UNIT CELL DIMENSIONS AND IONIC SUBSTITUTIONS IN COMMON CLINOPYROXENES

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ABSTRACT

The unit cell dimensions of eight analysed-clinopyroxenes are presented. In the light of the recent researches on the cummingtonites and orthopyroxenes, the discrepancy in the clinopyroxene correlation diagram, suggested by Brown (1960), is pointed out. Though linear regression equations are found to hold good for the optical properties and the specific gravity of clinopyroxenes (Winchell, 1961), they fail to give a satisfactory correlation between the lattice constants and the chemical composition. This is found to be due to the fact that the increases in the lattice constants, especially \( a \) and \( \beta \) (consequently \( a \sin \beta \)), caused by \( \text{Mg}^{2+} - \text{Fe}^{2+} \) substitution, seem to be influenced by the amount of calcium present. On the basis of these observations, a modification of Brown's correlation diagram is suggested.

Kuno and Hess (1953), Kuno (1955), Brown (1960) and Winchell (1960) have made an attempt to correlate the cell dimensions and compositions in clinopyroxenes. Details of previous work in this field have been given by Brown and Winchell. Brown showed that the two dimensions \( a \sin \beta \) and \( b \) exhibit a linear variation with the substitution of \( \text{Mg}^{2+} \) by \( \text{Fe}^{2+} \), of \( \text{Mg}^{2+} \) by \( \text{Ca}^{2+} \) and of \( \text{Fe}^{2+} \) by \( \text{Ca}^{2+} \) respectively. Winchell (1960) calculated the regression coefficients of the lattice constants on the composition of clinopyroxenes. The author (1963) observed that the relationship between \( a \sin \beta \) and the composition is not strictly linear within the calcium-rich clinopyroxenes.

While working on the problem "Optical, chemical and x-ray studies of the mineral suites of some South Indian rocks," the author determined the compositions and cell dimensions of eight clinopyroxenes (Specimens A to H, Tables 1, 2). The cell dimensions of these specimens were determined by the method described elsewhere (Viswanathan, 1964) and the errors in their determination are expected to lie within \( \pm 0.010 \) Å and that in \( \beta \pm 10' \). All these pyroxenes were analysed carefully twice and it was observed that the discrepancy between the two values (especially for the major constituents like \( \text{SiO}_2 \), \( \text{FeO} \), \( \text{MgO} \) and \( \text{CaO} \)) was never greater than 3% of the first value. The means of these two values were taken as final values for all the constituents. The analyses are given in Table 1 recast as atoms per 6000 oxygen. All these specimens were examined under microscope and were found to be free from exsolution.

Besides these eight specimens, the cell dimensions and compositions of twenty-six more pyroxenes, taken from literature, are presented in this paper. Of these thirty-four, twenty-five specimens (Table 1) are free from exsolution (in twelve of them, this was determined microscopically; in
others it was assumed to be so, because they are from metamorphic or volcanic rocks). The other nine pyroxenes (Table 3) show exsolved lamellae. As the cell dimensions determined in these cases are those of the hosts, the chemical compositions of these specimens have to be corrected to get the accurate composition of the host (Brown, 1960). To make this correction, the exact composition of the exsolved lamellae (including those of the minor constituents like Al₂O₃, Fe₂O₃ . . . etc.) and the exact proportion of the lamellae to the host have to be determined. As this is almost an impossibility, especially when the lamellae are very thin and as the exact information concerning these details are lacking, the available

