CHAPTER III

X-RAY AND IR STUDY OF THE MINERALS
A. X-RAY STUDY OF THE MINERALS

INTRODUCTION

Powder diffractograms of orthopyroxenes, calcic pyroxenes, hornblendes and garnets were taken, with cobalt Kα radiation and iron filter, on micronet-II, Czech-made X-ray diffractometer. The scanning speed was 1° per min. On the chart scale of 1 cm for 1°/min. The mineral powders (<2 µ) were mounted as thin eams on a glass slide by mixing them thoroughly with celluloid solution. Care was taken to have uniform thickness on the glass slide. The voltage, current and slit opening varied from sample to sample. First the scanning was done (to adjust the highest intensity peak) for 2θ = 70°. Several check points were taken to locate exactly the positions of the angles on the diffractogram paper. Much attention was not paid to the intensity of the lines. Only comparative intensity of the lines was taken into account to enable comparison with other data, and indexing of the lines. The scale of the diffractogram paper was kept at 3 x 10². The unit cell dimensions a, b, c and β angles have been calculated from the reciprocal parameters of three suitable indexed planes and the X-ray data is presented in Tables X, XI, XII and XIII.
1) Orthopyroxenes

Warren and Medal (1930) were the first to study the structure of enstatite and Mg-rich hypersthene. They established that the orthopyroxenes have a space group \( V_n \), that is \( P_1 b c a \). Ramberg and DeWolfe (1951) studied the changes in the optical properties and the unit cell dimensions of the orthopyroxenes with the composition. On plotting the unit cell dimensions 'a' and 'b' against the corresponding composition, they found that there was not a linear relationship and so they concluded that the orthopyroxenes do not form an ideal mixed crystal series.

Hess (1952) determined the unit cell dimensions of a number of orthopyroxenes of Bushwald type. He found that the cell dimensions of orthopyroxenes vary in a linear fashion with the change in chemical composition, gradually increasing towards the iron end. He expressed the linear relationship in the form of following equations.

\[
\begin{align*}
a &= 19.225 \text{ Å}^0 + 0.00205 (100 - \text{Mg}) \text{ Å}^0 \\
b &= 8.805 \text{ Å}^0 + 0.00255 (100 - \text{Mg}) \text{ Å}^0 \\
c &= 5.105 \text{ Å}^0 + 0.00073 (100 - \text{Mg}) \text{ Å}^0
\end{align*}
\]

where

\[
\text{Mg} = \frac{100 \times \text{Mg}^{2+}}{\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+}}
\]
The 'd' values were accurately determined using the \( \sin^2 \theta \) values the peaks were indexed as follows.

The interplanar spacing for the orthorhombic system can be written as

\[
\theta = \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

\[
\frac{1}{d_{hkl}} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}
\]

and the Bragg equation can be written in the form

\[
\frac{1}{d_{hkl}} = \frac{n \sin \theta_{hkl}}{\lambda}
\]

If the two equations are squared and combined, the following relation is obtained

\[
\frac{4 \sin^2 \theta_{hkl}}{\lambda^2} = \frac{1}{d_{hkl}^2} = \frac{1}{\lambda^2}
\]

\[
= h^2 \frac{1}{a^2} + k^2 \frac{1}{b^2} + l^2 \frac{1}{c^2}
\]

\[
\sin^2 \theta_{hkl} = h^2 \frac{\lambda^2}{4a^2} + k^2 \frac{\lambda^2}{4b^2} + l^2 \frac{\lambda^2}{4c^2} \quad \text{.... (1)}
\]

\[
= h^2 a^2 + k^2 b^2 + l^2 c^2 \quad \text{.... (2)}
\]
The cell dimensions of these three orthopyroxenes are plotted against their compositions in Fig. 10 and the plots of these points agree well with the values given by Hess, thereby suggestive of linear relationship of cell dimensions with the compositions of the analysed orthopyroxenes excepting the values of 'b' dimensions. The values of 'b' dimension are slightly lower ranging from 8.90 Å to 8.93 Å. Ramberg and Devore (1951) have also observed that the intermediate orthopyroxenes generally contain much Al2O3 and consequently they deviate from the linear relationship. The present samples are richer in Al2O3 (0.04 to 0.08). Consequently there is a considerable decrease in the 'b' dimension and Hess attributes that this is due to the replacement of Mg2+ and Fe2+ by the smaller Al3+ ion. Houle (1963) has pointed out the effect of Al in octahedral site on 46 orthopyroxenes from granulites. Ghose (1969) showed from X-ray diffraction data of metamorphic pyroxenes, that most of the iron was in octahedral site M2 and most of the magnesium in M1 site. Smith et al. (1969) showed that for all orthopyroxenes 'a' dimension is increased by Fe and it has affected little by Al and markedly increased by Ca, 'c' dim is increased by Fe and probably by Ca. The marked increase of 'a' by Ca and decrease of 'b' by Al is

