Canadian Mineralogist
Vol. 19, pp. 493-500 (1981)

SITE-OCCUPANCY INTERPRETATION OF THE DISTRIBUTION OF Mg and Fe BETWEEN ORTHOPYROXENE AND CLINOPYROXENE IN METAMORPHIC ROCKS

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ABSTRACT

A new compilation of data on the distribution of Mg and Fe^{2+} between orthopyroxene (Opx) and clinopyroxene (Cpx) in granulite-facies rocks from India, Australia and North America shows that the compositional dependence of the distribution coefficient is evidently a linear relation that extends over the entire range of composition. The relation is, approximately, $K_D = 2.0–0.45\ X^{Opx}$, where $K_D = [X^{Opx}/(1–X^{Opx})] \div [X^{Cpx}/(1–X^{Cpx})]$ and $X = Fe^{2+}/(Mg + Fe^{2+})$. This information, together with experimental (Mössbauer and X-ray) data on the distribution of Mg and Fe^{2+} between *M*1 and *M*2 sites in orthopyroxene and in clinopyroxene at 800°C, serves to define a slightly sigmoidal isotherm for the distribution of Mg and Fe^{2+} between *M*1 of orthopyroxene and *M*1 of associated clinopyroxene.

Keywords: granulite facies, orthopyroxene, clinopyroxene, Mg–Fe^{2+} distribution, site preference.

SOMMAIRE

A la lumière d'une nouvelle compilation de données sur le partage de Mg et de Fe^{2+} entre orthopyroxène (Opx) et clinopyroxène (Cpx) dans les roches à facies granulite de l'Inde, de l'Australie et de l'Amérique du Nord, l'influence de la composition sur le coefficient de distribution est une relation linéaire qui s'étend sur tout le domaine de composition. Cette relation peut s'écrire $K_D = 2.0 - 0.45\ X^{Opx}$, où $K_D = [X^{Opx}/(1–X^{Opx})] \div [X^{Cpx}/(1–X^{Cpx})]$, $X = Fe^{2+}/(Mg+Fe^{2+})$. Le paramètre K_D et les données expérimentales (Mössbauer, diffraction X) sur la distribution de Mg et Fe^{2+} sur *M*1 et *M*2 de l'orthopyroxène et du clinopyroxène à 800°C définissent un isotherme légèrement sigmoïde régissant la distribution de Mg et Fe^{2+} sur *M*1 de l'orthopyroxène et *M*1 du clinopyroxène associé.

(Traduit par la Rédaction)

Mots-clés: facies granulite, orthopyroxène, clinopyroxène, distribution Mg–Fe^{2+}, préférence de site.

INTRODUCTION

Jen & Kretz (1981) have prepared a new compilation of the distribution of Mg and Fe^{2+} between associated orthopyroxene and clinopyroxene in high-grade metamorphic terranes, including the Madras area in India (Howie 1955), the Quairading area in Western Australia (Davidson 1968) and the northeastern Adirondacks (Jen 1975, Jaffe *et al.* 1978). This compilation, which spans most of the Mg:Fe^{2+} range, shows (1) that the distribution coefficient for Mg-rich and intermediate pyroxenes is remarkably similar in the three widely separated terranes (see Fig. 7 of Jen & Kretz 1981) and (2) that the slight decrease in this coefficient with increasing Fe, discovered by Binns (1962) and Davidson (1968), evidently extends well into the Fe-rich part of the range, as shown in Figure 1.

Common orthopyroxene and clinopyroxene of metamorphic rocks possess two distinct (Mg, Fe^{2+})-bearing sites (*M*1 and *M*2); the observed between-mineral distribution of Mg and Fe^{2+} was presumably determined by the following three between-site distributions, acting in unison: (a) *M*1–*M*2 orthopyroxene, (b) *M*1–*M*2 clinopyroxene, and (c) *M*1 orthopyroxene – *M*1 clinopyroxene. The fourth, (d) *M*2 orthopyroxene – *M*2 clinopyroxene, may be regarded as a distribution that is dependent on the first three, which are here chosen as independent.

Experimental information, obtained by Virgo & Hafner (1969), Saxena & Ghose (1971) and McCallister *et al.* (1976), is available for (a) and (b), but no such information is available for (c). Hence the question arises: what pattern of distribution for (c), when combined with experimental data for (a) and (b), is consistent with the between-mineral distribution shown in Figure 1?