**Table 1. Analyses of Clinopyroxenes, ABC₂O₆, Recast as Atoms per 6000 Oxygen, Showing Assignment to Formula Positions A, B, C and Symbol X₁ Used in Computation**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>X₁</th>
<th>X₂</th>
<th>X₃</th>
<th>X₄</th>
<th>X₅</th>
<th>Sum</th>
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<tr>
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<td>126</td>
<td>55</td>
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<tr>
<td>B</td>
<td>1822</td>
<td>178</td>
<td>65</td>
<td>22</td>
<td>4</td>
<td>816</td>
</tr>
<tr>
<td>C</td>
<td>1820</td>
<td>175</td>
<td>5</td>
<td>3</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>1918</td>
<td>82</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>687</td>
</tr>
<tr>
<td>E</td>
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<td>16</td>
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<tr>
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<td>1907</td>
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<td>585</td>
</tr>
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<td>1866</td>
<td>134</td>
<td>31</td>
<td>45</td>
<td>9</td>
<td>823</td>
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<tr>
<td>H</td>
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<td>85</td>
<td>2</td>
<td>22</td>
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<td>812</td>
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<td>37</td>
<td>21</td>
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<tr>
<td>J</td>
<td>1933</td>
<td>1841</td>
<td>21</td>
<td>13</td>
<td>7</td>
<td>740</td>
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<td>K</td>
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<td>41</td>
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<td>55</td>
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<td>R</td>
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<td>21</td>
<td>942</td>
<td></td>
</tr>
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<td>917</td>
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<td>1956</td>
<td>1826</td>
<td>5</td>
<td>7</td>
<td>988</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>1990</td>
<td>10</td>
<td>40</td>
<td>14</td>
<td>2</td>
<td>334</td>
</tr>
<tr>
<td>W</td>
<td>1986</td>
<td>14</td>
<td>3</td>
<td>11</td>
<td>1</td>
<td>932</td>
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<td>Y</td>
<td>1851</td>
<td>149</td>
<td>65</td>
<td>22</td>
<td>11</td>
<td>827</td>
</tr>
</tbody>
</table>

* Includes Cr.

References to the analyses: A to H, (Viswanathan, 1963, nos. 1 to 7 and 9); 1, (Weibel and Locher, 1964, diopside); 2, (Morimoto et al, 1960, pigeonite); 3, (Burnham, 1965); 4, (Brown, 1966, diopside); 5, 6 and 7, (Brown, 1960, nos. 1, 10 and 11 in Table 2); 8, (Hess, 1949, no. 18; Kuno and Hess, 1953, no. 6); 9, (Kuno, 1955, no. 15); 10, (Kuno, 1955, no. 9); 11, (Kuno, 1955, no. 5); 12, (Kuno, 1955, no. 6); 13, (Kuno and Nagashima, 1952, no. 3; Kuno and Hess, 1953, no. 2); 14, (Hess, 1949, no. 16; Kuno and Hess, 1953, no. 5); 15, (Hess, 1949, no. 8); Kuno and Hess, 1953, no. 4); 16, (Kuno and Hess, 1953, no. 11); 17, (Kuno, 1955, no. 1).
UNIT CELLS OF CLINOPYROXENES

Table 2. Cell Dimensions and Optical Properties of Clinopyroxenes, Whose Compositions are Given in Table 1