\[ a = \frac{x^2}{4a^2}, \quad b = \frac{x^2}{4b^2}, \quad \text{and} \quad c = \frac{x^2}{4c^2} \]
quite common. The orthopyroxenes of Sivasonadram charnockites have higher alumina content which affects the 'b' dimension (lower values). The 'a' dimension of these samples is slightly greater than the values given by Kuno (1954).

11) Clinopyroxenes

Kuno and Ross (1953) first showed that there was a gradual change in the unit cell dimensions in the clinopyroxene trapezium (diopside-clinoenstatite, ferrosalite-hedenbergite). The diopside-pigeonite series was studied in detail by Kuno (1955). He showed that the substitution of Fe$^{2+}$ for Ca$^{2+}$ (Mg being constant) has considerable effect on the unit cell dimensions. Brown (1960) investigated the clinopyroxenes from Skevsgard intrusion, which showed a continuous replacement of Mg$^{2+}$ by Fe$^{2+}$ and he constructed the diopside-hadenbergite, clinoenstatite-ferrosalite trapezium, which showed a series of straight lines representing a variation in a Sin $\beta$ and 'b' dimension of the pyroxenes against chemical composition. He also examined the effect of Al$^{3+}$ content in sixfold coordination on unit cell dimensions.

The author has studied the clinopyroxenes from the charnockites by optical, chemical and X-ray methods to correlate their relationships. The indexing of the powder diffractograms was done with the help of Kuno's powder pattern and also following the procedure of Buerger and Asaroff.
brief summary of which is given below.

The interplanar spacing for monoclinic system is

\[ d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{2hl \cos \beta}{a c \sin^2 \beta} + \frac{k^2}{b^2}}} \quad \ldots (1) \]

If \( l = 0 \), the equation (1) reduces to

\[ d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2}}} \quad \ldots (2) \]

Bragg equation can be written as:

\[ \frac{1}{d_{hkl}} = \frac{2 \sin \theta_{hkl}}{\lambda} \quad \ldots (3) \]

If equations (2) and (3) are squared and combined the following relation is obtained

\[ \frac{4 \sin^2 \theta_{hko}}{\lambda^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} \quad \ldots (4) \]

\[ = h^2 \frac{\lambda^2}{4a^2 \sin^2 \beta} + k^2 \frac{\lambda^2}{4b^2} \quad \ldots (5) \]

\[ = h^2 \lambda + k^2 \mu \quad \ldots (6) \]
where
\[ A = \frac{\gamma^2}{4a^2 \sin^2 \beta} \quad \text{and} \quad B = \frac{\gamma^2}{4b^2} \]

Similarly \( \sin^2 \phi_{hkl} = k^2 B + l^2 C \) \( \cdots (7) \)

where
\[ B = \frac{\gamma^2}{4b^2} \quad \text{and} \quad C = \frac{\gamma^2}{4c^2 \sin^2 \beta} \]

The equation (1) can be written as

\[ \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{l^2}{c^2 \sin^2 \beta} + \frac{2hl \cos \beta}{ac \sin^2 \beta} + \frac{k^2}{b^2} \cdots (8) \]

or

\[ \sin^2 \phi_{hkl} = h^2 + l^2 c + 2hl \sqrt{ac \cos \beta} + k^2 \]

\[ \cdots (9) \]

once the values of \( A, B, \) and \( C \) are determined \( \beta \) can be determined by using eq. (9). From the values \( A, B \) and \( C \) and knowing \( \beta \) \( a, b \) and \( c \) can be calculated.

Brown (1960) has shown the variation in 'b' dimension with \( \text{Mg}^{2+}, \text{Fe}^{2+} \) and \( \text{Ca}^{2+} \) content of the calcic pyroxene. As all the three samples under study have the calcium content ranging from 41 to 43% and the 'b' values are plotted in Brown's figure which is reproduced as Fig. 11. Brown has examined the effect of the substitution of \( \text{Ca}^{2+} \) by \( \text{Fe}^{2+} \) on \( a \sin \beta \). (\( \text{Mg} \) remaining constant at 50%) and has shown that
the change is linear (Fig. 12).

