

EFFECT OF TEMPERATURE ON THE DISTRIBUTION OF Mg AND Fe²⁺ BETWEEN CALCIC PYROXENE AND HORNBLLENDE

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ABSTRACT

A compilation of data on coexisting calcic pyroxene and hornblende, including some new analyses from the Grenville province, shows that, within the temperature range represented by upper amphibolite and lower granulite facies metamorphism, the Mg-Fe²⁺ distribution coefficient decreases from 1.7 to 1.3 with rising temperature. With further rise in temperature, to the range represented by the crystallization of ultramafic and gabbroic rocks, the distribution coefficient is more variable but apparently increases sharply to about 2. This relationship forms a potential geological temperature indicator.

SOMMAIRE

Les données disponibles sur les pyroxènes calciques qui coexistent avec la hornblende, comprenant de nouvelles analyses de roches de la province Grenville, montrent que, dans le domaine de température caractéristique du métamorphisme à faciès amphibolite-supérieur et granulite-inférieur, le coefficient de distribution Mg-Fe²⁺ diminue de 1.7 à 1.3 à mesure qu'augmente la température. À plus haute température, dans le domaine de cristallisation des roches ultramafiques et gabbroïques, ce coefficient varie davantage, mais croît rapidement jusqu'à environ 2. Cette relation permet d'entrevoir des applications en géothermométrie.

INTRODUCTION

The distribution of magnesium and ferrous iron between calcic pyroxene and hornblende in some metamorphic, ultramafic and volcanic rocks was examined by Onuki (1966), who concluded that the distribution coefficient is only slightly affected by temperature. The distribution coefficient (eq. 1), was found to *increase*

$$K_D = \frac{X^{Cpx}}{1 - X^{Cpx}} \cdot \frac{1 - X^{Hbl}}{X^{Hbl}} \quad (1)$$

with rising temperature, being on the average 1.2 for rocks of the amphibolite facies, 1.6 for rocks of granulite facies, and 1.9 for ultramafic and volcanic rocks. In the above equation, X is the atomic ratio Mg/(Mg + Fe²⁺), and Hbl and Cpx refer to hornblende and calcic pyroxene.

We have obtained some new information on the distribution of Mg and Fe²⁺ in amphibolite-facies and granulite-facies rocks of the Grenville province (Canadian Precambrian Shield), where the distribution coefficient, as defined above, apparently *decreases* with rising temperature, in disagreement with the trend proposed by Onuki (1966). We have therefore prepared a new compilation of data and a revised proposal for the relationship between the distribution coefficient and temperature.

THEORY

The distribution of Mg and Fe²⁺ between coexisting ferromagnesian minerals was examined in relation to the concept of chemical equilibrium by Ramberg & DeVore (1951), and this approach was applied to the mineral pair calcic pyroxene-calcic amphibole by Mueller (1960), Kretz (1960), and Onuki (1966). Mueller (1960) showed that the relationship between the atomic ratio Mg/(Mg + Fe²⁺) in calcic pyroxene and the same ratio in calcic amphibole in some metamorphic rocks from the Canadian Shield can be adequately expressed by use of the distribution equation (1), where the distribution coefficient (K_D) is independent of X^{Cpx} and X^{Hbl} . Ramberg & DeVore (1951), Ramberg (1952), Kretz (1963) and Onuki (1966) have shown, by use of chemical theory, that the distribution coefficient is, in general, a function of temperature, pressure and compositional variations (*e.g.*, the Al content of amphibole).

COMPILATION

In addition to the work of Onuki (1966), referred to above, compilations of data on the distribution of Mg and Fe²⁺ between calcic pyroxene and hornblende have been prepared by DeVore (1957), Saxena (1969), Leelanandam (1970), Sen (1970, 1973) and Perchuk (1973); however, many more data are now available than were included in these compilations.

Our compilation takes the form of a sequence of distribution diagrams, in which X^{Cpx} is plotted against X^{Hbl} for all mineral analyses

available to us by the end of 1976, a total of 143 mineral pairs. Only those minerals were included for which the ferrous iron content was determined or estimated. Sodium-rich minerals were excluded. The results of this compilation are as follows: (1) In rocks of the upper-amphibolite facies, K_D for calcic pyroxene-actinolite pairs (less than 3.2 wt. % Al_2O_3) is 1.0; for calcic pyroxene-hornblende pairs it is about 1.7. (2) In rocks transitional between the amphibolite and granulite facies, K_D for calcic pyroxene-hornblende pairs is about 1.6. (3) In rocks of the hornblende granulite facies, K_D for calcic pyroxene-hornblende pairs ranges from 1.5 to 1.3; some values less than 1.3 were found, particularly in rocks from Madras, India. (4) In ultramafic, gabbroic and volcanic rocks, K_D for calcic pyroxene-hornblende pairs falls in the range 1.3-3.0; excluding certain gabbroic rocks, all values are greater than 1.7. (5) Coexisting synthetic calcic pyroxene and hornblende above solidus temperatures (820-1100°C) give distribution coefficients that range from less than 1 to 3.2. (6) Within a terrain of uniform metamorphic grade, the distribution coefficient is evidently independent of the Mg/Fe²⁺ ratio; hence, the simple distribution equation may be used without modification.

