CHAPTER V

ORTHOPYROXENE-CLINIC PYROXENE-HORNBLende EQUILIBRUM
INTRODUCTION

An understanding of the phase relations existing among ortho and calcic pyroxenes and hornblendes which form solid solutions, can be attempted on the basis of their compositional relations. The compositional data has been presented in the previous chapter. Among the phases (op. cit.) the hornblendes are complex multicomponent phases and the graphical projections cannot be carried out satisfactorily. Therefore analyses of equilibrium relations or phase relations only be attempted in terms of the distribution of common elements in either phase. This approach has some additional advantages. Firstly it provides fairly sensitive indicator of chemical equilibrium and secondly the numerical values of distribution constants can be employed to measure a shift of mineral equilibrium. It is also noteworthy that the inherent assumptions in this method are fewer than in graphical analyses.

Theoretical considerations

The theoretical foundations of distribution of chemical species between different phases in a chemical system at equilibrium are well understood. Through the work of Remberg and DeWaele (1951) Kratz (1961, 1963) Mueller (1960), Albee (1965) and others, who have done pioneering studies on such equilibria in metamorphic rocks, it has been
found that a regular distribution of chemical species between coexisting mineral phases.

For coexisting orthopyroxene and calcic pyroxene, the magnesium-iron exchange reaction can be written as follows.

\[
CaMgSi_2O_6 + FeSiO_3 \rightleftharpoons CaFeSi_2O_6 + MgSiO_3 \quad (1)
\]

\[\Delta G^\circ, \text{ in } \text{Cpx} + \text{Fe in } \text{Cpx} = \text{h}_0, \text{ in } \text{Cpx} + \text{Kn in } \text{Cpx}.\]

At equilibrium:

\[
\frac{x_{(\text{MgFe})\text{Cpx}}}{1-x_{(\text{MgFe})\text{Cpx}}} \cdot \frac{1-x_{\text{Mg}}}{x_{\text{Mg}}} = \frac{\frac{f_{(\text{MgFe})\text{Opx}}^{\text{Mg}}}{f_{\text{Fe}}^{(\text{MgFe})\text{Cpx}}}}{\frac{f_{\text{Mg}}^{(\text{MgFe})\text{Cpx}}}{f_{(\text{MgFe})\text{Opx}}}} \cdot \frac{f_{\text{Fe}}^{(\text{MgFe})\text{Cpx}}}{f_{(\text{MgFe})\text{Opx}}} \cdot \frac{f_{(\text{MgFe})\text{Cpx}}^{\text{Mg}}}{f_{\text{Mg}}^{(\text{MgFe})\text{Cpx}}}
\]

\[\Delta F^\circ = RT\ln \left( \frac{x_{(\text{MgFe})\text{Cpx}}}{1-x_{(\text{MgFe})\text{Cpx}}} \cdot \frac{1-x_{\text{Mg}}}{x_{\text{Mg}}} \right)
\]

where \( x_{(\text{MgFe})\text{Cpx}} \) = Concentration of Mg in (MgFe) orthopyroxene

\( f_{(\text{MgFe})\text{Opx}}^{\text{Mg}} \) = Activity coefficient of Mg in (MgFe) orthopyroxene

and \( \Delta F^\circ \) = Standard free energy change of the reaction 1.

The left hand side of the equation (2) is the
equilibrium constant $K$ and the concentration coefficient is the distribution ratio $K_D$.

Therefore,

$$K = K_D, \quad K_f = e^{-\Delta F^0/RT} \quad \ldots \quad (1)$$

and for ideal mixtures $K = K_D$, ($K_f$ being unity). It should be mentioned that as soon as the number of exchangeable cations exceeds one in the individual formula, exponents appear in the $K_D$ term. However, recent work has amply justified the usual practice of writing exchangeable reactions as if there were only one ion to be exchanged. In terms of graphical depiction $x^\alpha_{Mg}$ versus $x^\beta_{Mg}$ will describe hyperbolic curves giving Rozeboom type of diagrams. If on the other hand $x^\alpha_{Mg}/(1-x^\alpha_{Mg})$ is plotted against $x^\beta/(1-x^\beta)$, a straight line passing through the origin would result.