The change with the total replacement of Ca$^{2+}$ by Fe$^{2+}$ is 0.30 Å. He drew a $\sin \beta$ line at all values of Mg (10 to 100%) the change in a $\sin \beta$ with the replacement of Ca$^{2+}$ by Fe$^{2+}$ is the same. Therefore the cell dimensions of clinopyroxenes of Sivasamudram charnockites agree with the composition variation as drawn by Brown (1960).

iii) Amphiboles

Berman classified the amphiboles on the basis of the values of WXY and Z groups where

\[ W = \text{Ca, Na, K} \]
\[ X = \text{Mg, Fe}^{2+} \text{ Mn} \]
\[ Y = \text{Fe}^{3+}, \text{Al, Ti} \]
and \[ Z = \text{Si + Al} \text{ into hornblende, edenite, hastingite, glaucoephane and arvedsonite as below.} \]

\[
\begin{align*}
W & \quad X & \quad Y & \quad Z = (\text{Si + Al}) \\
3 & \quad 5 & \quad 0 & \quad 7:1 \quad \text{Hbl. Edn} \\
3 & \quad 4 & \quad 1 & \quad 6:3 \quad \text{Hastingite} \\
3 & \quad 3 & \quad 2 & \quad 8:0 \quad \text{Glaucophane} \\
3 & \quad 4 & \quad 1 & \quad 8:0 \quad \text{Arvedsonite}
\end{align*}
\]
According to bin? isarag&site lies between hornblende-adénite and hastingsite.

The W X Y and 2 values of the analysed amphiboles are presented below:

<table>
<thead>
<tr>
<th>Ref.No.</th>
<th>W</th>
<th>X</th>
<th>Y</th>
<th>2 (Si:Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.4</td>
<td>4.2</td>
<td>.95</td>
<td>6.5 : 1.5 (approx)</td>
</tr>
<tr>
<td>2</td>
<td>2.4</td>
<td>4.2</td>
<td>.83</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>4.4</td>
<td>.99</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>4.3</td>
<td>.89</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.7</td>
<td>4.0</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.6</td>
<td>4.1</td>
<td>.93</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.4</td>
<td>4.1</td>
<td>.99</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>4.4</td>
<td>.96</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.2</td>
<td>4.4</td>
<td>.87</td>
<td></td>
</tr>
</tbody>
</table>

The X-ray powder data for four hornblende samples is given in Table XII. As the 'd' values of these minerals are very close to each other and there is not much difference in chemical analyses also, it has not been possible to predict the influence of chemical composition on the cell dimensions.

iv) Garnet

Winchell (1958) has given two diagrams to determine
the chemical composition of the garnets from their physical properties. He plotted the refractive index against cell dimensions. These properties determined the shape of the diagrams and on these diagrams, contours representing the variation in Sp. Gr. were superposed. Each corner of the diagrams represented a particular type of garnet. But even this as Winchell (op.cit) himself observed, at times gives two of three compositions for a set of physical properties. Moreover the accurate determination of the amount of FeO present in this mineral is rather difficult. The specific gravity is normally not accurate because of small inclusions of other minerals in the garnet. The garnets under study contain appreciable amount of iron and cobalt radiation is used for X-ray analyses and if the diffraction goniometer is well aligned the \( d_{420} \) garnet line may be directly converted to \( d_{420} \) by using cobalt radiation tables. Because garnet is cubic \( a^2 = d_{hkl}^2 \) \((h^2 + k^2 + l^2)\)

\[
a^2 = 20 d_{420}^2 \quad \text{and} \quad a, (\text{\AA}) = 4.472 d_{420}
\]

The X-ray data along with other physical properties of Sivagamadram garnets is given in Table XIII. The cell edges \((a = 11.62 \quad \text{and} \quad a = 11.64)\) with Sp.Gr. and refractive index values, when superposed on the diagrams (Fig. 13, 14 and 15) of Winchell (1958), the composition of the end members obtained is as follows.
Almandine mol. 55, pyrope mol. 25 and grossular mol. 15. This composition when compared to the chemical composition (analysed) show slightly lower percentage of almandine and higher percentage of pyrope molecules. This may be accounted partly due to determination of ferrous iron in garnets.

