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Mg$^{2+}$ Fe$^{2+}$ ORDER-DISORDER IN ORTHOPYROXENE AND THE Mg$^{2+}$ Fe$^{2+}$ DISTRIBUTION BETWEEN COEXISTING MINERALS

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JULY 1970

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GREENBELT, MARYLAND

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CATEGORY
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Mg$^{2+}$-Fe$^{2+}$ ORDER-DISORDER IN ORTHOPYROXENE AND THE Mg$^{2+}$-Fe$^{2+}$ DISTRIBUTION BETWEEN COEXISTING MINERALS

by
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ABSTRACT

An approximate temperature of crystallization of rocks and important information on the thermodynamic nature of a crystalline solution, coexisting with orthopyroxene, can be obtained by using the experimental Mg$^{2+}$-Fe$^{2+}$ intra-crystalline distribution data in orthopyroxenes at various temperatures and the Mg$^{2+}$-Fe$^{2+}$ inter-crystalline distribution data in natural assemblage. Ca-pyroxene Ca(Mg, Fe)Si$_2$O$_6$ with the M2 site nearly filled by Ca, is a 'simple mixture' (Guggenheim, 1967) of Mg$^{2+}$ and Fe$^{2+}$ components with an energy constant $w$ approximately 1100 cal/mole at 600°C. The estimated temperature of ion-exchange equilibrium between coexisting cummingtonite and orthopyroxene in Biwabik Iron Formation, Minnesota is ~610°C. Cummingtonite also approximates to a 'simple mixture' with $w$ as 700 cal/mole at 600°C.
INTRODUCTION

The distribution of Fe$^{2+}$ and Mg$^{2+}$ between two coexisting ferromagnesian minerals such as ortho- and calcic-pyroxene by Kretz (1963) has been studied on the assumption that the Fe and Mg components mix ideally in each of the minerals. Mueller (1961, 1962) considered the possibility of intra-crystalline partitioning of the cations among the different structural sites in a mineral and for cummingtonite found it desirable to assume a 'regular solution' model. Matsui and Banno (1965), Banno and Matsui (1966) and Grover and Orville (1969) assumed ideal mixing of Fe$^{2+}$ and Mg$^{2+}$ on each site in orthopyroxene and interpreted the inter-crystalline Mg$^{2+}$-Fe$^{2+}$ distribution between coexisting ortho- and ca-pyroxene on that basis.

Saxena and Ghose (1970a) have shown that the mixing of Fe$^{2+}$ and Mg$^{2+}$ on M1 and M2 sites is better approximated by a 'simple mixture' model (Guggenheim, 1967) for each site individually. The orthopyroxene crystalline solution as a whole is found to be non-ideal asymmetric particularly at 500 and 600°C (Saxena and Ghose, 1970b). By using the intra-crystalline Mg$^{2+}$-Fe$^{2+}$ distribution data in orthopyroxene and the information on its solution behavior, the inter-crystalline Mg$^{2+}$-Fe$^{2+}$ distribution between orthopyroxene and another coexisting mineral can be interpreted more reliably. The study of Mg$^{2+}$-Fe$^{2+}$ distribution between orthopyroxene and another mineral yields important information on the temperature of crystallization of the host rock and on the thermodynamic nature of mixing of the Mg and Fe components in the other mineral.
The following notations and symbols are used:

Opx – orthopyroxene, Cpx – calcic pyroxene

Cum – cummingtorite

\( K_a \) – equilibrium constant for a reaction (a)

\( X_{Fe}^a \) – mole fraction \( Fe^{2+}/(Fe^{2+} + Mg^{2+}) \) in a phase \( a \) as on a site \( a \) in a phase

\( a_A^a \) – activity of a component A in a phase \( a \) or on a site \( a \); in the latter case they are referred to as 'partial' activity

\( w \) – an energy constant for 'simple mixture' (see Guggenheim, 1967)

\( \Delta G^0_a \) – standard free energy change for a reaction (a).