Therefore,

$$K_D = \frac{x^\alpha (1-x^\beta)}{(1-x^\alpha) x^\beta}$$

Mueller (1960) and Kretz (1961) showed that the metamorphic orthopyroxenes and calcic pyroxenes exhibit equilibrium in Mg-Fe distribution. Kretz's compilation of natural pyroxene pairs (1963) shows that the distribution constants, $K_{Opx-Cpx}^D$ ($Mg$-$Fe$) are different for metamorphic and igneous pairs, while the same from ultrabasics do not have a distinctive range. The range of $K_D$ values for metamorphic
pyroxenes is 0.51 to 0.65 and that for igneous pyroxenes is 0.65 to 0.86. Bartholome (1962) pointed out that \( F_d \) values for Mg-Fe distribution bear a relation to the mole fractions of \( \text{CaSiO}_3 \) in calcic pyroxenes in such a way that \( X_{\text{Cpx-Cpx}} \), calculated as \( \frac{\text{Mg/Fe in Cpx}}{\text{Mg/Fe in Cpx}} \), values are less than 0.52 where \( X_{\text{Ca}} \) values in Cpx are greater than 0.45 and where greater than 0.62, the latter was less than 0.45. Generally \( X_{\text{CaSiO}_3} > 0.45 \) in metamorphic calcic pyroxenes and \( < 0.45 \) in igneous cases.

Since these researches, a number of publications have added to our knowledge of cation fractionation in coexisting pyroxenes from various metamorphic rocks. The recent contributions summarized are given hereunder:

1. Though theoretically Mg\textsuperscript{2+}-Fe\textsuperscript{3+} mixing can not be ideal because of crystal field effects associated with Fe\textsuperscript{2+} ions, no significant departure from ideality has been seen for Mg\textsuperscript{2+}-Fe\textsuperscript{3+} distribution between coexisting pyroxenes.

2. Determination of detailed structure of pyroxenes and amphiboles (Norimoto, Applemann and Evans, 1960, Close 1961) revealed the presence of non-equivalent sites. Orthopyroxenes are now known to possess two kinds of sites (\( M_1 \) and \( M_2 \)) with Fe distinctly preferring one site over the other. The Mg-Fe
distribution between pyroxenes as advanced by Mueller (op. cit) and Kretz (op. cit) were on the basis of one site model and hence needed modification. Natsui and Banno (1965) and Banno and Natsui (1966) have shown that apparent non-ideal behaviour of a solid solution may be due to the presence of sub-lattices. The Mg-Fe distribution in pyroxenes is further complicated by the fact that both the minerals have two structurally distinct cation sites and in such cases the deviation in one phase may tend to cancel that in another in exchange between two double site phases and consequently the degree of apparent nonideality may be negligible.

Kretz (1959) has shown that the distribution coefficient with respect to exchange between two chemical species is often seen to be dependent on the concentration of a third element. It has been amply borne out by later investigation that the Mg-Fe distribution among coexisting ferromagnesian silicates is dependent on Al (hbl-biot) and Mn-Ca (garnet) of the phases. It is interesting to observe that these "third element" are usually the members of the major end member components in addition to Mg-Fe components. In a later paper Kretz (1961) has developed a thermodynamic explanation for such
dependence. On the other hand for the purpose of
a general understanding of this dependence a
crystallo-chemical approach is more feasible. For
example it is a fairly established observation that
in calciferous amphiboles Al in tetrahedral coordi-
nation increases the affinity for Fe, presumably
by changing the polarizability or electronegativity
of oxygen shared between tetrahedral and octahedral
sites (Rambarg 1952). In the present state of our
knowledge it is not possible to go beyond such
empirical and general correlations and integration
of thermodynamic theory of complex mixtures with the
crystallo-chemical aspects of dependence of $K_D$ on
other elements is practically unattainable yet. With
respect to Mg"-Fe" distribution between pyroxenes,
the elements whose concentrations are most likely
to influence $K_D$ are Ca and Al. This is because the
major end members in the pyroxenes, especially the
diopsidic ones are CaSiO$_3$, FeSiO$_3$ and MgSiO$_3$ and Al
which sometimes reaches to a considerable concentra-
tion in the pyroxenes is known to affect such parti-
tioning as mentioned earlier. Pyroxenes from
Sivagumudram area are having Al contents mostly
comparable ones from each other (0.10 in the formula
per six oxygens). Hence the dependence of $K_D$ Mg-Fe
on Al is not expected and review of the published data did not reveal any such dependence either. The concentration of Ca then be the major influencing factor, if any such influence is seen to exist. The fact that Ca occupies MII position in calcic pyroxenes and Fe also prefers MII, hence the concentration of Ca would tend to lower the Fe content of calcic pyroxenes.