B. INFRARED ABSORPTION SPECTROSCOPY

INTRODUCTION

Infrared spectroscopic experiments have been chiefly employed for the structural analysis of organic materials. The application of IR to the mineralogical studies started in 1950. R. J. P. Lyon (1962) made a systematic IR study of almost all the mineral groups. In recent years the American mineralogists have published a number of papers dealing with the applications of IR to the silicate minerals. Now it is clear that IR spectrum of a mineral obtained by absorption reflection, or emission techniques is characteristic of the mineral. The structural formula of the mineral can be determined without any chemical analysis (semi quantitative analysis). The frequency of an IR absorption band is determined mainly by bond "elasticity" and relative masses of the bonded atoms. The shifts in frequency of IR are also, due to the nature, size and electronegativity of the neighbouring atoms,
due to phase changes and hydrogen bonding. Therefore an IR spectra yields an entirely different 'view' of the analysed material than the X-ray analysis. X-ray yields the periodic arrangement of atoms in the crystal lattice and on the other hand IR is more sensitive to the short range ordering on neighbouring atoms. Infrared techniques are capable of distinguishing minerals with following main groups.

1. Minerals of relatively constant chemical composition.

2. Minerals that exhibit marked differences in composition of major elements (plagioclases, garnets pyroxenes and amphiboles).

3. The polymorphic modifications of the minerals (Muscovite - orthoclase).

4. The variation in chemical composition with structural modification (Plagioclases).

Infrared study of minerals is intended now mainly to the variable properties of a mineral or the mineral groups, like atomic substitution (not for trace elements) solid solution, structural modification and hydration. In this connection the work of Lyon and Tuddenham (1960) is very extensive. They have been able to measure quantitatively the substitution of aluminium for silicon in the tetrahedral sites of the minerals. They have also employed IR for the
model analysis of rocks (both artificial and natural).

Analytical method adopted

The mineral sample required for this study is very little (about 0.5 mg). But the purity of the mineral is very important. The impurities like quartz and carbonates even 1% in the sample produce marked variations in the nature of the spectrum produced. The size of the sample also affects the spectrum and for optimum spectra the sample particle size should be below the wavelength of the radiation being used. To avoid the scattering effect of the material the sample is mixed with Nujol mull. As the minerals under investigation are silicates, the strongest absorptions will be in the region of 9.0 to 10.0 μ (1100 to 1000 cm⁻¹) and also near 13.3 μ to 25 μ (750 to 400 cm⁻¹).

Interpretation

The IR spectral chart compared to the X-ray diffractogram is simple and the peaks are diagnostic in shape and a fewer in number. The peaks of IR show less variation for a mineral species. Therefore the interpretation of spectra involves recognition of peaks with their shapes. The identified peaks are compared with the known mineral spectra. Therefore the identification is rather empirical. The nature of spectra of analysed minerals are as follows,
(i) Potash feldspars

The order-disorder nature of the feldspars is indicated by a definite peak of 648 cm$^{-1}$ as ordered K-feldspars. The substitution of Fe$^{3+}$ for Al$^{3+}$ is not seen in these minerals as the peaks 648 cm$^{-1}$ donot change to 514 cm$^{-1}$ region. Therefore the potash feldspars selected from gneisses, granites and mylonites donot show any change in composition and in structural disorder. They all belong to the ordered mica-clines (see Fig. 16), and the potash feldspars from charnockites were not studied as the mineral was perthitic.

(ii) Orthopyroxenes

Five samples of orthopyroxenes were analysed for IR and the peak positions clearly shift with the substitution in Mg$^+$ by Fe$^+$ in this group. The orthopyroxenes show the characteristic absorption at about 490 cm$^{-1}$. But the next peak varies from 525 to 550 cm$^{-1}$, which is due to the variation in composition (atomic substitution). 525 cm$^{-1}$, peak is for ferrohypersthene and this shifts to 545 cm$^{-1}$ in bronzite (Fig. 17A).

The peaks at 635, 675 cm$^{-1}$ and at 890 and 950 and 1025 cm$^{-1}$ are characteristic peaks which are common for ferrohypersthene. Therefore the orthopyroxenes under investigation are mostly ferrohypersthene and no polymorphic
modifications are indicated.