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>a Å</th>
<th>b Å</th>
<th>c Å</th>
<th>α sin β</th>
<th>β</th>
<th>γ</th>
<th>2V</th>
<th>Z/Ap/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.725</td>
<td>8.918</td>
<td>5.245</td>
<td>74°54'</td>
<td>9.354</td>
<td>1.683</td>
<td>1.690</td>
<td>1.711</td>
</tr>
<tr>
<td>B</td>
<td>9.723</td>
<td>8.913</td>
<td>5.241</td>
<td>74°60'</td>
<td>9.350</td>
<td>1.683</td>
<td>1.689</td>
<td>1.709</td>
</tr>
<tr>
<td>D</td>
<td>9.749</td>
<td>8.937</td>
<td>5.228</td>
<td>74°36'</td>
<td>9.398</td>
<td>1.692</td>
<td>1.699</td>
<td>1.718</td>
</tr>
<tr>
<td>E</td>
<td>9.752</td>
<td>8.940</td>
<td>5.239</td>
<td>74°36'</td>
<td>9.401</td>
<td>1.694</td>
<td>1.701</td>
<td>1.720</td>
</tr>
<tr>
<td>F</td>
<td>9.761</td>
<td>8.949</td>
<td>5.250</td>
<td>74°22'</td>
<td>9.401</td>
<td>1.696</td>
<td>1.703</td>
<td>1.724</td>
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<tr>
<td>G</td>
<td>9.745</td>
<td>8.925</td>
<td>5.251</td>
<td>73°59'</td>
<td>9.366</td>
<td>1.684</td>
<td>1.694</td>
<td>1.715</td>
</tr>
<tr>
<td>H</td>
<td>9.734</td>
<td>8.929</td>
<td>5.260</td>
<td>74°07'</td>
<td>9.362</td>
<td>1.687</td>
<td>1.694</td>
<td>1.715</td>
</tr>
<tr>
<td>I</td>
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<td>8.951</td>
<td>5.251</td>
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<td>1.690</td>
<td>1.694</td>
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</tr>
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<td>K</td>
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<td>5.244</td>
<td>71°54'</td>
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<td>1.614</td>
<td>1.617</td>
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<td>L</td>
<td>9.734</td>
<td>8.907</td>
<td>5.246</td>
<td>73°51'</td>
<td>9.350</td>
<td>1.682</td>
<td>1.687</td>
<td>1.709</td>
</tr>
<tr>
<td>M</td>
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<td>8.910</td>
<td>5.268</td>
<td>73°53'</td>
<td>9.363</td>
<td>1.691</td>
<td>1.694</td>
<td>1.715</td>
</tr>
<tr>
<td>N</td>
<td>9.802</td>
<td>9.004</td>
<td>(5.252)</td>
<td>74°45'</td>
<td>9.457</td>
<td>1.676</td>
<td>1.679</td>
<td>1.701</td>
</tr>
<tr>
<td>O</td>
<td>9.754</td>
<td>9.024</td>
<td>5.263</td>
<td>75°40'</td>
<td>9.458</td>
<td>1.723</td>
<td>1.730</td>
<td>1.751</td>
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<tr>
<td>P</td>
<td>9.712</td>
<td>8.959</td>
<td>5.251</td>
<td>71°27'</td>
<td>9.208</td>
<td>1.713</td>
<td>1.720</td>
<td>(1.734)</td>
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<tr>
<td>Q</td>
<td>9.716</td>
<td>8.944</td>
<td>5.242</td>
<td>72°20'</td>
<td>9.238</td>
<td>1.711</td>
<td>1.713</td>
<td>1.739</td>
</tr>
<tr>
<td>S</td>
<td>9.722</td>
<td>8.925</td>
<td>5.242</td>
<td>73°57'</td>
<td>9.295</td>
<td>1.691</td>
<td>1.697</td>
<td>1.718</td>
</tr>
<tr>
<td>T</td>
<td>9.692</td>
<td>8.917</td>
<td>5.239</td>
<td>71°27'</td>
<td>9.185</td>
<td>1.695</td>
<td>1.698</td>
<td>1.722</td>
</tr>
<tr>
<td>U</td>
<td>9.804</td>
<td>8.980</td>
<td>5.259</td>
<td>74°46'</td>
<td>9.400</td>
<td>1.708</td>
<td>1.714</td>
<td>1.736</td>
</tr>
<tr>
<td>V</td>
<td>9.750</td>
<td>8.930</td>
<td>5.249</td>
<td>74°50'</td>
<td>9.380</td>
<td>1.672</td>
<td>1.679</td>
<td>1.701</td>
</tr>
<tr>
<td>X</td>
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<td>8.901</td>
<td>5.268</td>
<td>73°55'</td>
<td>9.361</td>
<td>1.690</td>
<td>1.696</td>
<td>1.715</td>
</tr>
</tbody>
</table>

Values in parentheses are of doubtful accuracy (Brown, 1960) and hence they were not used for the calculation of regression coefficients.

Errors in the refractive indices, 2v and Extinction angles of specimens A to H are ± 0.005, ± 2° and ± 2° respectively.