**COEXISTING ORTHO- AND CALCIC-PYROXENE**

**The Ion-exchange Reactions**

The ion-exchange reactions between orthopyroxene \( (Fe, Mg)_{2}Si_{2}O_{6} \) with M1 and M2 sites and Ca-pyroxene \( Ca(Mg, Fe)_{2}Si_{2}O_{6} \) with M2 site completely occupied by Ca are:

1. \( Mg(M1) + Fe(M1) \rightleftharpoons Fe(M1) + Mg(M1) \)
2. \( Mg(M2) + Fe(M1) \rightleftharpoons Fe(M2) + Mg(M1) \)
3. \( Mg(M1) + Fe(M2) \rightleftharpoons Fe(M1) + Mg(M2) \)
The equilibrium constants for these reactions are:

\[ K_1 = \frac{a_{\text{Mg}}^{\text{Mg}} a_{\text{Cpx}}^{\text{Cpx}}}{a_{\text{Mg}}^{\text{Mg}} a_{\text{Cpx}}^{\text{Cpx}}} \]
\[ K_2 = \frac{a_{\text{Fe}}^{\text{Fe}} a_{\text{Cpx}}^{\text{Cpx}}}{a_{\text{Fe}}^{\text{Fe}} a_{\text{Cpx}}^{\text{Cpx}}} \]
\[ K_3 = \frac{a_{\text{Fe}}^{\text{Fe}} a_{\text{Mg}}^{\text{Mg}}}{a_{\text{Fe}}^{\text{Fe}} a_{\text{Mg}}^{\text{Mg}}} \]

where \( a_{\text{Fe}}^{\text{Fe}} \) represents the partial activity of \( \text{Fe}^{2+} \) referred to the M1 site in orthopyroxene and similarly \( a_{\text{Mg}}^{\text{Mg}} \), \( a_{\text{Fe}}^{\text{Fe}} \) and \( a_{\text{Mg}}^{\text{Mg}} \) represent other partial activities. \( a_{\text{Cpx}}^{\text{Cpx}} \) or \( a_{\text{Cpx}}^{\text{Cpx}} \) are activities of the Fe and Mg components in Ca-pyroxene. In the present case, they are the same as the partial activity of Fe or Mg on the M1 site in Ca-pyroxene. The inter-crystalline ion-exchange reaction between

\[
\text{Mg} (\text{M1}) + 1/2 \text{Fe} (\text{M1} + \text{M2}) \rightleftharpoons \text{Fe} (\text{M1}) + 1/2 \text{Mg} (\text{M1} + \text{M2})
\]

The equilibrium constant for (4) is

\[ K_4 = \frac{a_{\text{Cpx}}^{\text{Cpx}} a_{\text{Opx}}^{\text{Opx}}}{a_{\text{Cpx}}^{\text{Cpx}} a_{\text{Opx}}^{\text{Opx}}} = \frac{a_{\text{Cpx}}^{\text{Cpx}} (a_{\text{Mg}}^{\text{Mg}} a_{\text{Mg}}^{\text{Mg}})^{1/2}}{a_{\text{Mg}}^{\text{Mg}} a_{\text{Mg}}^{\text{Mg}}} \]

Transforming \( K_4 \) in terms of \( K_1 \) and \( K_2 \), we have

\[ K_4 = K_1^{1/2} K_2^{-1/2} \]

\( K_1, K_2 \) and \( K_3 \) are interrelated as

\[ K_3 = K_1 K_2^{-1} \]
As discussed by Kretz (1963) and Grover and Orville (1969), the effect of pressure on these equilibrium constants is small. Therefore, we shall be mainly concerned with the temperature effect.

**Distribution of Mg\(^{2+}\) and Fe\(^{2+}\) between Ca-pyroxene and M1 Site in Coexisting Orthopyroxene**

The intra-crystalline Mg\(^{2+}\)-Fe\(^{2+}\) distribution data between M1 and M2 sites in orthopyroxene (Saxena and Ghose, 1970a) can be used to obtain the inter-crystalline distribution between M1 or M2 site in orthopyroxene and M1 site in clinopyroxene if the equilibrium temperature of the inter-crystalline ion-exchange is known. In absence of any experimental data on the Mg\(^{2+}\)-Fe\(^{2+}\) distribution between ortho- and Ca-pyroxenes in the temperature range of 500-800°C, the data available from natural assemblages are used. This involves both uncertainty in the temperature of crystallization as well as the non-stoichiometry of Ca in the M2 site in clinopyroxene. Both the pyroxenes in natural assemblages also contain small amounts of Al\(^{3+}\), Fe\(^{3+}\), Ti\(^{4+}\) and Mn\(^{2+}\). All these factors shall affect the quantitative results obtained by using the chemical data from natural assemblages.