Copies of the distribution diagrams and a list of references may be obtained at nominal cost from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa K1A 0S2.

DISCUSSION

Compositional effect

The effect of Al^{IV} in amphibole on the distribution of Mg and Fe²⁺ between this mineral and calcic pyroxene is shown in Figure 1, where most of the data points pertain to the amphibolite facies. The Al^{IV} effect also appears in the granulite facies, where it was detected by Sen (1973); two such trends are shown as lines D and M in Figure 1. Note that an increase of Al^{IV} in amphibole causes this mineral to acquire a larger relative share of Fe²⁺, compared to that of the coexisting mineral, as was predicted by Ramberg (1952).

Pressure effect

The effect of pressure on the distribution coefficient was estimated and found to be very small. The estimate is based on a volume change for the exchange reaction of $-0.30 \text{ cm}^3/\text{gram}$ -formula weight of $CaMgSi_2O_6$, as obtained from density measurements compiled by Deer *et al.*

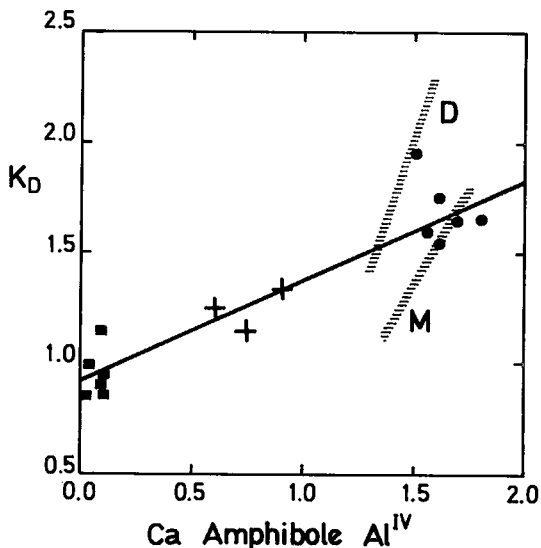


FIG. 1. Variation in the Mg-Fe²⁺ distribution coefficient for calcic pyroxene-calcic amphibole pairs as a function of the number of atoms of four-coordinated Al in amphibole per standard formula. Squares and circles represent mineral pairs from the amphibolite facies (Mueller 1960, Kretz 1978), crosses represent granitic rocks (Haslam 1968); lines D and M are trends obtained from two granulite-facies terrains (Sen 1973).

(1963). Thus, at 730°C the distribution coefficient is displaced by a negligible factor of 1.02 as the result of an increase in pressure from 1 to 5000 bars.

Temperature effect

The effect of temperature on the distribution coefficient is shown in Figure 2, where the data points represent average distribution coefficients for certain well-studied rock bodies or terrains,

TABLE 1. SELECTED DATA ON COEXISTING CALCIC PYROXENE AND HORNBLENDE

Facies/rocks	No. of pairs	Av. K_D	Est. T °C	Symbol (Fig. 2) and Reference
Amphibolite (opx. rare)	9	1.65	650*	K (Kretz 1978) ¹
Amphibolite-granulite (opx. not abundant)	5	1.58	700	E (Engel <i>et al.</i> : 1964) ²
Granulite (opx. abundant)	7	1.56	700	J1 (Jen 1967) ³
	7	1.49	750	B (Binns 1965a, b) ⁴
	9	1.44	750	D (Davidson 1968, 1971) ⁵
	8	1.41	750	J2 (Jen 1975) ⁶
	4	1.28	750	H (Howie 1955) ⁷
	7	1.27	750	R (Ray & Sen 1970) ⁸
Magmatic rocks (ultramafic, gabbroic)	7	1.86	900	O (Onuki 1965) ⁹
	5 [†]	2.39	1000	G (Gandhi 1970) ¹⁰
Experimental results	2	1.60	875	+ (Helz 1973)
	3	1.53	930	+ (Helz 1973)
	2 [†]	2.05	970	+ (Helz 1973)
	3	3.55	1000	+ (Helz 1973)

* estimated $\pm 50^\circ\text{C}$ associated with each value, except for the data of Helz (1973) which are run temperatures. Localities: ¹ Québec; ² Adirondacks, N.Y.; ³ Ontario; ⁴ Broken Hill, Australia; ⁵ Western Australia; ⁶ Adirondacks, N.Y.; ⁷ and ⁸ Madras, India; ⁹ Northern Japan; ¹⁰ Mont Yamaska, Québec. [†] excluding one ($K_D = 3.64$) from Gandhi (1970) and one ($K_D = 2.68$) from Helz (1973).