* X = b for Nos. 13 and 16 only; others have Y = b.

Table 3. Unit Cell Dimensions and Major Cation Contents of the Clinopyroxenes, the Compositions of Which Have Been Corrected for Exsolution

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Ca2+</th>
<th>Mg2+</th>
<th>Fe2+</th>
<th>AlIV</th>
<th>AlIII</th>
<th>a Å</th>
<th>b Å</th>
<th>c Å</th>
<th>β</th>
<th>α sin β</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.3</td>
<td>43.2</td>
<td>12.5</td>
<td>0.699</td>
<td>0.023</td>
<td>9.751</td>
<td>8.926</td>
<td>5.260</td>
<td>74°57'</td>
<td>9.371</td>
<td>Brown, 1960, No. 2, Table 2</td>
</tr>
<tr>
<td>2</td>
<td>44.6</td>
<td>40.3</td>
<td>15.1</td>
<td>0.096</td>
<td>0.015</td>
<td>9.753</td>
<td>8.928</td>
<td>5.259</td>
<td>74°56'</td>
<td>9.373</td>
<td>Brown, 1960, No. 3, Table 2</td>
</tr>
<tr>
<td>3</td>
<td>42.3</td>
<td>38.7</td>
<td>19.0</td>
<td>0.084</td>
<td>0.018</td>
<td>9.754</td>
<td>8.940</td>
<td>5.270</td>
<td>74°59'</td>
<td>9.375</td>
<td>Brown, 1960, No. 4, Table 2</td>
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<tr>
<td>4</td>
<td>41.6</td>
<td>37.0</td>
<td>21.4</td>
<td>0.077</td>
<td>0.011</td>
<td>9.751</td>
<td>8.945</td>
<td>5.267</td>
<td>74°02'</td>
<td>9.376</td>
<td>Brown, 1960, No. 5, Table 2</td>
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<tr>
<td>5</td>
<td>40.5</td>
<td>36.5</td>
<td>23.0</td>
<td>0.086</td>
<td>0.019</td>
<td>9.753</td>
<td>8.944</td>
<td>5.267</td>
<td>74°03'</td>
<td>9.378</td>
<td>Brown, 1960, No. 6, Table 2</td>
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<td>6</td>
<td>40.9</td>
<td>34.5</td>
<td>24.6</td>
<td>0.091</td>
<td>0.010</td>
<td>9.757</td>
<td>8.948</td>
<td>5.251</td>
<td>74°06'</td>
<td>9.383</td>
<td>Brown, 1960, No. 7, Table 2</td>
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<tr>
<td>7</td>
<td>41.0</td>
<td>31.4</td>
<td>27.6</td>
<td>0.058</td>
<td>0.011</td>
<td>9.758</td>
<td>8.954</td>
<td>5.255</td>
<td>74°07'</td>
<td>9.385</td>
<td>Brown, 1960, No. 8, Table 2</td>
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<tr>
<td>8</td>
<td>40.2</td>
<td>27.6</td>
<td>32.2</td>
<td>0.063</td>
<td>0.012</td>
<td>9.763</td>
<td>8.965</td>
<td>5.272</td>
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<td>9.395</td>
<td>Brown, 1960, No. 9, Table 2</td>
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<td>9</td>
<td>47.8</td>
<td>26.0</td>
<td>26.2</td>
<td>0.049</td>
<td>0.016</td>
<td>9.771</td>
<td>8.966</td>
<td>5.249</td>
<td>74°36'</td>
<td>9.420</td>
<td>Blinn, 1962, clinopyr. No 5</td>
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</tbody>
</table>