A deductive (nontheoretical) approach is used here to answer this question. Distribution coefficients are employed only as convenient expressions of the relative Mg:Fe^{2+} ratios of two sites or two minerals; no attempt is made to derive equilibrium constants or other thermodynamic parameters of sites and minerals. The approach is thermodynamic only in the sense that exchange equilibrium is assumed through-

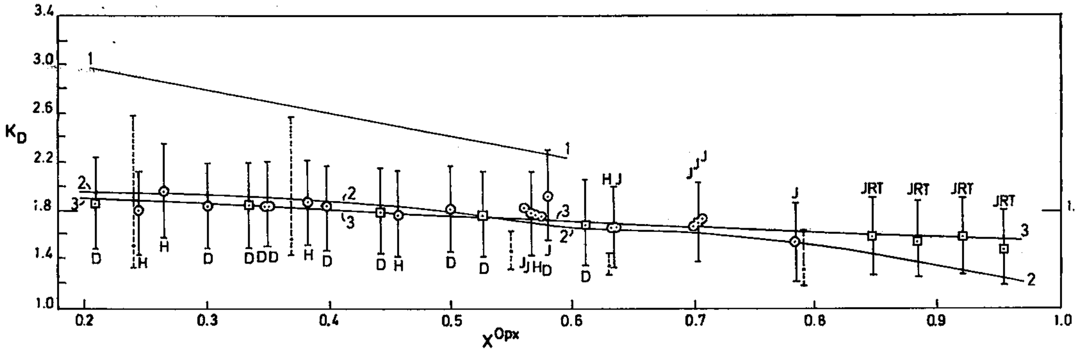

FIG. 1. The distribution coefficient (K_D) for Fe^{2+}–Mg exchange between orthopyroxene and clinopyroxene in metamorphic rocks from India (H, Howie 1955), Australia (D, Davidson 1968) and the Adirondacks in North America (J, Jen 1975; JRT, Jaffe *et al.* 1978), plotted against the $Fe^{2+}/(Mg+Fe^{2+})$ ratio of orthopyroxene (X^{Opx}). Vertical bars on the data points represent maximum error; normally, considerable cancellation of error occurs in the calculation of K_D from mineral analyses. Open squares are mineral pairs selected for modeling. Curves 1, 2 and 3 correspond to models 1, 2 and 3a in the text. Small dots represent "best values" experimentally determined at 810°C by Lindsley *et al.* (1974), with dashed bars defining "maximum" and "minimum" values.

out. Three principal models are considered, and within this framework earlier models are reviewed and a new one is presented.

The modeling procedure requires an estimate of the temperature of granulite-facies metamorphism. An estimate of ≧ 750°C for the northeastern Adirondacks was obtained by Bohlen & Essene (1977), based on two-feldspar and magnetite–ilmenite temperature indicators. A temperature of 800°C is here adopted initially; the preferred model is constructed for both 800 and 700°C.

SYMBOLS AND EQUATIONS

The following symbols and equations will be used:

Opx, Cpx: orthopyroxene, Ca-rich clinopyroxene

$M1$, $M2$: structural sites

n: number of sites (relative to 6 oxygen atoms) occupied by (Fe^{2+}, Mg)

n_r: n^{M2}/n^{M1}

x: $Fe^{2+}/(Mg+Fe^{2+})$ on site; atomic fraction

X: $Fe^{2+}/(Mg+Fe^{2+})$ in crystal; atomic fraction

k_D: between-site distribution coefficient, defined as follows:

$$k_D{}^{Opx} = \frac{x^{OpxM2}}{1 - x^{OpxM2}} \cdot \frac{1 - x^{OpxM1}}{x^{OpxM1}} \quad \ldots\ldots\ldots\ (1)$$

$$k_D{}^{Cpx} = \frac{x^{CpxM2}}{1 - x^{CpxM2}} \cdot \frac{1 - x^{CpxM1}}{x^{CpxM1}} \quad \ldots\ldots\ldots\ (2)$$

$$k_D{}^{M1-M1} = \frac{x^{CpxM1}}{1 - x^{CpxM1}} \cdot \frac{1 - x^{OpxM1}}{x^{OpxM1}} \quad \ldots\ldots\ (3)$$

