

DISTRIBUTION OF IRON AND MAGNESIUM BETWEEN  
COEXISTING GARNET AND CLINOPYROXENE IN  
ROCKS OF VARYING METAMORPHIC GRADE

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

ABSTRACT

The distribution of Fe and Mg between coexisting garnet (with little Mn) and clinopyroxene in rocks of glaucophane schist facies, granulite facies and eclogites is studied. The average distribution coefficient (Fe-Mg) in each of the following cases—glaucophane schist facies, granulite facies and in certain eclogites is distinctly different. This difference could not be correlated with variation in the concentration of Ca in garnet and is probably due to changing  $p$  and  $T$ . The variation in the distribution coefficient in several eclogitic rocks, however, is difficult to interpret at present.

INTRODUCTION

In many ferrous iron-magnesium silicates such as pyroxenes, there is virtually complete substitution of Mg by  $\text{Fe}^{2+}$ . As the two ions are closely similar in their properties, they tend to form a nearly ideal solution in some of the silicates. In garnets the nature of their solution is influenced by the presence of Mn and Ca which also share the eight-coordinated sites. A previous study (Saxena, 1968*a*) indicates that in garnets (with little Mn) the role of Ca in high-grade metamorphic rocks may be mainly one of dilution, *i.e.*, Mg and Fe end members of garnet form a nearly ideal solution and the variation in the concentration of Ca does not significantly affect their relationship. On theoretical grounds (Saxena, 1968*a*), it is probable that in low-grade rocks the binary solution is not ideal, but the deviations may not be large. If both garnets (with little Mn) and the coexisting clinopyroxene are nearly ideal binary solutions of  $\text{Fe}^{2+}$  and Mg, the distribution coefficient for such pairs may be useful in recognizing the metamorphic grade of the rocks in which they occur.

The coefficient for the distribution of Mg and Fe is defined as

$$K_{D(\text{Fe})}^{\text{Cpx-Gar}} = \frac{X_{\text{Fe}}^{\text{Cpx}}}{1 - X_{\text{Fe}}^{\text{Cpx}}} \cdot \frac{1 - X_{\text{Fe}}^{\text{Gar}}}{X_{\text{Fe}}^{\text{Gar}}}$$

where  $X_{\text{Fe}}$  is the mole fraction  $\text{Fe}/(\text{Fe} + \text{Mg})$  and *Cpx* and *Gar* stand for clinopyroxene and garnet respectively. If Ca influences the ideal solution (for example in high-grade rocks, Ca may replace little more of Mg than Fe, see Saxena, 1968*a*),  $K_{D(\text{Fe})}$  might vary as a function of its concentration in rocks of the same metamorphic grade. As rocks of a single facies form within a  $p$ - $T$  field, constant  $K_D$  values cannot be expected even if both the minerals are binary ideal. However  $K_D$  values

for rocks of different metamorphic facies might form distinct groups and the mean of  $K_D$  values for rocks of one facies might differ distinctly from the mean of  $K_D$  values for rocks of another facies.

Analyses for coexisting pairs of garnet (with little Mn) and clinopyroxene are taken from the literature (Table 1). Rocks where a certain estimate of  $p$  and  $T$  can be made are preferred. The data from rocks of the glaucophane schist facies are limited to a single locality. The results of this article, therefore, would require a further confirmation by more data on coexisting garnet and clinopyroxene from elsewhere. Some eclogitic rocks of uncertain origin are included for comparison.

### RESULTS AND DISCUSSIONS

*Distribution of Fe and Mg.* Figure 1 shows the distribution of Fe and Mg between coexisting clinopyroxene and garnet. The advantage of plotting  $X_{Fe}/(1-X_{Fe})$  instead of  $X_{Fe}$  is that in such diagrams the symmetric curves for ideal solutions are represented by straight lines. Scatter on such plots is easily noted and the equation to the best fit straight line can be obtained statistically for rocks of one metamorphic grade. The best fit lines follow the relations:

$$\frac{X_{Fe}^{Cpx}}{1 - X_{Fe}^{Cpx}} \cdot \frac{1 - X_{Fe}^{Gar}}{X_{Fe}^{Gar}} = K_{D(Fe)}^{Cpx-Gar} = 0.044 \text{ (glaucophane schist facies)}$$

$$= 0.138 \text{ (granulite facies)}$$

*Variation of  $K_D$  as a function of chemical composition.* The garnets of the granulite facies rocks used here contain little Mn but even small variations in the concentration of Mn may cause a change in  $K_{D(Fe)}$ , particularly if the concentration of Mg is small (Saxena, 1968b). This is demonstrated in Figure 2. A large part of the scattering in these distribution points, therefore, may be attributed to variation in the concentration of Mn in garnets.