AlIV and AlIII denote the amount of aluminum in the tetrahedral and octahedral positions respectively.
The compositions of these specimens are not considered adequately accurate for inclusion along with the other twenty-five specimens for the purposes of calculating the regression coefficients. They are only plotted in the final correlation diagram presented (Fig. 3). The pyroxene (No. 1, Table 1) is from a contact rock from Bregg Valley, Switzerland (Weibel and Locher, 1964). It was found to be free from exsolution (Weibel, pers. comm.). The pyroxene (No. 9, Table 3) is from a two-pyroxene granulite from Broken Hill, New South Wales (Binns, 1962) and was found to contain exsolution lamellae of clinohypersthene containing 69 mol. per cent of the clinoferrosilite molecule (Binns and Long, 1963). The analysis of this pyroxene, which was not corrected for exsolution, is given elsewhere (clinopyroxene No. 5, Binns, 1962). A rough estimate of the abundance of (001) clinohypersthene lamellae, based on electron probe traverse is approximately 10% (Binns, pers. comm.). On this basis, the original analysis was corrected by the author, and the corrected composition is given in Table 3 in terms of Ca²⁺, Mg²⁺ and Fe²⁺ atomic per cent. The cell dimensions of these two pyroxenes were determined by the author, following the procedure described by Viswanathan and Ghose (1965). The probable errors in the cell dimensions of these specimens are expected to lie within ±0.005 Å and the error in β±5°.

The following values were obtained for the a sin β and b dimensions of clinoenstatite and clinoferrosilite from Fig. 5 of Brown (1960).

<table>
<thead>
<tr>
<th></th>
<th>a sin β</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>clinoferrosilite</td>
<td>9.330 Å</td>
<td>9.098 Å</td>
</tr>
<tr>
<td>clinoenstatite</td>
<td>-9.030 Å</td>
<td>-8.840 Å</td>
</tr>
<tr>
<td></td>
<td>0.300 Å</td>
<td>0.258 Å</td>
</tr>
</tbody>
</table>

The total increase in a sin β in the clinoenstatite-clinoferrosilite series, according to Brown, is 0.300 Å, whereas the total increase in b dimension is 0.258 Å. This means that the Mg²⁺—Fe²⁺ substitution causes a greater increase in a sin β direction and less in b direction. It is interesting to compare this result with the orthopyroxene series and cummingtonite series. All these three series are essentially groups of minerals formed by Mg²⁺—Fe²⁺ substitution. As reported earlier (Viswanathan and Ghose, 1965), there is a remarkable similarity in the anisotropic expansions of the cell dimensions of the orthopyroxenes and cummingtonites, caused by the substitution of Mg²⁺ by Fe²⁺. It was noted that the substitutional coefficients of expansion¹ α for the corresponding cell dimensions in both

¹ In the original paper (Viswanathan and Ghose, 1965) the actual increase in the cell dimensions has been referred to, by mistake, as the “coefficient of expansion.” In a correction to this paper (to be published), the term “substitutional coefficient of expansion” has been correctly defined.
minerals are approximately the same: e.g. $\alpha$ in $a$ direction of cummingtonite is 0.000135, $\alpha$ in $a$ direction of orthopyroxene is 0.000113 and $\alpha$ in $b$ direction of cummingtonite is 0.000288, $\alpha$ in $b$ direction of orthopyroxene is 0.000290. The rates of expansion in $b$ direction in both groups of minerals are almost double those in $a$ direction (or $a\sin\beta$ direction of cummingtonite). This similarity is very interesting when one considers the differences in the structures and systems of crystallisation of these two groups. It probably means that the rate of expansion is influenced more by the nature and size of the substituting ions than by the system of crystallisation. When the values of $a\sin\beta$ and $b$ of clinoenstatite and clinoferroilite, as given by Brown’s Fig. 5, are considered, it is found that the $\text{Mg}^{2+}-\text{Fe}^{2+}$ substitution causes a greater change in $a\sin\beta$ direction than in $b$. This result of Brown is incompatible with the above-mentioned observations and hence it is felt that Brown’s correlation diagram needs revision. But if the $b$ values of Brown are used and if the coefficient of expansion $(9.098-8.840/100\times8.840)$ is calculated, a value of 0.000292 is obtained, which agrees very well with the values 0.000290 and 0.000288 of orthopyroxenes and cummingtonites respectively. Therefore the discrepancy lies only in the values of $a\sin\beta$ and not in the $b$ values, assigned to clinoenstatite and clinoferroilite. This discrepancy is noted when the three pyroxenes (Nos'C', '2' and '17' Tables 1, 2) are plotted in Brown’s Fig. 5. All these show $a\sin\beta$ values about 0.025 Å higher than the experimentally determined values.