The data on the distribution of Fe\(^{2+}\) and Mg\(^{2+}\) between coexisting ortho- and Ca-pyroxene in six rocks of granulite facies, chosen arbitrarily from the data in literature, are presented in Table 1. Assuming that the temperature of inter-crystalline equilibrium was 600°C in these rocks, the data on \(X_{Fe}^{M1}\) in orthopyroxene
corresponding to each composition are obtained from Fig. 1 (reproduced here from Saxena and Ghose, 1970a, Fig. 1). Similarly, the data on $X^M_{Fe}$ in orthopyroxene at 700°C are obtained and listed in Table 1. The distribution coefficient $K'$ is:

$$K' = \frac{1 - X_{Fe}^{Cpx}}{X_{Fe}^{Cpx}} \cdot \frac{X^M_{Fe}}{1 - X^M_{Fe}}$$

(3)

$K'$ would correspond to the equilibrium constant $K_1$ if both Ca-pyroxene (M1 site) and the M1 site in orthopyroxene were ideal. The values of $K_1'$ in Table 1 show that one or both of the phases may be non-ideal. As the Ca-pyroxene in the six samples do not contain Ca$^{2+}$: (Mg$^{2+} + Fe^{2+}$) as 1:1, the $K_1'$ values may change as a function of Ca concentration. A plot of concentration of Ca$^{2+}$ in Ca-pyroxene against $K_1'$ does not show any significant correlation between the two. Fig. 2, however, shows that there is a definite correlation between $K_1'$ and $X_{Fe}^{Cpx}$.

Although Ca$^{2+}$ does not completely fill M2 site in the six Ca-pyroxenes, a one site quasi-binary model for Ca-pyroxene may still be assumed. The absence of any correlation between $K_1'$ and concentration of Ca$^{2+}$ in the pyroxene favors this assumption.

Since mixing on the M1 site in orthopyroxene is non-ideal (Saxena and Ghose, 1970a), the $K_1''$ values can be improved by considering another equilibrium constant $K_1''$ as
These values, also listed in Table 1, continue to be a function of $X_{Fe}$. Therefore, the mixing of Fe- and Mg-components in Ca-pyroxene should be non-ideal to a certain extent.

Estimation of Temperature of Crystallization

Figure 3 shows a plot of $X_{Fe}^{\text{M1}}$ in orthopyroxene against $X_{Fe}^{\text{Cpx}}$. The open circles are based on the assumption that the temperature of inter-crystalline ion-exchange equilibrium was 600°C. Similarly, the solid circles represent 700°C. The M1 site in orthopyroxene is a 'simple mixture' (Saxena and Ghose, 1970a) of Fe$^{2+}$ and Mg$^{2+}$. Assuming that the one site quasi-binary Ca-pyroxene is also a 'simple mixture', the log of the equilibrium constant for (1) is

$$\ln K_1'' = \ln K_1' + \frac{w_{\text{M1}}}{RT} (1 - 2 X_{Fe}^{\text{M1}}) - \frac{w_{\text{Cpx}}}{RT} (1 - 2 X_{Fe}^{\text{Cpx}})$$

Equation (10), in an exponential form, was derived by Mueller (1964) and later used by Saxena (1969) in the logarithmic form. In Fig. 3, the distribution curves are drawn using a least squares fit to the distribution data in Table 1 according to equation (10). Table 2 shows the resulting constants. From Saxena and Ghose (1970a), the experimental values of $w_{\text{M1}}/RT$ are 1.294 at 600 and 700°C respectively. The difference between the experimental $w_{\text{M1}}/RT$ and the calculated $w_{\text{M1}}/RT$ in Table 2 is due to the actual temperature of crystallization
being different from either 600 or 700°C. By plotting the experimental $w^{M1}/RT$ and the calculated $w^{M1}/RT$ in Table 2 against temperature, the temperature of crystallization can be determined graphically from the intersection of the straight lines, one joining the calculated $w^{M1}/RT$ and the other joining the experimental $w^{M1}/RT$. This method of temperature estimation is quite general and can be applied to a group of coexisting pyroxenes with sufficient degree of Mg:Fe variation in the range of temperatures for which the intra-crystalline $w^{M1}$ values are available. The present data yield 620°C as the temperature of inter-crystalline ion-exchange equilibrium (4). Corresponding to this temperature $w^{Cpx}/RT$ is 0.625 and $K_1$ is 0.85.