K_D: between-crystal distribution coefficient, defined as follows:

$$K_D = \frac{X^{Opx}}{1 - X^{Opx}} \cdot \frac{1 - X^{Cpx}}{X^{Cpx}} \quad \ldots\ldots\ldots\ldots\ldots\ (4)$$

By rearrangement of terms:

$$X^{Opx} = K_D/[(1/X^{Cpx}) + (K_D - 1)] \quad \ldots\ldots\ (5)$$

$$X^{Cpx} = 1/[K_D/X^{Opx}) - (K_D - 1)] \quad \ldots\ldots\ldots\ (6)$$

For any pyroxene mineral, x^{M1}, x^{M2} and X are interrelated by:

$$X = (n^{M2}\,x^{M2} + n^{M1}\,x^{M1})/(n^{M2} + n^{M1}) \ldots (7)$$

Also, equation (2) may be written:

$$x^{M2} = k_D/[(1/x^{M1}) + (k_D - 1)] \quad \ldots\ldots\ldots\ldots\ (8)$$

Substituting (8) in (7) produces the following relation among n_r, x^{M1}, X and k_D:

$$k_D n_r = [(n_r + 1)X - x^{M1}][(1/x^{M1}) + (k_D - 1)] . (9)$$

In orthopyroxene, n_r is approximately 1.0, and equation (9) is simplified to:

$$k_D = [2X - x^{M1}]\,[(1/x^{M1}) + (k_D - 1)] \ldots\ldots (10)$$

THE MODELS

Model 1

Mueller (1962) derived an equation to interrelate the orthopyroxene–clinopyroxene distribution coefficient (K_D) and the atomic fraction of Fe^{2+} in the $M1$ and $M2$ sites of orthopyroxene (x^{M1}, x^{M2}). The model was based on the following assumptions: (1) Ca in clinopyroxene is confined to $M2$, for which supporting evidence was later provided by Clark *et al.* (1969); (2) clinopyroxene is regarded as a one-site phase ($n^{CpxM2} = 0$); (3) the atomic fractions of Fe^{2+} in the $M1$ sites of orthopyroxene and clinopyroxene are equal ($x^{CpxM1} = x^{OpxM1}$). Mueller was thus able to derive an isotherm to represent the distribution of Fe^{2+} and Mg between $M1$ and $M2$ of orthopyroxene, based on $K_D = 1.82$, as obtained from natural mineral assemblages.

Matsui & Banno (1965) used the Mueller equation to show that K_D must decrease with increasing Fe^{2+}, provided the within-orthopyroxene distribution coefficient ($k_D{}^{Opx}$) remains constant. The calculated decrease, with $k_D{}^{Opx} = 3.3$, is slightly greater than that shown in Figure 1, falling from $K_D = 2.1$ in the Mg end to $K_D = 1.5$ in the Fe^{2+} end of the range. Some aspects of the Mueller model were adopted by Davidson (1968) to account for his observed decrease in K_D with increasing Fe^{2+}. However, the suggestions that Fe^{2+} in Mg-rich orthopyroxene is excluded from $M1$ and that the $M2$ sites become saturated in Fe^{2+} have not been confirmed by the experimental results of Virgo & Hafner (1969). Mueller's three assumptions also form a basis for the thermodynamic calculations of Grover & Orville (1969).

A simplified form of Mueller's equation may be obtained by writing equation (4) as

$$K_D = \frac{X^{Opx}/(1-X^{Opx})}{X^{Cpx}/(1-X^{Cpx})} \dots\dots\dots\dots\dots\dots (11)$$

Replacing X^{Cpx} by x^{OpxM1} (by assumptions 2 and 3),

$$K_D = \frac{X^{Opx}/(1-X^{Opx})}{x^{OpxM1}/(1-x^{OpxM1})} \dots\dots\dots\dots\dots (12)$$

Now equation (1) may be rewritten:

$$x^{OpxM1}/(1-x^{OpxM1}) = [x^{OpxM2}/(1-x^{OpxM2})]/k_D{}^{Opx} \quad (13)$$

Substituting (13) in (12) yields

$$K_D = \frac{X^{Opx}/(1-X^{Opx})}{x^{OpxM2}/(1-x^{OpxM2})} \cdot k_D{}^{Opx} \dots\dots (14)$$