(iii) Clinopyroxenes

Four samples of clinopyroxenes from charnockites are subjected to infrared absorption spectra. All the samples of clinopyroxenes show absorption peaks in the regions 512 to 515 cm⁻¹ characteristic of diopside pyroxenes and also at 634 cm⁻¹, 670 cm⁻¹ and 860-875 cm⁻¹ region. But the peaks in the region 960 show variations from 960 cm⁻¹ to 980 cm⁻¹. This variation when compared to the chemical composition of the clinopyroxenes may be ascribed to Ca and Mg components. The last peak at 1070 cm⁻¹ common for all the samples is very sharp. This peak is also noticed for augites. Therefore the clinopyroxenes from basic charnockites don't show any marked variations in the general nature excepting in the region 960 to 980 cm⁻¹ region. All of them indicate diopside to augite composition. The absence of any peaks at 730 to 745 cm⁻¹ range also indicates that aenite, omphacite and jadeite are not present. The strong absorption peak at 922 cm⁻¹ also indicates diopside (See Fig. 173).

(iv) Hornblende

Five samples of hornblende from acid to basic charnockite and amphibolite are studied by IR and all of them show characteristic absorption peaks at 455 to 465 cm⁻¹ region,
excepting one sample which showed first absorption at 440
\text{cm}^{-1} (No. 25). But this sample also shows absorption at
455 \text{cm}^{-1}. Neither glaucophane nor riobackite have both peaks
(at 440 and 455 \text{cm}^{-1}). As amphiboles permit greater Al, Si
substitutions in the \text{Si}_4\text{O}_{11} chain and greater degree of
atomic substitution, their interpretation is more complicated.

The second peak varies from 504 to 515 \text{cm}^{-1} in the
analyzed samples from charnockites and amphibolites, indic-
ating them to be common hornblende, similarly the peak at
635 \text{cm}^{-1} and at 690 \text{cm}^{-1} is conspicuous for hornblendes. The
peak at 653 \text{cm}^{-1} varies from 946 to 960 \text{cm}^{-1} again. Therefore
it is clear that even though there is a slight variation in
the peak number they belong to only hornblende group but not
to the alkali amphibole group and as the author has not got
the data for other minerals of this group, the interpretation
of the variation of the peaks is not carried out (see
Fig. 17C).

(v) Garnets

Two samples of garnet one from metamorphosed ferrug-
inosus sediments and the other from charnockite were subject-
ed for IR absorption spectra. The general pattern of both
the samples do not vary much from the pyrocholite group.
There is a gradual variation in the peak positions. The
maximum variation is about 5 \text{cm}^{-1}. The garnet from
metamorphosed ferruginous sediments is nearer to the almandine compositions but the peak numbers 452 cm$^{-1}$ and 563 cm$^{-1}$ are similar to spessartite garnet. The other peaks are similar to those shown by almandine. This variation in wave number may be due to substitution of other cations or due to impurities. The garnet from the charnockite is quite similar in peak positions shown by almandine. Therefore the two garnets from the different rock types from Sivasmudram do not show any variation either in composition or in the structure (see Fig. 179). The peak numbers of IR spectra of different minerals are given in Table XIV.
investigated (on 36 oxygens) can be listed as below.

1) $\text{Al}^{IV}$ ranges from 1.34 to 1.55
2) $\text{Al}^{VI}$ ranges from 0.31 to 0.60
3) $(\text{Al}^{VI} + \text{Fe}^{3+} + \text{Ti})$ range from 0.85 to 1.01.
4) $(\text{Mg} + \text{Fe}^{2+})$ value range from 4.0 to 4.4.
5) $(\text{Na} + \text{K})$ value range from 0.42 to 0.72.
6) $\text{Ti}$ ranges from 0.11 to 0.23 and
7) $\text{Mg} (\text{Mg} + \text{Fe}^{2+})$ varying between 0.42 to 0.59.

These values indicate that these amphiboles have close eclogitic and tschermakitic affinities or in other words both kinds of coupled substitutions viz $\text{Na} + \text{K}$ (in vacant site) = $\text{Al}^{IV}$ and $(\text{Al}^{VI} + \text{Fe}^{3+} + \text{Ti}) = (\text{Al}^{VI})$ have been operative. With respect to $\text{Mg} = \text{Fe}$ substitution most of these are very close to 1:1 ratio. The Ti content of these amphiboles varies considerably (0.11 to 0.23). Generally the hornblende in granulite facies are rich in Ti unless tita-niferrous magnetite or ilmenite is formed as a product during transformation. The composition of the hornblende is plotted in Fig. 18 and 19 after Deer et al., 1963 (PL 72-273).