Recently Burnham (1965) determined the cell dimensions of synthetic clinoferroilite (No. 3, Tables 1, 2). Using these data and the data of synthetic cinoenstatite (No. 16, Tables 1, 2), the coefficients of expansion for the corresponding cell dimensions of these synthetic clinopyroxenes can be calculated:

<table>
<thead>
<tr>
<th></th>
<th>$a\sin\beta$ Å</th>
<th>$b$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>clinoferroilite</td>
<td>9.221</td>
<td>9.098</td>
</tr>
<tr>
<td>clinoenstatite</td>
<td>9.128</td>
<td>8.828</td>
</tr>
<tr>
<td></td>
<td>0.093</td>
<td>0.270</td>
</tr>
</tbody>
</table>

Coefficient of expansion in $a\sin\beta$ direction = 0.093/100 × 9.128 = 0.000102
Coefficient of expansion in $b$ direction = 0.270/100 × 8.828 = 0.000306. It should be noted that these values agree very well with those of naturally occurring orthopyroxenes and cummingtonites. The coefficients of expansion for the corresponding cell dimensions in the natural clinoenstatite-clinoferroilite series may not, therefore, differ much from that of synthetic pyroxenes. It is most likely that they are equal. Therefore, for all practical purposes, it can be assumed that the natural clinoenstatite and clinoferroilite have the same cell dimensions as the synthetic ones.
and that they show the same amount of expansion in their cell dimensions for Mg\textsuperscript{2+}—Fe\textsuperscript{3+} substitution. Further both these minerals as well as the pigeonites, whose compositions approach the intermediate members of the clinoenstatite-clinoferrosilite series, possess the same structure (space group $P2_1/c$). Considering this fact and their similarity to the orthopyroxenes and cummingtonites, a linear increase in their cell dimensions due to Mg\textsuperscript{2+}—Fe\textsuperscript{3+} substitution can be safely assumed. Using the values of the synthetic clinoenstatite and ferrosilite and considering a linear relationship, the $a \sin \beta$ and $b$ values for the clinohypersthene of the composition $\text{Mg}_{50}\text{Fe}_{50}$ can be calculated.

\[
\begin{align*}
    a \sin \beta &= (9.128 + 0.047) = 9.175 \text{ Å} \\
    b &= (8.828 + 0.135) = 8.963 \text{ Å}
\end{align*}
\]

The remarkable agreement of these values with those arrived at by Brown ($a \sin \beta = 9.18 \text{ Å}$, $b = 8.97 \text{ Å}$) adds much weight for accepting these assumptions. Hence the above-referred $a \sin \beta$ values have been assigned to clinoenstatite, clinoferrosilite and clinohypersthene ($\text{Mg}_{50}\text{Fe}_{50}$) in Fig. 1.

In this figure the compositions of the 25 pyroxenes, given in Table 1, have been plotted in terms of $\text{Mg}^{2+}$, $\text{Fe}^{3+}$ and $\text{Ca}^{2+}$ atomic per cent. Only the $a \sin \beta$ values have been marked with a view to avoid confusion. Considering the $a \sin \beta$ values of the two pyroxenes (Nos. 4 and 15, Tables 1, 2), which lie near the diopside corner, a value of 9.375 Å has been assigned to diopside ($\text{Ca}_{50}\text{Mg}_{50}$) arbitrarily. Similarly considering the $a \sin \beta$ values of pyroxenes (Nos. 6, 7 and 8, Tables 1, 2), an approx-