TABLE 1. DISTRIBUTION OF Mg AND Fe^{2+} IN ORTHOPYROXENE*

	x^{M1}	x^{M2}	k_D^{Opx}
800°C	0.069	0.293	5.59
	0.187	0.575	5.88
	0.252	0.657	5.69
	0.298	0.701	5.52
	0.429	0.811	5.72
	0.579	0.860	4.46
	0.794	0.926	3.25
700°C	0.059	0.303	6.93
	0.156	0.605	8.29
	0.225	0.685	7.49
	0.360	0.800	7.11
	0.410	0.829	6.98
	0.790	0.929	3.48

*Saxena & Ghose (1971)

This equation may be used to derive a relation between K_D and X^{Opx} for a given value of $k_D{}^{Opx}$. As a demonstration of this equation, the Saxena & Ghose (1971) 800°C isotherm will be chosen for values of $k_D{}^{Opx}$. Although these authors adopted a simple-solution model for Fe^{2+}–Mg substitution on the two sites, thus allowing $k_D{}^{Opx}$ to vary with increasing Fe^{2+}:Mg, Table 1 shows that $k_D{}^{Opx}$ does in fact remain constant over a wide range in composition. Within this range ($k_D{}^{Opx} = 5.7 =$ constant), K_D and a relation between K_D and X^{Opx} may be calculated, as shown in Table 2 and in Figure 1, curve 1. Although model 1 provides an explanation for the observed decrease in K_D with increasing X^{Opx}, it yields K_D values that are much too high. This model must therefore be regarded as inadequate, presumably because assumptions 2 or 3 (or both) are invalid.

Model 2

Model 1 can be improved by taking into consideration the presence of some Fe^{2+} and Mg atoms in the $M2$ sites of clinopyroxene, these being not completely filled with Ca and Na. Thus, assumption 2 is removed; 1 and 3 are retained.

A model of this kind was adopted by Fleet (1974), who referred to the Saxena & Ghose

TABLE 2. MODEL 1

$x^{Opx\,M2}$	X^{Opx}	K_D
0.2	0.121	3.15
0.3	0.185	3.02
0.4	0.252	2.88
0.5	0.325	2.74
0.6	0.404	2.58
0.7	0.500	2.44
0.8	0.606	2.19

(1971) data to obtain estimates of k_D^{Opx}, assumed $k_D^{M1-M1}=1.00$ and then calculated k_D^{Cpx} for several metamorphic mineral pairs, chiefly from India. This led to highly variable and some unrealistic (negative) values of k_D^{Cpx}, which are obviously due to small errors in the chemical analyses of MgO and FeO. A small miscalculation in the Mg:Fe^{2+} ratio of clinopyroxene will give rise to large errors in the Mg:Fe^{2+} ratio of the relatively few atoms that are assigned to $M2$; these errors will, in turn, produce a large error in calculated k_D^{Cpx}. The mean value of k_D^{Cpx} (as defined by equation 2) was found to be about 20. An improvement in Fleet's model may be obtained by referring to recent experimental data to obtain estimates of k_D^{Cpx}, and by utilizing mineral analyses that cover the entire range of Mg:Fe^{2+} ratio.

The present calculation begins by selecting from Figure 1 the ten representative mineral pairs that are listed in Table 3; the include five from Davidson (1968), one of three nearly identical mineral pairs from Jen & Kretz (1981) and the four Fe-rich mineral pairs of Jaffe *et al.* (1978). For each of the ten clinopyroxenes, the composition of a hypothetical coexisting orthopyroxene is calculated, leading to a value of K_D (calculated) that may be compared with K_D (observed). The data needed for the calculation are n_r^{Cpx}, n_r^{Opx}, k_D^{Opx}, k_D^{Cpx} and assumption 3 ($x^{\mathrm{Opx}M1}=x^{\mathrm{Cpx}M1}$).

