.
- SUBRAMANIAM, A. P. (1960) Petrology of the Charnockite Suite of rocks from the type area around St. Thomas Mount and Pallavaram near Madras city, India. *Int. Geol. Congr. Rep. 21st Session Norden*, **13**, 394-403.
- WAARD, D. DE. (1965) The occurrence of garnet in the granulite facies terrane of the Adirondack Highlands. *J. Petrology*, **6**, 165-191.
- WINCHELL, H. (1958) The composition and physical properties of garnets. *Amer. Mineral.*, **43**, 595-600.