Mg$^{2+}$-Fe$^{2+}$ Partitioning in Metamorphic and Igneous Pyroxenes:

Assuming that both orthopyroxene and Ca-pyroxene approach ideal solution closely at high temperatures corresponding to igneous rocks (1150°C), $K_4$ can be taken as 0.73 as obtained by Kretz (1963). $w^{Cpx}/RT$ at 600°C is then 0.650 (or $w$ is 1100 cal/mole) and the activity-composition relation (Fig. 4) in Ca-pyroxene Ca (Mg, Fe) Si$_2$O$_6$ is:

$$a^{Cpx}_{Fe} = x^{Cpx}_{Fe} \exp 0.650 (1 - x^{Cpx}_{Fe})^2$$

(11)

where $a^{Cpx}_{Fe}$ refers to the activity of Fe$^{2+}$ in the pyroxene crystalline solution and should be similar in magnitude to the activity of the end-member CaFe$_2$Si$_2$O$_6$. The equation (11) is for the 'simple mixture' as defined by Guggenheim (1967).
By taking $K_1$ as 0.85 at 600°C and combining it with $K_3$ as 0.2516 (from the experimental results in Saxena and Ghose, 1970a), $K_2$ is 3.38. $K_4$ is calculated to be 0.59 and $\Delta G_4^0$ is 915 cal/mole. The distribution curve at 600°C for the inter-crystalline Mg$^{2+}$-Fe$^{2+}$ distribution according to these data is shown in Figure 5. The ideal distribution curve with $K_4$ as 0.73 is also plotted.

It was noted by Saxena and Ghose (1970a) that the intracrystalline ion-exchange free energy $\Delta G_4^0$ does not change significantly with changing temperature. It is probable that $\Delta G_4^0$ also does not vary much with temperature. If we assume 1150°C for $K_4$ as 0.73, $\Delta G_4^0$ is 890 cal/mole which is of the same order of magnitude as $\Delta G_4^0$ at 600°C. The different distribution isotherms in the range of 600-1200°C shall be quite closely spaced. As a result, they cannot yield the temperature estimates very accurately.

COEXISTING ORTHOPYROXENE AND CUMMINGTONITE

Estimation of Temperature

The data on the distribution of Mg$^{2+}$ and Fe$^{2+}$ between coexisting orthopyroxene and cummingtonite in twelve metamorphic samples from Biwabik Iron Formation, Minnesota (Bonnichsen, 1969) are listed in Table 2. The ion-exchange reaction between cummingtonite and M1 site in orthopyroxene is written as

$$\frac{1}{7} \text{Fe} - \text{(all sites)} + \text{Mg} - \text{M1} \rightleftharpoons \frac{1}{7} \text{Mg} - \text{(all sites)} + \text{Fe} - \text{M1} \quad (12)$$

Cum \hspace{1cm} Op \hspace{1cm} Cum \hspace{1cm} Op
Disregarding the different sites in cummingtonite and assuming that the crystal as a whole is a 'simple mixture', the equilibrium constant for (12) is

$$\ln K_{12} = \ln K_D + \frac{w^{\text{Fe}^2+}}{RT} \left( 1 - 2 X_{\text{Fe}^2+} \right) - \frac{w^{\text{cum}}}{RT} \left( 1 - 2 X_{\text{Fe}^2+} \right)$$  \hspace{1cm} (13)

Assuming that the temperature of equilibrium in (12) is 500, 600 and 700°C, a least squares fit according to (6) for the data in Table 2 at each temperature is obtained. The results are shown in Table 3. The values of calculated $w^{\text{Fe}^2+}/RT$ in Table 3 are plotted against temperature and so also the experimental values of $w^{\text{Fe}^2+}/RT$ in orthopyroxene from Saxena and Ghose (1970a). A crossing of the two curves gives the temperature of inter-crystalline equilibrium (12) as 610°C.