The reported clinopyroxene formulas were used to calculate n^{M2} and n^{M1}; n^{M2} was taken as the number of $M2$ sites remaining after all Ca, Na and K ions were assigned to this site, and n^{M1} as the remaining (Fe^{2+}+Mg) ions (Table 3). In orthopyroxene, if Ca and Na are assigned to $M2$, and Fe^{3+}, Ti and Al^{VI} to $M1$, then n^{M2} and n^{M1} are very nearly equal; n_r was taken as 1.0. The 800°C isotherm of Saxena & Ghose (1971) was adopted to provide values of k_D^{Opx} (Table 1). In the Fe^{2+}-rich end of the composition range, where k_D^{Opx} decreases, appropriate values for a given $x^{\mathrm{Opx}M1}$ were obtained by interpolation. The chosen estimate of k_D^{Cpx} (800°C) was based on the experimental data (crystal-structure refinement) of McCallister *et al.* (1976), who determined k_D^{Cpx} as a function of temperature for two crystals with 0.67 and 0.72 as the fraction of $M2$ occupied by (Ca + Na). A value k_D^{Cpx} (800°C) for each clinopyroxene was first obtained by interpolation (to give k_D^{Cpx} = 7 and 10, respectively). A bold extrapolation was then used to estimate k_D^{Cpx} for crystals with about 0.9 of the $M2$ sites filled with (Ca + Na), the approximate average for the ten selected clinopyroxenes of the present study (Fig. 2). This gave k_D^{Cpx} = 19, which is nearly identical to the mean value estimated by Fleet (1974); this is now assumed to remain constant over the entire range of composition. Considerably higher values were obtained or implied by Hafner *et al.* (1971) and Saxena *et al.* (1974) in their Mössbauer study of clinopyroxene; however, because of the difficulty in interpreting Mössbauer spectra in Ca-rich clinopyroxenes, as pointed out by Dowty & Lindsley (1973), the X-ray results may be preferable.

The procedure followed in the construction of model 2, using the above constants, is indicated in Table 3. First, $x^{\mathrm{Cpx}M1}$ was obtained by an iterative solution of equation (9). This, using assumption 3, gave $x^{\mathrm{Opx}M1}$ for the hypothetical coexisting orthopyroxene. With $x^{\mathrm{Opx}M1}$, X^{Opx} (calc.) could be obtained from equation (10). Entering this value with X^{Cpx} of the clinopyroxene in equation (4) produced K_D (calc.), as listed in Table 3 and plotted as curve 2 in Figure 1.

The K_D values predicted by model 2 agree closely with the observed values, particularly in the middle part of the Fe^{2+}:Mg range. Furthermore, a slight decrease of K_D with increas-

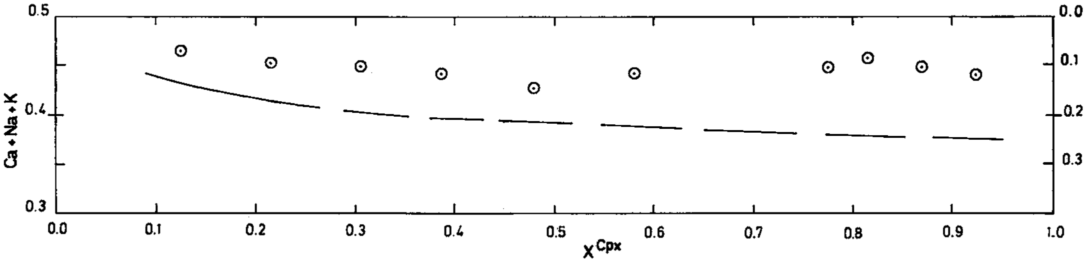

FIG. 2. Ca+Na+K atoms *per* 3 oxygen atoms in ten selected clinopyroxenes (Table 3), plotted against $Fe^{2+}/(Mg+Fe^{2+})$ in the crystals, denoted X^{Cpx}. Numbers on right vertical axis indicate the fraction of $M2$ sites occupied by (Fe^{2+},Mg) assuming all Ca, Na and K in $M2$, and Al^{VI}, Ti and Fe^{3+} in $M1$. Dashed curve shows experimental results (810°C, 15 kbar) of Lindsley *et al.* (1974).