**Interrelation between rock and hornblende chemistry**

If the temperature and pressure are held constant, (so in case of granulites) the chemical composition of solid
solution minerals like hornblends, particularly with reference to major elements should reflect the relative availabilities of those elements with chemical environments at the time of their formation. The best available measure of the relative concentration of different chemical species in the environment is provided by the chemical analyses of the parent rocks. It is worthwhile to examine from this viewpoint, the relation between the chemical composition of hornblends and those of the rocks.

Among the major elements Ca and Na of the amphiboles either taken individually or as ratios do not show any correlation with that of the rocks, because the plagioclase of different composition is present in large amounts in these rocks. Regarding the lack of correlation with respect to Ca; Na ratios, it is worthwhile to remember that the states of Na - Vis - a Vis Ca is very much different between amphibole and plagioclase structure. $K/(K + Na)$ ratios on the other hand should reflect the relative availabilities of these two elements because with the physical conditions constant, K-Na replacement in plagioclase structure is similar to that in amphiboles. Consequently both should be a function of relative availabilities. It is seen from the Fig. 20 that $K_2O/(K_2O + Na_2O)$ mol. ratios show a crudely developed positive correlation. The Al contents or $Al_2O_3/(Al_2O_3 + SiO_2)$ ratios of the amphiboles are functions of both physical conditions of
Fig 20: Plot of mol $K_2O/(K_2O + Na_2O)$ in hornblende versus rock.
metamorphism and rock chemistry. Again under the same physical conditions these ratios should be related to those of rocks. However the spread of molecular $\frac{Al_2O_3}{(Al_2O_3 + SiO_2)}$ ratios, particularly in rocks is very small and does not allow a satisfactory test.

There is a strong correlation between molecular $\frac{MgO}{(MgO + FeO)}$ ratios of rocks and hornblendes almost in a 1:1 fashion. This suggests that Mg - Fe replacement in hornblendes was determined by the chemical environment.

<table>
<thead>
<tr>
<th>Mol.$\frac{MgO}{(MgO+FeO)}$ in charnockites</th>
<th>0.51</th>
<th>0.41</th>
<th>0.56</th>
<th>0.46</th>
<th>0.61</th>
<th>0.32</th>
<th>0.46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol.$\frac{MgO}{(MgO+FeO)}$ in hornblende</td>
<td>0.59</td>
<td>0.44</td>
<td>0.38</td>
<td>0.42</td>
<td>0.49</td>
<td>0.45</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The manganese contents of the hornblendes and the rocks have almost same positive correlations.

<table>
<thead>
<tr>
<th>Wt.% MnO in charnockites</th>
<th>0.20</th>
<th>0.17</th>
<th>0.10</th>
<th>0.05</th>
<th>0.20</th>
<th>0.12</th>
<th>0.13</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% MnO in hornblendes</td>
<td>0.19</td>
<td>0.16</td>
<td>0.17</td>
<td>0.10</td>
<td>0.24</td>
<td>0.10</td>
<td>0.10</td>
<td>0.20</td>
</tr>
</tbody>
</table>
(b) **Orthopyroxenes**

The chemistry of orthopyroxenes from charnockites and related granulites has been a subject of renewed interest. The Fe"\textsuperscript{II}-Mg"\textsuperscript{II} ratio of coexisting ortho and calcic pyroxenes, a subject which will be discussed later and the contents of the some of the elements like Al"\textsuperscript{IV} and Al"\textsuperscript{VI}, Ca and alkalis, in ortho pyroxenes are discussed hereunder. The chemical analyses of the orthopyroxenes and the calculated formulae on the basis of six oxygen atoms is given in Table XVI. The orthopyroxenes are ferrohypersthene in terms of Eu-Fe molecules. The Al contents of the orthopyroxenes are known to be appreciable. The contents of Al replacing Si range from 0.03 to 0.14. Escola (1957) correlated higher content of Al in orthopyroxenes with higher pressure of formation and experimental work of Boyd and England (1960) lent some support to this contention. But several later workers like Banno (1964) have shown that even natural orthopyroxenes from different pressure environments show wide variation. The Ti, Fe\textsuperscript{3+} and Mn contents of orthopyroxenes are uniformly low and negligible. The contents of Ca which measure the formation of wollastonite end member range in terms of calculated wollastonite molecules from 1.40 to 3.9%.