The Mg$^{2+}$–Fe$^{2+}$ Distribution between Coexisting Orthopyroxene and Cummingtonite at 600°C

At 600°C the approximate value of $w^{\text{cum}}/RT$ is 0.42. The activity of Fe$^{2+}$ in cummingtonite at 600°C is:

$$a_{\text{Fe}}^{\text{Cum}} = X_{\text{Fe}}^{\text{Cum}} \exp \left( 0.42 (1 - X_{\text{Fe}}^{\text{Cum}})^2 \right)$$  \hspace{1cm} (14)

The value of the energy constant $w$ is 728 cal/mole at 600°C. The activity of Fe component in orthopyroxene may be calculated by using the analytical expression for the activity-coefficient (Saxena and Ghose, 1970b)

$$\log f_{\text{Fe}} = X_{\text{Mg}}^2 \left( 0.280 + 0.118 (3 X_{\text{Fe}} - X_{\text{Mg}}) + 0.190 (X_{\text{Fe}} - X_{\text{Mg}}) (5 X_{\text{Fe}} - X_{\text{Mg}}) \right)$$  \hspace{1cm} (15)
or graphically from Fig. 3 in Saxena and Ghose (1970b). The ion-exchange reaction between coexisting cummingtonite and orthopyroxene is:

\[
\frac{1}{7} \text{Mg} + \text{Cum} + \text{Fe} + \text{Opx} \rightleftharpoons \text{Mg} + \text{Opx} + \frac{1}{7} \text{Fe} + \text{Cum} \quad (16)
\]

The equilibrium constant for (16) is

\[
K_{16} = \frac{\alpha_{\text{Fe}}^{\text{Cum}} \alpha_{\text{Fe}}^{\text{Opx}}}{\alpha_{\text{Fe}}^{\text{Opx}} \alpha_{\text{Fe}}^{\text{Cum}}} \quad (17)
\]

Table 4 shows the value of \( K_{16} \) in six samples, selected to represent a wide composition range. The values of \( K_{16} \) using \( x_{\text{Fe}}^{\text{Cum}} \) as \( \alpha_{\text{Fe}}^{\text{Cum}} \) are also listed for comparison. The values of \( K_{16} \) are more uniform but they still vary with \( x_{\text{Fe}}^{\text{Cum}} \) or \( x_{\text{Fe}}^{\text{Opx}} \). It is probable that cummingtonite, similar to orthopyroxene (Saxena and Ghose, 1970b) is asymmetric crystalline solution and not the 'simple mixture' assumed in the preceding section. However, the deviations from a 'simple mixture' model is probably not great. The \( \Delta G_{16} \) at 600°C, assuming \( K_{16} \) as 0.79, is 400 cal/mole.

**DISCUSSION**

The availability of the intra-crystalline Mg\(^{2+}\)-Fe\(^{2+}\) distribution data in orthopyroxene at various temperatures when used with the Mg\(^{2+}\)-Fe\(^{2+}\) distribution data for the coexisting ortho- and Ca-pyroxene in natural assemblages makes it possible to interpret such inter-crystalline Mg\(^{2+}\)-Fe\(^{2+}\) distributions
without making various assumptions which were necessarily used by previous workers. In particular, it is not necessary to assume 1) the ideal mixing of Mg\(^{2+}\) and Fe\(^{2+}\) on individual sites in a pyroxene and 2) the equivalence of M1 site in Ca-pyroxene to the M1 site in orthopyroxene. The second assumption was introduced by Mueller (1962) and was used along with the first assumption by Banno and Matsui (1965) and Grover and Orville (1969). Although these assumptions are no longer required in the present work, a binary solution model for a multi-component phase has still to be used. Ca-pyroxene should be treated as a phase with three major components (Fe\(^{2+}\), Mg\(^{2+}\) and Ca\(^{2+}\)) distributed between two non-equivalent sites. The solution model for cummingtonite, a quasi-binary four site phase, is not yet definite.