TABLE 3. MODEL 2

		Cpx				Opx					K_D	
		X	n^{M2}	n^{M1}	x^{M1}	x^{M1}	x^{M2}	k_D	X(calc)	X(obs)	calc	obs
1.	D 11	.123	.069	.933	.085	.085	.346	5.7	.216	.208	1.96	1.87
2.	D 12	.217	.089	.927	.166	.166	.532	5.7	.350	.334	1.94	1.87
3.	D 10	.305	.099	.915	.245	.245	.649	5.7	.447	.443	1.84	1.81
4.	D 7	.384	.114	.934	.321	.321	.729	5.7	.525	.526	1.77	1.77
5.	D 4	.480	.141	.920	.411	.411	.799	5.7	.605	.611	1.66	1.70
6.	J 103	.580	.109	.946	.537	.537	.853	5.0	.695	.703	1.65	1.71
7.	JRT 1	.776	.099	.917	.754	.754	.915	3.5	.835	.848	1.46	1.59
8.	JRT 2	.816	.082	.922	.801	.801	.928	3.2	.865	.883	1.45	1.69
9.	JRT 3	.872	.096	.883	.859	.859	.943	2.7	.901	.918	1.34	1.62
10.	JRT 4	.927	.113	.860	.918	.918	.963	2.3	.941	.954	1.26	1.56

ing Fe^{2+} is predicted, as observed. However, for Mg-rich mineral pairs, K_D (calc.) is slightly greater than K_D (obs.), and for Fe^{2+}-rich mineral pairs, K_D (calc.) is somewhat less than K_D (obs.).

Model 3

The reason for the lack of perfect agreement between K_D (calc.) and K_D (obs.) may possibly lie in assumption 3 ($x^{OpxM1} = x^{CpxM1}$), which was adopted for model 2. Although the $M1$ sites in the two minerals are geometrically similar, x^{M1} is not necessarily identical on the two sites. Indeed, this was anticipated by Mueller (1962). Model 3 was designed to determine to what extent x^{OpxM1} and x^{CpxM1} must differ from each other to bring K_D (obs.) and K_D (calc.) into perfect agreement.

Some estimates on the distribution of Fe^{2+} and Mg between the two sets of $M1$ sites were reported previously. Banno & Matsui (1966) showed that in the low-granulite-facies rocks at Broken Hill (Binns 1962), good agreement between K_D (calc.) and K_D (obs.) is obtained if $M1$ in clinopyroxene contains more Fe^{2+} than $M1$ in orthopyroxene, with k_D^{M1-M1} (equation 3) = 1.24. However, when extended over the whole Fe^{2+}:Mg range, their model produces unrealistic values for K_D, ranging from 3.2 at the Mg end to 1.4 at the Fe^{2+} end. This may be a consequence of the fact that they retained assumption 2, which is here regarded as unacceptable. Saxena (1971) calculated $M1$ orthopyroxene – M1 clinopyroxene isotherms, which are sigmoidal in form and generally display a considerable difference in composition between the two sets of sites; he also retained assumption 2. Blander (1972) referred to Virgo & Hafner (1969) for estimates of k_D^{Opx} and k_D^{Cpx} at 900°C and reported that agreement with K_D from Mg-rich meteorites was achieved with k_D^{M1-M1} (equation 3) = 0.83. However, Bunch & Olsen (1974), who obtained several additional analyses of pyroxenes from meteorites, suggested that this value is too low.

Model 3a (800°C) was constructed by first calculating x^{CpxM1} as was done for model 2. A similar calculation for orthopyroxene, using an iterative solution of equation (10), produced corresponding estimates of x^{OpxM1}. These values, listed in Table 4 and plotted in Figure 3, show in effect how Fe^{2+} and Mg must distribute themselves between the two sets of $M1$ sites when curve 2 (model 2) is rotated and brought into coincidence with line 3, which is a visual fit of a straight line to the ten data points selected. Only a slight difference in x^{CpxM1} and x^{OpxM1} will produce the desired effect, with k_D^{M1-M1} ranging from 1.05 to 0.75.

A similar model, 3b, was constructed to examine the effect that a different choice of k_D^{Cpx} and k_D^{Opx} would have on k_D^{M1-M1}. The calculation required for model 3a was repeated using k_D values appropriate to 700°C, namely, $k_D^{Cpx} = 30$ and $k_D^{Opx} = 7.3$, decreasing to 2.5 (Table 1). These calculations (Table 4) show that a slightly greater variation in k_D^{M1-M1} is required to accommodate the larger values for both k_D^{Cpx} and k_D^{Opx}. The reason K_D is generally insensitive to k_D^{Cpx} is found in the relation $n^{CpxM2} \ll n^{CpxM1}$, so that a large change in k_D^{Cpx} produces a small change in x^{CpxM1}, and hence in X^{Cpx}. Thus, the uncertainty in the estimate of k_D^{Cpx} does not create a serious defect within models 2 and 3.