Garnets range in CaO weight percent from 6.4 to 13.6. The variations in  $K_{D(Fe)}$  within the granulite facies do not appear to be related to these changes. In the samples of glaucophane schist facies, garnets range in CaO weight percent from 9.5 to 13.7.  $K_{D(Fe)}$  for the granulite facies is distinctly different from  $K_{D(Fe)}$  for the glaucophane schist facies. The range of concentration of Ca in garnets in the two cases is similar and cannot account for the change of  $K_{D(Fe)}$  from one to the other. The difference in  $p$ - $T$ , on the other hand, is certainly large and the change in  $K_{D(Fe)}$  is more likely due to a change in the metamorphic grade.

*Relative influence of  $p$  and  $T$  on  $K_D$ .* For the exchange equilibrium

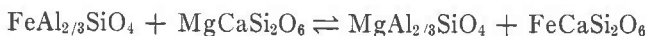


TABLE 1. MOLE FRACTIONS (Fe/(Fe+Mg)) AND DISTRIBUTION COEFFICIENTS FOR COEXISTING CLINOPYROXENE AND GARNET IN ROCKS OF DIFFERENT METAMORPHIC GRADE

No.	$X_{Fe}^{Cpx}$	$X_{Fe}^{Grt}$	$K_D^{Cpx-Grt}$	Rock no.	Locality	Reference	Estimate of pressure and temperature
1	0.211	0.834	0.053	113-RGC-58	California	Coleman <i>et al.</i> (1965)	Glauconite schist facies, Essen, Fyfe and Turner (1965) estimate 5-10 kbar and 150-300°C.  Granulite facies, 600-800°C and 4-8 kb, estimated on the basis of Fyfe and Turner (1966). There may be a difference of as much as 4 kbar of crystallization in the Varberg rocks (Saxena, 1968b). Samples 7, 8 and 11 representing lower $p$ and samples 9 and 10 higher.  1300°C } For clinopyroxene, estimate of Davis and Boyd 1000°C } (1966) at 30 kb. 1000°C } Uncertain $p$ and $T$ . Most of the rocks occur in the granulite facies terrain.
2	0.185	0.821	0.049	100-RGC-58	California	Coleman <i>et al.</i> (1965)	
3	0.183	0.848	0.040	207-RGC-59	California	Coleman <i>et al.</i> (1965)	
4	0.286	0.809	0.045	62-RGC-58	California	Coleman <i>et al.</i> (1965)	
5	0.173	0.862	0.033	102-RGC-58	California	Coleman <i>et al.</i> (1965)	
6	0.215	0.860	0.044	36-RGC-62	California	Coleman <i>et al.</i> (1965)	
7	0.219	0.583	0.200	1	Varberg	Saxena (1968b)	
8	0.324	0.726	0.180	2	Varberg	Saxena (1968b)	
9	0.368	0.876	0.082	3	Varberg	Saxena (1968b)	
10	0.648	0.922	0.156	6	Varberg	Saxena (1968b)	
11	0.316	0.700	0.198	7	Varberg	Saxena (1968b)	
12	0.353	0.796	0.139	3/66	Varberg	Saxena (unpub. i. h. e. d.)	
13	0.661	0.927	0.153	V <sub>5</sub>	Varberg	Saxena (1968b)	
14	0.407	0.805	0.166	Ch-199	India	Subramanian (1962)	
15	0.424	0.837	0.143	13	Adirondack	Buddington (1952)	
16	0.593	0.922	0.123	14	Adirondack	Buddington (1952)	
17	0.074	1.108	0.666	E <sub>11</sub>	South Africa	Nixon <i>et al.</i> (1963)	
18	0.052	1.186	0.239	G <sub>12</sub>	South Africa	Nixon <i>et al.</i> (1963)	
19	0.042	1.164	0.224	A <sub>3</sub>	South Africa	O'Hara and Mercy (1963)	
20	0.115	0.447	0.160	E <sub>4</sub>	South Africa	Nixon <i>et al.</i> (1963)	
21	0.150	0.334	0.380	E <sub>10</sub>	Scotland	Nixon <i>et al.</i> (1963)	
22	0.202	0.699	0.107	35090	Yoder and Tilley (1962)	Yoder and Tilley (1962)	
23	0.274	0.722	0.146	35083	Yoder and Tilley (1962)	Yoder and Tilley (1962)	
24	0.053	0.415	0.079	958	Germany	Yoder and Tilley (1962)	
25	0.051	0.372	0.091	"weiss"	Germany	Yoder and Tilley (1962)	
26	0.129	0.240	0.466	66118	Oahu	Yoder and Tilley (1962)	
27	0.088	0.315	0.209	N 23	Tafjord, Norway	O'Hara and Mercy (1963)	
28	0.052	0.245	0.169	N 69	Almklovdalen, Norway	O'Hara and Mercy (1963)	
29	0.051	0.257	0.156	N 70	Almklovdalen, Norway	O'Hara and Mercy (1963)	
30	0.049	0.267	0.140	N 71	Almklovdalen, Norway	O'Hara and Mercy (1963)	
31	0.097	0.307	0.247	N 26	Tafjord, Norway	O'Hara and Mercy (1963)	
32	0.060	0.201	0.244	A 2	Switzerland	O'Hara and Mercy (1963)	