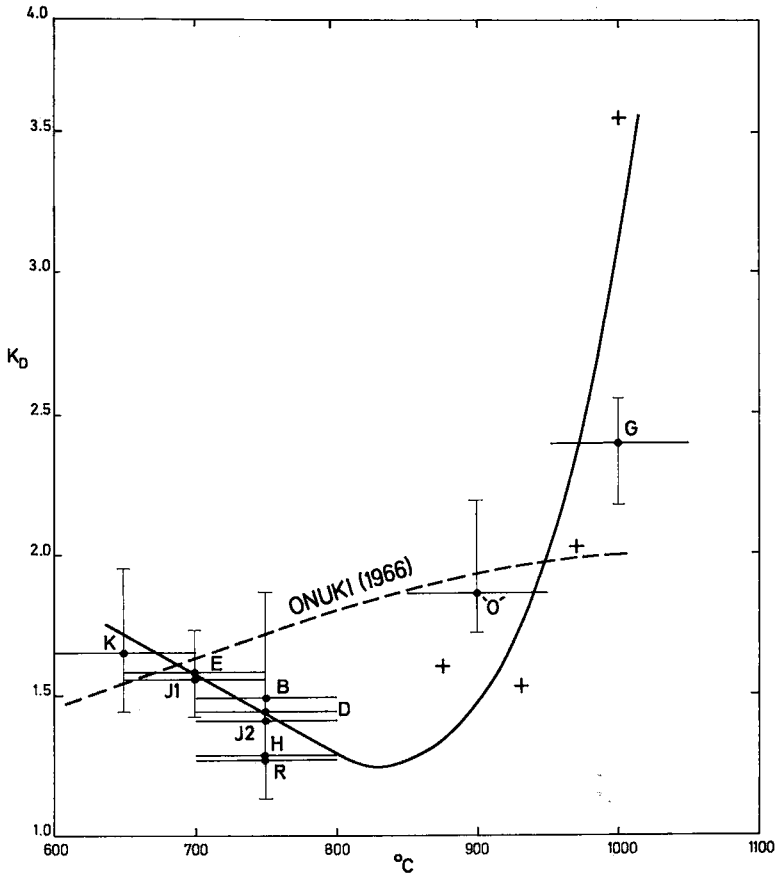


FIG. 2. Variation in the Mg-Fe²⁺ distribution coefficient for calcic pyroxene-hornblende pairs (K_D) as a function of temperature (°C). Data are from Table 1. Circles represent data from rocks; crosses, from experimental studies. Vertical lines through circles indicate observed range in K_D ; horizontal lines indicate presumed uncertainty in temperature estimates. The broken curve is the relationship initially proposed by Onuki (1966).

as listed in Table 1. Temperature estimates are 650°C for the upper amphibolite facies, based on the Goldsmith-Newton carbonate reaction (Kretz 1978), 700°C for the amphibolite-granulite transitional facies (Turner 1968), and 750°C for the hornblende granulite facies, based on various reactions (Jen 1975). The estimate of 900°C for ultramafic rocks from Japan is that given by Onuki (1965), whereas that of 1000°C attributed to the Mont Yamaska intrusion studied by Ghandi (1970) is our own rough estimate. The experimental results of Helz (1973) are also shown in Figure 2.

In general, an increase in temperature may displace a distribution coefficient toward or away from unity, depending on how the thermodynamic properties of the mineral solid solu-

tions are affected by temperature. The data on Figure 2 do not produce a straight-line plot on a $\ln K_D$ vs. $(1/T)$ graph, as could have been expected (Kretz 1963); we have, therefore, used the simple K_D vs. T plot in Figure 2.

The presence of a pronounced minimum in the K_D vs. temperature curve is a surprise; this relationship resembles that found for the pair calcic pyroxene-olivine by Bartholomé (1960).