Model 3 was based on the assumption that k_D^{Cpx} remains constant over the whole com-

TABLE 4. MODEL 3

	a) 800°C				b) 700°C			
	x^{CpxM1}	k_D^{Opx}	x^{OpxM1}	k_D^{M1-M1}	x^{CpxM1}	k_D^{Opx}	x^{OpxM1}	k_D^{M1-M1}
1	.085	5.7	.081	1.05	.079	7.3	.068	1.19
2	.166	5.7	.156	1.08	.157	7.3	.135	1.21
3	.245	5.7	.241	1.02	.240	7.3	.217	1.14
4	.321	5.7	.322	1.00	.317	7.3	.297	1.10
5	.411	5.7	.418	0.97	.407	7.3	.395	1.05
6	.537	5.0	.547	0.96	.535	5.9	.534	1.00
7	.754	3.5	.773	0.89	.753	4.2	.764	0.95
8	.801	3.2	.827	0.84	.801	3.5	.823	0.87
9	.859	2.7	.883	0.81	.859	3.0	.880	0.83
10	.918	2.3	.937	0.75	.918	2.5	.935	0.78

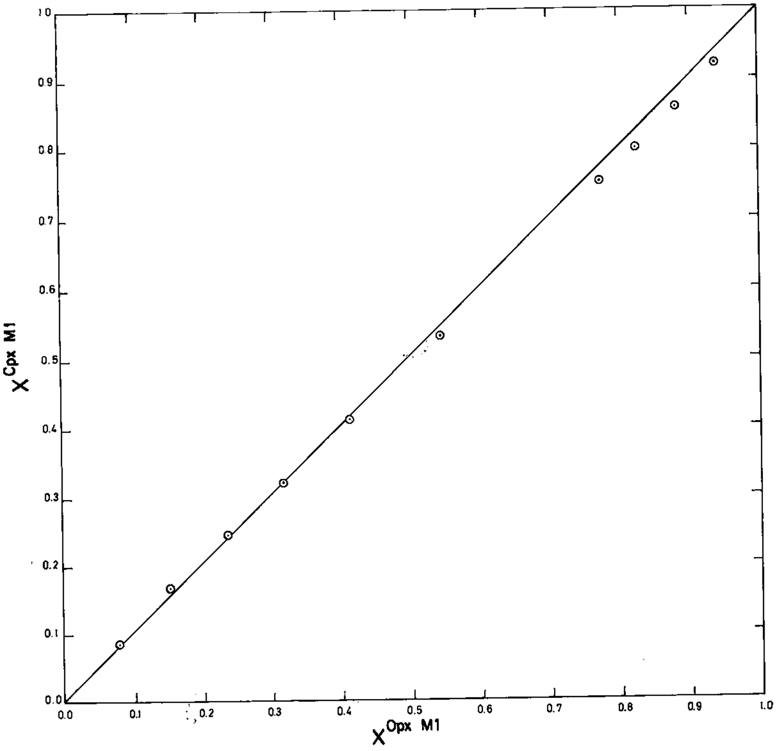

FIG. 3. Calculated distribution (model 3a, Table 4) of Fe^{2+} and Mg between *M*1 sites of clinopyroxene and *M*1 sites of orthopyroxene; $x = Fe^{2+}/(Mg+Fe^{2+})$. The straight line of unit slope is shown for comparison.

positional range, extending from Mg-rich to Fe-rich crystals. An alternative interpretation of the inadequacy of model 2 in the Mg and Fe extremes of the range might be that $k_D{}^{Cpx}$ decreases with increasing Fe while $k_D{}^{M1-M1}$ remains fixed at 1.00. However, a calculation shows that this decrease would have to extend from about 28 near the Mg end (specimens 1 and 2) to about 0.40 near the Fe end (specimens 9 and 10), a variation that appears excessive. Thus, model 3 is preferred to this alternative interpretation.