Samples 7 to 13—total Fe, others—Fe<sup>2+</sup>. The chemical data from literature are for the wet chemical analyses. Although no reference to zoned garnets is mentioned, the possibility cannot be ruled out. In Varberg samples 7, 8, 10 and 13 the garnets do not show significant zoning or inhomogeneity. In samples 9 and 11, the garnets are inhomogeneous and  $K_D$  may vary by 10 percent.

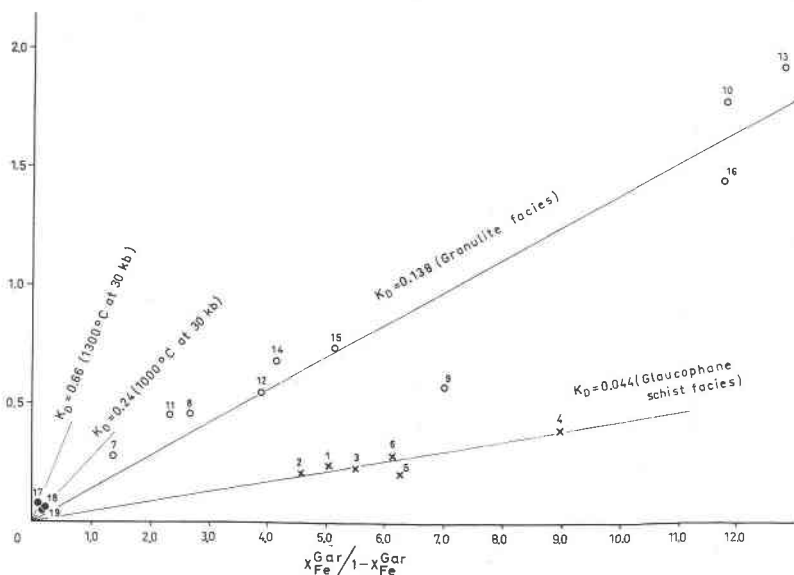


FIG. 1. Distribution of iron between coexisting garnet and clinopyroxene in rocks of varying metamorphic grade. Cross—glaucophane schist facies, open circles—granulite facies, solid circles—eclogite facies (according to Davis and Boyd, 1966, the clinopyroxenes in samples 17, 18 and 19 may have crystallized at 1300°C, 1000°C and 1000°C respectively at 30 kbars). The straight lines for glaucophane schist facies and granulite facies are  $X = 0.009 + 0.044 Y$  and  $X = 0.061 + 0.138 Y$  respectively. The difference in the distribution coefficient  $K_{D(Fe)}$  is mainly due to the variation in  $p$  and  $T$ .

$\Delta V$  is 3.12 cc (molar volumes from a 1962 report later published by Robie, Beardsley and Bethke, 1967;  $FeCaSi_2O_6$  value from Kretz, 1963). Calculations by using the equation

$$\left( \frac{\partial \ln K_D}{\partial p} \right) = \frac{\Delta V}{RT}$$

for 1000°C and  $\Delta p$  (5000–15) atmospheres show that  $K_D$  may change by a factor of 0.85.  $K_{D(Fe)}$  is, therefore, not only a function of  $T$  alone but also of  $p$ .