The role of Ca in orthopyroxene structure should be similar to that of dilute solution. Examination of calcium contents of natural orthopyroxenes reveals that the upper limit of most of them is about 0.07. In other words Ca's contribution to free energy will be negligible. It should also be mentioned that the concentration of Ca being very low in orthopyroxenes the errors in Ca estimation by gravimetric and titrimetric methods tend to be greater. On the basis of these considerations Ca in calcic pyroxene should be the most likely element whose concentration may affect the partitioning of Mg and Fe between two pyroxenes. It can be seen that despite geographical separation, $K_{Dpx-Cpx}$ values from granulites are quite similar even after allowing for slight modification owing to the third element concentration like Ca in Cpx. Such restrictions
of $K_D$ values is indeed striking and has yet to be explained.

The partitioning of common elements particularly Mg and Fe between coexisting pyroxenes presently analysed will now be discussed against this background.

(1) Magnesium and iron distribution

a) Orthopyroxene-calcic pyroxene: The magnesium-iron distribution between orthopyroxenes and calcic pyroxenes of the analysed granulites is shown in Fig. 22 and the numerical values are presented in Table XVII. The range of $K_D$ values is from 0.52 to 0.64. The presence or absence of hornblende generally affects the $K_D$ values and higher values above (0.57) for hornblende poor pyroxene granulites and lower values (0.58) for hornblende rich pyroxene granulites are often seen. The variation in the $K_D$ values are apparently due to calcium contents of the calcic pyroxene. If we calculate the $K_{Opx-Cpx}$ as $\frac{Mg/Fe \text{ in Opx}}{Mg/Fe \text{ in Cpx}}$ and the inverse relation between calcium contents and $K_D$ can only mean that calcium plays a complementary role to iron in the crystal structure as it prevents the intake of iron. In addition, the ferric content of the calcic pyroxene is comparatively high and if the ferric iron is derived by oxidation of Fe$^{2+}$ as it seems likely, the $K_D$ value with respect to Mg-Fe is
affected. Therefore the varying amounts of Ca in Cpx, provide a reasonable explanation of variation of $C_{\text{Cpx-Cpx}}^{\text{Opx}}$. The calcium content of orthopyroxenes should also play a role but because of their dilute concentration no conspicuous relations can be deciphered.

Engel and Engel (1962) and others have established that in the hornblende-pyroxene granulites, the pyroxenes are derived by the break-down of hornblende. As the calcic pyroxenes of the present study are confined only to the basic charnockites, the basic granulites can be taken to represent arrested stages of hbl - 2 pyroxene break-down equilibrium and Mg-Fe mixing place in hornblende also. Therefore if the Mg-Fe distribution among the three phases is seen, the hornblende are found to have lower Mg/Fe ratios for most of the samples than the coexisting calcic pyroxenes but higher ones than the orthopyroxenes. Examination of the published data shows that similar situation is valid for such rocks. The Mg/Fe ratios of the hornblende could be matched by the Mg/Fe ratios of the two pyroxenes combined. In general Mg/(Mg+Fe) ratios of the rocks also matching (in 1:1 fashion) with hornblende, inspite of varying modal proportions of the two pyroxenes. In other words the $K_{\text{Opx-hbl}}$ i.e. $(\text{Mg/Fe})$ in Opx/$(\text{Mg/Fe})$ in hbl has varied directly with $K_{\text{Opx-hbl}}^D(\text{Mg-Fe})$ and the hornblende can be said to have acted as a "buffer" in orthopyroxene-calcic pyroxene
FIG. 22: PLOT OF $X \times Mg^+$ IN CO-EXISTING ORTHO AND CLINOPYROXENES.
Mg-Fe exchange equilibrium.

b) Hornblende-pyroxene

Table XVIII shows that the \( k_{D(Mg-Fe)}^{Cpx-hbl} \) and \( k_{D(Mg-Fe)}^{Crx-hbl} \) values have considerable variation in \( K_D \) values but when considered the differing tetrahedral Al contents of the hornblendes which are affecting the Mg-Fe distribution between hornblendes and other ferromagnesian silicates (Gretz 1960, Coxina 1962) a systematic relation emerges.

Ramsberg (1952a) has pointed out that in a general way, increasing Al\(^{IV} \) in hornblendes results in a greater affinity for Fe\(^{2+} \), hence \( k_{D(Mg-Fe)}^{Cpx-hbl} \) as calculated here should increase.