DISCUSSION AND CONCLUSION

Model 3a was designed to provide an understanding of (1) the observed between-crystal distribution coefficient in ten selected mineral pairs and (2) its observed dependence on the Fe^{2+} content of orthopyroxene, as shown by curve 3, Figure 1, or the corresponding equation:

$$K_D = 2.0 - 0.45X^{Opx} \qquad (15)$$

This model views the between-crystal distribution coefficient as determined principally by the following chemical processes, each of which is presumed to have attained equilibrium during granulite-facies metamorphism at about 800°C: (1) solid solution of $(Fe^{2+},Mg)SiO_3$ in clinopyroxene, to produce an equilibrium solvus concentration of (Ca + Na + K) of about 0.45 atoms *per* 3 oxygen atoms, corresponding to about 90% of the *M*2 sites occupied by (Ca + Na + K); (2) Fe^{2+}–Mg exchange between *M*1 and *M*2 of orthopyroxene, resulting in a within-crystal distribution coefficient of 5.7, decreasing in Fe-rich crystals to about 3; (3) Fe^{2+}–Mg exchange between *M*1 and *M*2 of clinopyroxene, resulting in a within-crystal distribution coefficient of about 19; (4) Fe^{2+}–Mg exchange between *M*1 of orthopyroxene and *M*1 of clinopyroxene, resulting in slightly more Fe^{2+} in *M*1 of clinopyroxene at low Fe concentrations, and *vice versa* at high Fe concentrations, as expressed by a between-site distribution coefficient that ranges from 1.1 to 0.8.

An examination of the numerous chemical analyses of pyroxene minerals that are now available and the corresponding values of K_D, as compiled by Grover & Orville (1969) and others, seems to indicate that some variability in K_D will persist no matter how accurate the chemical analyses may be. This variability may be attributed, in part, to perturbations produced by minor elements and to other causes not understood. It is curious, for example, that Maxey & Vogel (1974) reported an *increase* in K_D with increasing X^{Opx}, opposite to that shown in Figure 1.

Some experimental information on K_D is available for comparison. Using synthetic pyroxenes at 810°C and 15 kbar, Lindsley *et al.* (1974) determined distribution coefficients of about 1.45 and noted that their results (Fig. 1) are consistent with a slight decrease in K_D with increasing Fe. They also determined the Ca content of the Ca-pyroxene phase, as shown in Figure 2. Compared with the experimental data, the data for the natural assemblages, for both K_D and the Ca content of clinopyroxene, represent conditions that might be expected at temperatures considerably lower than 800°C. The reason for this disagreement may lie in the substantial concentrations of minor elements, especially in clinopyroxene; these were not present in the synthetic pyroxenes.

Mori (1978), also using synthetic pyroxenes, determined K_D at 1200°C and 30 kbar (Fe–Mg exchange not reversed). He found a decrease in K_D from about 1.1 at $X^{\mathrm{Cpx}} = 0$ to 0.8 at $X^{\mathrm{Opx}} = 1.0$, producing an apparently linear relation, similar to that shown by curve 3 in Figure 1, but with a slightly greater slope (–0.45 compared with –0.30). Mori also estimated the distribution of Fe^{2+} and Mg between $M1$ sites of orthopyroxene and clinopyroxene at 1200°C by a procedure similar to that used in model 3. He found k_D^{M1-M1} (as defined in equation 3) to range from 1.11 to 0.83 with increasing X^{Opx}, values that are almost identical to estimates here obtained for 800°C. This suggests that, unlike the $M1$–$M2$ distribution coefficients, the $M1$–$M1$ distribution coefficient may be virtually insensitive to a temperature change of about 400°C.

Abundant information is now available on the distribution of Mg and Fe between associated ferromagnesian minerals in metamorphic rocks; the approach used in the present study could be applied to various mineral systems provided that experimental data on within-crystal distribution coefficients are available. Although the "macroscopic" approach to element distribution has been very rewarding, it is clear that a full understanding of between-crystal distribution relations cannot be obtained without taking the individual sites into consideration.

ACKNOWLEDGEMENTS

The manuscript was reviewed by M.E. Fleet, who kindly corrected an unintentional omission.

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Received September 1980, revised manuscript accepted May 1981.