In Varberg rocks Saxena (1968*b*) estimated on the basis of the compositions of coexisting garnet and plagioclase that rocks (9 and 10) from one locality may differ from the rocks (7, 8 and 11) in another locality in the  $p$  (probably tectonic) of formation by 4 kbars. The scatter in these samples in Figure 1 may be due to the differences in  $p$ , samples 9 and 10 representing higher  $p$  than samples 7, 8 and 11. However it is not possible to decide if these differences in the  $K_{D(Fe)}$  in Varberg rocks are due to changes of pressure or changes in the con-

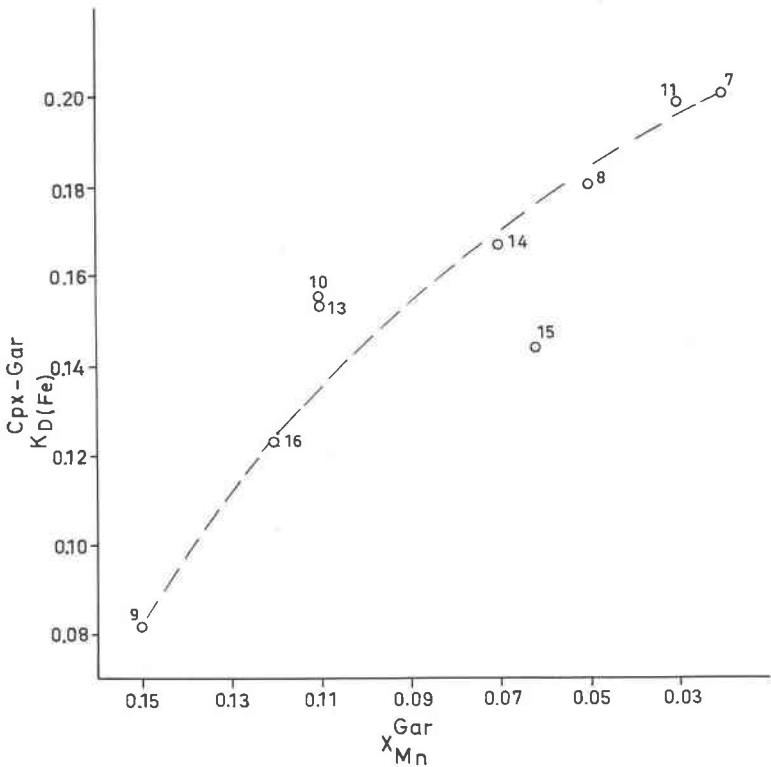


FIG. 2. Scattering of distribution points of the granulite facies as related to the concentration of Mn (number of ion in the formula) in garnet. As the concentration of Mn increases,  $K_{D(Fe)}$  decreases. A varying concentration of Mn, therefore, affects the concentration of Mg (which is small) more than the concentration of Fe in garnet. The partial analysis of garnet in sample 12 does not contain Mn.

centration of Mn in garnet (Fig. 2). The latter varies with bulk chemical composition but may also vary with changes of pressure.

Estimates of  $p$  and  $T$  by Essene, Fyfe and Turner (1965) for the formation of Franciscan glaucophane schist facies rocks (samples 1 to 6) are 5–10 kbar and 150–300°C. A reasonable estimate for granulite facies rocks could be 600–800°C and 4–8 kbar. There could not be any significant variation in  $p$  between Varberg rocks and rocks represented by samples 1 to 6. The difference of  $T$  is considerable and the large change in  $K_{D(Fe)}$  from one metamorphic facies to the other should be attributed to it.

Three samples of eclogites (17, 18 and 19) are included in Figure 1. Estimates of the possible  $p$  and  $T$  of crystallization of pyroxene in these

samples were made by Davis and Boyd (1966). These estimates suggest that for 1000°C and 30 kbar (samples 18 and 19)  $K_{D(\text{Fe})}$  is 0.24 and for 1300°C and 30 kbar (sample 17)  $K_{D(\text{Fe})}$  is 0.66. With increase in temperature  $K_{D(\text{Fe})}$  approaches unity. For the ion-exchange equilibrium (Fe-Mg) between clinopyroxene and garnet, the effect of increasing pressure is opposite to that of temperature. If samples 18 and 19 formed at rather high pressure (compared to that of granulite facies) the comparatively small difference between  $K_{D(\text{Fe})}$  for samples 18 and 19 (0.24) and for sample 7 (0.20) can be explained.

$K_{D(\text{Fe})}$  in rocks of uncertain origin. Eclogitic rocks may form under a variety of  $p$ - $T$  conditions. They usually contain clinopyroxene and garnet. The distribution coefficient could be useful in indicating the probable  $p$ - $T$  of crystallization. It is not intended to investigate the origin of different occurrences of eclogitic rocks and, therefore, only few such samples are included in Table 1. The samples contain garnet with less than one percent MnO and with CaO around five percent by weight. These could be classified according to  $K_{D(\text{Fe})}$  and the  $p$ - $T$  may be inferred from Figure 1 approximately: (1) samples 21 and 26 ( $K_{D(\text{Fe})}$  = 0.38 to 0.46); (2) samples 27, 31 and 32 ( $K_{D(\text{Fe})}$  = 0.21 to 0.25); (3) samples 20, 23, 28, 29 and 30 ( $K_{D(\text{Fe})}$  = 0.14 to 0.17); (4) samples 22, 24 and 25 ( $K_{D(\text{Fe})}$  = 0.08 to 0.10). Samples 17 and 20 both from Basutoland show very different  $K_{D(\text{Fe})}$  and the suggested difference in  $p$  and  $T$  on this basis is difficult to understand. Some other evidences are desirable to interpret the variation of  $K_{D(\text{Fe})}$  in these rocks of uncertain origin.