The Mg-Fe distribution in hornblende-pyroxene of Willyama samples (Binns 1965a, 1965b) shows that there is an increase of \( k_{D(Mg-Fe)}^{Cpx-hbl} \) from A to B correlative with increasing Al\(^{IV} \) in hornblendes. In Adirondack samples also (Engel et al. 1964) same effect is seen but they show a very narrow range of variation. Therefore the effect of Al\(^{IV} \) in hornblende on \( k_{D(Mg-Fe)}^{Cpx-hbl} \) has been tested.

The effect of calcium contents in hornblendes is not clear. However it is generally true that in basic granulites of a particular area the range of variation of calcium is much less than that in calcic pyroxene and
calcium contents of hornblendes can be taken to be more or less constant.

Regarding the Mg-Fe distribution between hornblendes and pyroxenes the following points are clear:

i) The major controlling factor is \( A^VI \) in hornblendes, with minor role played by calcium in pyroxenes and ferric to ferrous ratios in hornblendes.

ii) The intergroup displacements in hbl-cpx and hbl-cpx distribution lines are in the same direction; this is the graphical expression of direct variation of numerical values of the two \( K_D \) s.

iii) The calcium content of calcic pyroxene is superimposed even in hbl-pyroxene equilibrium. Hence \( K_{cpx-cpx}^{D(Mg-Fe)} \) is ultimately affected by calcium in calcic pyroxene. It should also be noted that \( K_{cpx-hbl}^{D(Mg-Fe)} \) values tend to be less variable than \( K_{cpx-hbl}^{D(Mg-Fe)} \) values (Table XVII).

iv) The modification of \( K_{cpx-hbl}^{D(Mg-Fe)} \) and \( K_{cpx-hbl}^{D(Mg-Fe)} \) by \( (Ca)_{Cpx} \) is such as would be expected if Ca were to compete for the same site as Fe in calcic pyroxene structure, supporting thereby the results of site preference studies in pyroxenes.
v) Mg-Fe distribution between two pyroxenes as well as between hornblendes and pyroxenes can be explained on the basis of ideal mixing if modifying influence of a third element like Al in hornblende is considered.

A few comments on Mg-Fe distribution trends among pyroxenes and amphiboles as correlated with different crystal sites (Suessman 1968) are pertinent in this connection. With respect to Mg-Fe distribution between calciferous amphiboles and pyroxenes, Suessman (op. cit) argues that $M_4$ and $M_{II}$ sites will be taken up by Ca and of the remaining sites $M_1$ and $M_3$ of amphiboles are similar in environment to $M_1$ of pyroxenes but $M_2$ in amphiboles is known to be preferred by Fe. Thus according to him Fe-Mg ratio will tend to be higher in the amphibole. In addition to pointing out the observational data that this trend never applies to coexisting calciferous amphibole-orthopyroxene (as already shown) it is worth noting that $M_1$ and $M_2$ have strictly no parallel in pyroxene structure and tetrahedral substitution by Al can change the electronegativity of the oxygen. In amphibole structure, it is true that there is a preference of Fe over Mg in $M_2$ site, but in $M_1$ and $M_3$ sites as revealed by recent structural investigations, Mg is preferred over Fe. In view of the multiple controls exerted by crystal field stabilization energy of Fe, entropy effects due to randomization over
different sites and modification of chemical bonding due to preference of Al in tetrahedral coordination, the generalizations advanced by Russman (op.cit) are seem to be over simplified.

**Partitioning of other cations**

The fractionation of Mg and Fe is of prime importance in understanding Cpx-Cpx-hbl phase relations, because as a first approximation, compositions of these phases can be expressed in terms of different degrees of combination of Mg and Fe end members. Secondary it can be stated that the different behaviour of 
MgO and FeO (or MgSiO$_3$, FeSiO$_3$ etc) components in silicate phase relations is a well established fact and, experimental as well as theoretical studies in petrology have greatly emphasised the Mg-Fe composition, among coexisting ferromagnesian silicates have brought out many significant observations relating to partitioning of other elements like Mn, Ti, Ca etc. The distribution of these elements among orthopyroxene, calcic pyroxene and hornblende will now be examined.