Intercrystalline and intracrystalline exchange

A change in the intercrystalline distribution coefficient, resulting from a change in temperature, may be brought about by a change in one or more intracrystalline distribution relationships, themselves affected by temperature. But the intercrystalline distribution coefficient could al-

so be affected by a change in the number of atomic positions available to $(Mg + Fe^{2+})$ in one or both crystals. For example, a decrease in the Ca content of calcic pyroxene with increasing metamorphic grade, as shown by Binns (1965a), would make a larger proportion of $M2$ sites available to $(Mg + Fe^{2+})$; as the $M2$ sites prefer Fe^{2+} (McCallister *et al.* 1976), we would expect that with increasing grade, the calcic pyroxene crystal will take up more and more Fe^{2+} relative to that in the coexisting hornblende. This would effectively decrease the distribution coefficient, even though all intracrystalline distributions remain virtually undisturbed. However, calculations show that this "available site" effect is small; for example, an increase from 9 to 14% $(Mg + Fe^{2+})$ in $M2$ in calcic pyroxene would cause the distribution coefficient to drop from 1.7 to 1.6.

CONCLUSIONS

A decrease in the $Mg-Fe^{2+}$ distribution coefficient with increasing metamorphic grade appears well established. The correlation, as shown in Figure 2, would be considerably improved by supposing that the granulite-facies rocks of Madras crystallized near $800^{\circ}C$. The higher-temperature rocks show more variation; this cannot be correlated with the Al content of hornblende, and may be due to other factors, such as a more important departure from exchange equilibrium. Even more variation is found in the experimental results; however, these are in general agreement with those obtained from natural rocks. The change in slope of the K_D vs. T curve may possibly reflect a change in sign of ΔH , the heat of the exchange reaction. Additional experimental work will undoubtedly provide an improved calibration of the K_D vs. T relationship.

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REFERENCES

- BARTHOLOMÉ, P. (1960): L'interprétation pétrogénétique des associations d'olivine et orthopyroxène. *Soc. géol. Belg., Ann.* 83, 319-344.
- BINNS, R. A. (1965a): The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, New South Wales. Part I. Hornblendes. *Mineral. Mag.* 35, 306-326.
- (1965b): The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, New South Wales. Part II. Pyroxenes, garnets, plagioclases, and opaques oxides. *Mineral. Mag.* 35, 561-587.
- DAVIDSON, L. R. (1968): Variation in ferrous iron-magnesium distribution coefficients of metamorphic pyroxenes from Quairading, Western Australia. *Contr. Mineral. Petrology* 19, 239-259.
- (1971): Metamorphic hornblendes from basic granulites of the Quairading district, Western Australia. *Neues Jahrb. Mineral. Monatsh.*, 344-359.
- DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1963): *Rock-Forming Minerals. 2. Chain Silicates*. Longmans, London.
- DEVORE, G. W. (1957): The association of strongly polarizing cations with weakly polarizing cations as a major influence in element distribution, mineral composition, and crystal growth. *J. Geol.* 65, 178-195.
- ENGEL, A. E. J., ENGEL, C. G. & HAVENS, R. G. (1964): Mineralogy of amphibolite interlayers in the gneiss complex, Northwest Adirondack Mountains, New York. *J. Geol.* 72, 131-156.
- GHANDI, S. S. (1970): Petrology of the Monteregean intrusions of Mount Yamaska, Quebec. *Can. Mineral.* 10, 452-484.
- HASLAM, H. W. (1968): The crystallization of intermediate and acid magmas at Ben Nevis, Scotland. *J. Petrology* 9, 84-104.
- HELZ, R. T. (1973): Phase relations of basalts in their melting range at $P_{H_2O} = 5kb$ as a function of oxygen fugacity. I. Mafic phases. *J. Petrology* 14, 249-302.
- HOWIE, R. A. (1955): The geochemistry of the charnockite series of Madras, India. *Roy. Soc. Edin. Trans.* 62, 725-768.
- JEN, L. S. (1967): *Petrochemical Study of Amphibolitic Gneisses from the Tichborne and Westport Areas, Southeast Ontario*. M.Sc. thesis, Queen's Univ., Kingston, Ontario.
- (1975): *Spatial Distribution of Crystal and Phase Equilibrium in Charnockitic Granulites from the Adirondack Mountains, New York*. Ph.D. thesis, Univ. Ottawa, Ottawa, Ontario.
- KRETZ, R. (1960): The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles and biotites in skarns. *Geochim. Cosmochim. Acta* 20, 161-191.
- (1963): Distribution of magnesium and iron between orthopyroxene and calcic pyroxene in natural mineral assemblages. *J. Geol.* 71, 773-785.
- (1978): Distribution of Mg, Fe^{2+} , and Mn in some calcic pyroxene-hornblende-biotite-garnet gneisses and amphibolites from the Grenville province. *J. Geol.* 86, (in press).