ACKNOWLEDGMENTS

Thanks are due to Drs. R. F. Mueller and Dr. S. Ghose for very useful discussions.
REFERENCES


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<th>Sample</th>
<th>$X_{\text{Cpx}}^{\text{Fe}}$</th>
<th>$X_{\text{Op}}^{\text{Fe}}$</th>
<th>$X_{\text{M1}}^{\text{Fe}}$</th>
<th>$a_{\text{M1}}^{\text{Fe}}$</th>
<th>$a_{\text{M1}}^{\text{Mg}}$</th>
<th>$K'_1$</th>
<th>$K''_1$</th>
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<td>0.773</td>
<td>0.645</td>
<td>0.759</td>
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<td>0.978</td>
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<td>0.632</td>
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<td>0.500</td>
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<td>0.482</td>
<td>0.831</td>
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<td>0.855</td>
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$X = \frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}^{2+}}$, $a_{\text{Fe}}^{\text{M1}}$, partial activity referring to activity of Fe$^{2+}$ on M1 in orthopyroxene; the values are obtained from Fig. 1 of Saxena and Ghose (1970a).

$$K'_1 = \frac{X_{\text{M1}}^{\text{Fe}}}{1 - X_{\text{Op}}^{\text{Fe}}} \cdot \frac{1 - X_{\text{Cpx}}^{\text{Fe}}}{X_{\text{Op}}^{\text{Fe}}} \cdot \frac{1 - a_{\text{M1}}^{\text{Fe}}}{a_{\text{M1}}^{\text{Mg}} X_{\text{Cpx}}^{\text{Fe}}}$$

Samples: H-4-Metamorphic iron formation; northern Quebec; Kranck (1961). 115, 4642 A, 2941 and 2270-Charnockites from India; Howie (1955). Arendalite-From the type locality Arendal, southern Norway; collected by Saxena.
### TABLE 2

**Fe$^{2+}$-Mg$^{2+}$ Distribution Data in Coexisting Cummingtonite and Orthopyroxene**

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>$\chi_{Fe}^{Cum}$</th>
<th>$\chi_{Fe}^{Opx}$</th>
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<td></td>
<td></td>
<td></td>
<td>500°C</td>
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<tr>
<td>026</td>
<td>0.666</td>
<td>0.736</td>
<td>0.540</td>
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<td>0.573</td>
<td>0.631</td>
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<td>0.771</td>
<td>0.635</td>
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<td>304</td>
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Data on coexisting minerals from Bonnichsen (1969). Data on $X_{Fe}^{Opx}$ in orthopyxene from Fig. 1 (Saxena and Ghose, 1970a).
### TABLE 3

Equilibrium Constant $K_{12}$ and $w$ for the Data in Table 2

Using a Least Squares Program on Equation

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<th>$T^\circ C$</th>
<th>$K_{12}$</th>
<th>$w^{Cum}/RT$</th>
<th>$w^{Op}/RT$ (opx)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.36</td>
<td>-1.00</td>
<td>0.58</td>
</tr>
<tr>
<td>600</td>
<td>0.61</td>
<td>0.42</td>
<td>1.19</td>
</tr>
<tr>
<td>700</td>
<td>0.78</td>
<td>1.22</td>
<td>1.63</td>
</tr>
</tbody>
</table>

### TABLE 4

Calculation of Equilibrium Constants

<table>
<thead>
<tr>
<th>S. No.</th>
<th>$X^{Cum}_{Fe}$</th>
<th>$X^{Op}_{Fe}$</th>
<th>$a^{Cum}_{Fe}$</th>
<th>$a^{Cum}_{Mg}$</th>
<th>$a^{Op}_{Fe}$</th>
<th>$a^{Op}_{Mg}$</th>
<th>$K_1$</th>
<th>$K_1'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>0.274</td>
<td>0.310</td>
<td>0.341</td>
<td>0.749</td>
<td>0.420</td>
<td>0.725</td>
<td>0.78</td>
<td>0.65</td>
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<tr>
<td>304</td>
<td>0.353</td>
<td>0.416</td>
<td>0.421</td>
<td>0.681</td>
<td>0.530</td>
<td>0.640</td>
<td>0.75</td>
<td>0.66</td>
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<tr>
<td>073</td>
<td>0.573</td>
<td>0.631</td>
<td>0.620</td>
<td>0.490</td>
<td>0.740</td>
<td>0.430</td>
<td>0.73</td>
<td>0.78</td>
</tr>
<tr>
<td>026</td>
<td>0.666</td>
<td>0.736</td>
<td>0.698</td>
<td>0.402</td>
<td>0.810</td>
<td>0.360</td>
<td>0.77</td>
<td>0.88</td>
</tr>
<tr>
<td>082</td>
<td>0.722</td>
<td>0.771</td>
<td>0.746</td>
<td>0.346</td>
<td>0.825</td>
<td>0.320</td>
<td>0.86</td>
<td>1.04</td>
</tr>
<tr>
<td>234</td>
<td>0.743</td>
<td>0.787</td>
<td>0.764</td>
<td>0.324</td>
<td>0.840</td>
<td>0.310</td>
<td>0.87</td>
<td>1.07</td>
</tr>
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</table>