**ii) Manganese**

It can be seen from the compilation of Kretz (1963) that pyroxene pairs from granulites and related rocks exhibit a variable but not entirely erratic pattern, and the partitioning of Mn is dependent of Mg/Fe ratios of the
minerals. Distribution coefficients for Mn calculated as

\[
\frac{\text{Mn/(Mg+Fe+Mn)} \text { in Cpx}}{\text{Mn/(Mg+Fe+Mn)} \text { in Cpx,}}
\]

from the type area samples (Howie 1955, Subramaniam 1962) is found to vary from 0.9 to 1.5. Ray and Sen (1971) have studied the distribution of Mn between coexisting calcic pyroxenes and hornblendes showing a fairly good correlation obeying Nernst's law, but the fractionation between orthopyroxene and hornblende does not show any pattern. The \( K_D \) values range from 0.80 to 2.86, whereas the \( K_D \) values from calcic pyroxene and hornblende range from 0.95 to 2.26. The samples from Sivasamudram are having the values for Cpx-hbl, 0.70 to 1.61 and for Opx-hbl from 1.22 to 1.80 (See Table XX). Therefore it is reasonable to conclude that manganese shows a fairly close approach to equilibrium distribution among these ferromagnesian silicates and behaves as a dilute constituent obeying Nernst's distribution law.

iii) Titanium

The fractionation of Ti between ortho and calcic pyroxenes and pyroxene-hornblende is found to be erratic and wide scatter is observed in Sivasamudram samples. The \( K_D \) values, for (1) Cpx-hbl are 0.095 and 0.180 (2) Opx-hbl are 0.116, 0.086 and 0.455, and (3) for Opx-Cpx it is 1.37 and 0.48. It is a common experience of other investigators also
that titanium usually fails to attain an equilibrium partitioning between coexisting phases. Frequently small inclusions of ilmenite are found in the hornblends and pyroxenes and to get pure concentrates free from these inclusions is almost impossible. Secondly the concentration of titanium may be partially dictated by charge balance considerations (particularly in hornblends) and/or owing to a greater strength of Ti-O bonds, Ti may fail to achieve equilibrium distribution by communicating chemically with the rest of the environment. Roy and Sen (1971) did not find an equilibrium distribution for the type area samples, neither is it evident in willyama (Bins 1965b) and Adirondack (Engel et al. 1964) samples.

iv) Sodium-potassium-calcium

Sodium and potassium do not show any regular pattern in their distribution in hornblende-calcic pyroxene and orthopyroxene. When multicomponent phases like hornblends and pyroxenes coexist it is not necessary that all cations should show regular fractionation. After one or more cations achieve equilibrium distribution, the process of chemical exchange could come to a stop because the potentials with respect to these elements have been nullified, and the rest of the cations might not attain an equilibrium distribution. This is further complicated by the fact that concentrations
of Na and K, occupying vacant positions in hornblendes have
to meet the demands of charge balance owing to heterovalent
substitutions.

The distribution coefficient values for calcium in
coexisting calcic pyroxenes and hornblendes of Sivagamudram
area range from 1.33 to 1.80. However the calcium distribu-
tion between the two pyroxenes is not very regular. This may
be due to sizeable error in estimation of Ca in orthopyro-
oxenes. Generally the Ca content of the orthopyroxenes in
these samples is more or less same, whereas the Ca content of
the calcic pyroxene decreases with increasing Fe²⁺ (Binns
1962). Therefore it is reasonable to conclude that small
variations in Ca contents of orthopyroxenes have been masked
by analytical errors. The Kp values for calcium in different
phases in compiled in Table XIX, along with the values given
by Ray and Sen (1971) from type are charnockites (Madras).
These values are quite comparable.

In conclusion, the following results with respect
to equilibrium relations among orthopyroxene calcic pyroxene
and hornblendes of Sivagamudram area need to be emphasized.

1) Distribution of magnesium and iron shows a close
approach to chemical equilibrium in the present
samples.
2) Distribution pattern of Mg and Fe between hornblende calcic pyroxene, and orthopyroxene indicates the break-down reaction as follows.

\[
\text{Hornblende + quartz } \xrightarrow{\text{orthopyroxene + Calcic pyroxene}} \text{ + Plagioclase + Water}
\]

3) Partitioning study involving all the three phases strongly suggest that hornblende-pyroxene equilibrium was the controlling factor.

4) Mg-Fe distribution between two pyroxenes is modified by calcium contents of calcic pyroxenes, where as hornblende-pyroxene distribution is modified by mostly tetrahedral Al contents of the hornblende and also by the Ca contents of the calcic pyroxenes.

5) There is some indication that oxidation influences the Mg-Fe distribution by changing Mg/(Mg+Fe) ratios.

6) Finally the Mg-Fe distribution constants fall well within the range of metamorphic pyroxene pairs.