The soda content is rather uniform with a value of 0.3% Na\textsubscript{2}O and the potash is not found in any samples.
(c) Calcic pyroxenes

Monoclinic calcic pyroxenes of diopside - hedenbergite series are quite common in basic granulites and eclogites, all over the world and certain aspects of their chemistry like the presence of jadeite and 'techenhite' molecules have attracted the attention of many petrologists. It is worthwhile to collect more data on the elemental chemistry for the purpose of comparison and correlation with existing orthopyroxenes. The chemical analyses and the calculated formulas on six oxygen basis is presented in Table XVI. The calcic pyroxenes from the chenoehitites have the wollastonite mol. ranging from 40% to 44%. A survey of literature shows that in granulite calcic pyroxenes CaSiO$_3$ mol. % is 45±5, whereas igneous calcic pyroxenes quite commonly have much lower percentage of CaSiO$_3$ molecules. Siusma (1962) has noted a decreasing Ca content in calcic pyroxenes with increasing Fe content. Recent structural studies on these minerals (Zusman 1968) lend support to this view, because both Ca and Fe occupy the larger cation sites in the structure. It must be mentioned that such trends imply a greater degree of solid solution of orthopyroxenes, which will be controlled to a large extent by temperature, a set of samples equilibrated under similar temperatures is unlikely to show such a distinct pattern. Also as the solubility gap shrinks there should be an opposite relation between Ca
and Fe in coexisting orthopyroxenes. The samples of calcic-pyroxene given in Table XVII do not show any conspicuous trend. The best such trend revealed from granulite data is in Binns' samples and as Binns (1965b) has shown that the trend in igneous calcic pyroxenes is even better developed, with regard to orthopyroxenes. Calcic pyroxenes of Himmelberg and Phinney (1967) and to some extent of Leelanandan (1967) show similar relations. But again the orthopyroxene do not show any conspicuous slopes. It can be stated that even when there is no pronounced gradient in terms of temperature of formation, the trend of calcic pyroxenes is much more conspicuous than in orthopyroxenes. This might mean that the orthopyroxene limb of the solvus for these pyroxenes is steeper under these conditions. But this can only be settled by further experimental work. From the chemical data on the calcic pyroxenes of the area the following observations can be made:

1) Total Al is around 0.10 in the majority of the calcic pyroxene of all such areas, with present samples slightly towards higher values.

2) AlIV in most of the cases is slightly greater than AlVI and the difference is not pronounced. Generally AlVI is higher in garnetiferrous granulites of Madras (Sen and Ray 1971).
(Na + K) values in calcic pyroxenes are usually low (up to 0.04) in other areas but present samples have slightly higher values (up to 0.06). Between coexisting ortho and calcic pyroxene Na in calcic pyroxenes is distinctly higher than the orthopyroxenes.

White (1964) has drawn attention to some contrasts between the chemistry of calcic pyroxenes of granulites and eclogites. It has been felt desirable to test White's (op. cit) hypothesis using the present data (Fig. 21). With plots of Ti moleclue versus Jd of these calcic pyroxenes shows that though the majority fall in the granulite field some plotted points fall in White's vacant field and some even in the eclogite field. It must be emphasized that though Jd content measures roughly the Al⁶⁺ concentration in these minerals, which in turn reflects the pressure of formation (other parameters being same), White's method neglects many other complicating factors in addition to ignoring the varying Al and Na contents of the rocks. For instance the percentage of Jd is very much dependent on the total amount of Al available to the calcic pyroxene, Fe³⁺ content and Na/Fe³⁺ ratios. Secondly there are many alternatives in choosing Tschermak's mol. Coleman et al. (1965) noted that varying Jd contents of eclogitic calcic pyroxenes may be profoundly influenced by the amounts of Na₂O in bulk composition.
However, it is interesting to point out that the samples with comparable Fe$^{3+}$, the total Al contents versus Al$^{VI}$ will clearly distinguish the calcic pyroxene for eclogites and granulites. The correlation of rock chemistry versus the chemistry of the pyroxenes is not discussed, as the major elemental chemistry is closely related to those of amphiboles. Therefore, the calcic pyroxenes of Sivasamudram charnockites resemble in chemistry close to those formed under granulite facies conditions.