* $K_1 = \frac{a^{Cum}_{Fe} a^{Op}_{Mg}}{a^{Cum}_{Mg} a^{Op}_{Fe}}$  
$K_1' = \frac{X^{Cum}_{Fe} a^{Op}_{Mg}}{X^{Cum}_{Mg} a^{Op}_{Fe}}$
**FIGURE CAPTIONS**

Figure 1. Distribution of Mg$^{2+}$ and Fe$^{2+}$ between M1 site and M° site in orthopyroxene (from Saxena and Ghose, 1970a). The mole fractions $X_{Fe}^{M1}$ and $X_{Fe}^{M2}$ are determined by Mössbauer resonance spectroscopy on heated orthopyroxenes.

Figure 2. The distribution coefficient $K_1' = \left( \frac{1 - X_{Fe}^{Cpx}}{X_{Fe}^{Cpx}} - \frac{X_{Fe}^{M1}}{1 - X_{Fe}^{M1}} \right)$ plotted against $X_{Fe}^{Cpx}$ to show the non-ideal relationship.

Figure 3. The distribution of Fe$^{2+}$ and Mg between M1 in orthopyroxene and clinopyroxene. The curves are least squares fit according to the equation employing simple mixture model of Guggenheim (see Saxena and Ghose, 1970). The dashed curve uses the data on $X_{Fe}^{M1}$ in orthopyroxene at 600°C and the solid curve at 700°C.

Figure 4. Inferred activity-composition relation in calcic pyroxene Ca(Mg, Fe)Si$_2$O$_6$ at 600°C.

Figure 5. Distribution of Fe$^{2+}$ and Mg between ortho- and calcic-pyroxene. The data are from Kretz (1963). Open circles — metamorphic, crosses — igneous. The 600°C isotherm is based on activity-composition relations in clinopyroxene as shown in Fig. 3 and in orthopyroxene as listed in Table 1 (Saxena and Ghose, 1970b) $K_4$ is 0.59. The 1150°C isotherm is based on ideal solution model with $K_4$ as 0.73.
Figure 1. Distribution of Mg\(^{2+}\) and Fe\(^{2+}\) between M1 site and M2 site in orthopyroxene (from Saxena and Ghose, 1970a). The mole fractions \(X_{Fe}^{M1}\) and \(X_{Fe}^{M2}\) are determined by Mössbauer resonance spectroscopy on heated orthopyroxenes.
Figure 2. The distribution coefficient \( K' \) of \( \frac{1 - x^{Cpx}}{x^{Cpx}} \cdot \frac{x^{M1}}{1 - x^{M1}} \) plotted against \( x^{Cpx}_{Fe} \) to show the non-ideal relationship.
Figure 3. The distribution of Fe\textsuperscript{2+} and Mg between M1 in orthopyroxene and clinopyroxene. The curves are least squares fit according to the equation employing simple mixture model of Guggenheim (see Saxena and Ghose, 1970). The dashed curve uses the data on $X_{\text{Fe}}^{M1}$ in orthopyroxene at 600°C and the solid curve at 700°C.
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Figure 5. Distribution of Fe\(^{2+}\) and Mg between ortho- and clinopyroxene. The data are from Kretz (1963). Open circles — metamorphic, crosses — igneous. The 600°C isotherm is based on activity-composition relations in clinopyroxene as shown in Fig. 3 and in orthopyroxene as listed in Table 1 (Saxena and Ghose, 1970) \(x_{\text{Fe}}\) is 0.60. The 1150°C isotherm is based on ideal solution model with \(x_{\text{Fe}}\) = 0.73.