Some of the rocks considered here were also discussed before (Saxena, 1968a, Table 8). It was suggested that in an isochemical rock series, with increasing metamorphism Ca may be driven out of the garnet structure and Mg incorporated. Therefore we may find an approximate correlation between  $K_{D(\text{Fe})}^{\text{Cpx-Gar}}$  and Ca:Mg in the rocks of varying metamorphic grade. Note that changes of Ca:Mg in the bulk composition at constant  $p$  and  $T$  do not affect  $K_{D(\text{Fe})}$  significantly particularly in high grade metamorphic rocks.

#### SUMMARY

In certain rocks of glaucophane schist facies and granulite facies, the distribution of Fe and Mg between coexisting garnet (with little Mn) and clinopyroxene is consistent with an approximate binary ideal solution model of both the minerals. The average distribution coefficients for the glaucophane schist facies and granulite facies are 0.044 and 0.138 respectively. Departure from the binary model in garnet is expected with variations of Ca and Mn. No significant effect of a variable concentration of Ca in garnet on  $K_{D(\text{Fe})}$  could be found in the present

case. In the rocks of the granulite facies, however, even a small variation in the concentration of Mn in garnets caused significant change in  $K_{D(\text{Fe})}$ . The large variation in  $K_{D(\text{Fe})}$  for the rocks considered here may be mainly due to a variation in the  $p$  and  $T$  of crystallization. The chemical data on glaucophane schist facies from other areas are required to confirm the above conclusion.

## ACKNOWLEDGMENTS

Thanks are due to Prof. Hans Ramberg for valuable discussions, to Dr. Ralph Kretz for suggesting improvements, to Mrs. M. Dahl for the analytical work on Geoscan and to the Natural Science Research Council (Grant no. 2392-17) and Malmfonden (Grant no. 87) Sweden for financially supporting the work on Geoscan.

## REFERENCES

- BUDDINGTON, A. F. (1952) Chemical petrology of some metamorphosed Adirondack gabbroic, syenitic and quartz syenitic rocks. *Amer. J. Sci.* **Bowen Vol.**, 37-84.
- COLEMAN, R. G., D. E. LEE, L. B. BEATTY, AND W. W. BRANNOCK (1965) Eclogites and eclogites: their differences and similarities. *Geol. Soc. Amer. Bull.*, **76**, 483-508.
- DAVIS, B. T. C., AND F. R. BOYD (1966) The join  $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$  at 30 kilobars pressure and its application to pyroxenes from Kimberlites. *J. Geophys. Res.*, **71**, 3567-3576.
- KRETZ, R. (1963) Distribution of magnesium and iron between orthopyroxene and calcic pyroxene in natural mineral assemblage. *J. Geol.*, **71**, 773-785.
- NIXON, P. H., O. VON KNORRING, AND J. M. ROOKE (1963) Kimberlites and associated inclusions of Basutoland: A mineralogical and geochemical study. *Amer. Mineral.*, **48**, 1090-1132.
- O'HARA, M. J. AND E. L. P. MERCY (1963) Petrology and petrogenesis of some garnetiferous periodotites. *Trans. Roy. Soc. Edinburgh*, **65**, 251-314.
- ROBIE, R. A., P. M. BETHKE AND K. M. BEARDSLEY (1967) Selected X-ray data, molar volumes and densities of minerals and related substances. *Geol. Surv. Bull.* **1248**.
- SAXENA, S. K. (1968a) Distribution of elements between coexisting minerals and the nature of solid solution in garnet. *Amer. Mineral.*, **53**, 994-1014.
- (1968b) Chemical study of phase equilibria in charnockites, Varberg, Sweden. *Amer. Mineral.*, **53**, 1674-1695.
- SUBRAMANIAM, A. P. (1962) Pyroxenes and garnets from charnockites and associated granulites. *Geol. Soc. Amer.*, **Buddington Vol.**, 21-36.
- YODER, H. S., JR., AND C. E. TILLEY (1962) Origin of basalt magmas: An experimental study of natural and synthetic rock systems. *J. Petrology*, **3**, 342-532.

*Manuscript received, November 30, 1967; accepted for publication, August 21, 1968.*