---

**Fig. 1.** The plotted points refer to the clinopyroxenes for which the analyses are given in Table 1 and the cell dimensions are given in Table 2.
imate value of 9.530 Å has been assigned to hedenbergite corner. From this diagram, it is seen that a change of composition from Ca_{56}Mg_{56} to Ca_{50}Fe_{50} causes an expansion in $a \sin \beta$, which is approximately 0.155 Å, whereas a change from Mg_{56}Fe_{56} to Fe_{100} causes an expansion of only 9.220 - 9.175 = 0.045 Å. In other words, the increase in $a \sin \beta$ caused by Mg^{2+} - Fe^{2+} substitution, when Ca^{2+} = 50, is at least three times greater than that when Ca^{2+} = 0. Therefore the source of the discrepancy in Brown’s diagram lies in his assumption that, for all values of Ca^{2+} content, Mg^{2+} - Fe^{2+} substitution causes the same amount of increase in $a \sin \beta$.

It is seen in Table 1, that none of these twenty five pyroxenes contain large amounts of any constituent other than Si, Ca, Mg and Fe^{2+}. It may be further emphasised that this three-fold increase in $a \sin \beta$ cannot be attributed to the presence of some minor constituents. It must be attributed only to the influence of increasing calcium content and the accompanying changes in the structure. A consideration of the structure (Viswanathan and Ghose, 1965) also supports this observation. Ca^{2+} has a two-fold effect on $a \sin \beta$: (1) Because of its greater ionic size, it causes an expansion in the $a \sin \beta$ direction (2) Because it invariably occupies the M₂ site, it causes a decrease in $\beta$ (obtuse angle), thereby increasing the $a \sin \beta$ value (Whittaker, 1960). To quote Brown (p. 24, 1960), “In the $a \sin \beta$ graphs, the effect (of calcium) is more marked and when changes in this dimension with Mg^{2+}:Fe^{2+} substitution were graphed, the series had to be divided into a ‘high-calcium’ (50%) and a ‘low-calcium’ (40%) group.”

Again, by considering the $a$ and $\beta$ values of the four pyroxenes (Nos. 4, 15, 8 and 14, Tables 1, 2) and by similar reasoning, it can be shown that the lattice constants $a$ and $\beta$ increase more rapidly, when Ca^{2+} = 50, than when Ca^{2+} = 0. But it is apparent that the amount of increase in $a$ is smaller than that in $a \sin \beta$. The expansion in $b$ appears to be approximately of the same magnitude, both when Ca^{2+} = 50 and Ca^{2+} = 0. The expansion in $c$ due to Mg^{2+} - Fe^{2+} substitution is too little and irregular to be commented upon.

An attempt was made to calculate the regression coefficients of lattice constants on the compositions of clinopyroxenes. Only the twenty five pyroxenes given in Table 1 were considered for this purpose. Following Winchell (1960), the analyses are recast in the form of numbers of metal atoms relative to 6000 oxygen atoms. These relative numbers of atoms are distributed according to the order of increasing ionic radius in the positions C, B and A of the pyroxene formula ABC2O6, thus assuming a completely ordered distribution of the elements in these positions, even though that is known to be partially untrue for pyroxenes crystallized at
high temperatures. The reader is referred to Winchell (1960) for further details regarding the symbols and the reasons for choosing the following five independent variables for the regression equation. The five variables are:

- $X_1$: Si in C position;
- $X_2$: Al$^{3+}$ + Fe$^{3+}$ + Ti in B position;
- $X_3$: Mg in B position;
- $X_4$: Fe$^{2+}$ in A position;
- $X_5$: Ca in A position;

Table 4 gives the regression coefficients, Table 5 gives the lattice constants of interesting compositions of clinopyroxenes, calculated using the regression coefficients and Table 6 gives the differences between observed and estimated values of the cell constants for the relevant analyses. Table 6 shows satisfactory residuals for $b$ dimension (excepting specimen No. 2, Table 6, for which the author has no explanation at present), thereby indicating that the regression coefficients for $b$ are correct. But it shows a few large residuals for $a$ sin $\beta$, $a$ and $\beta$, which means that these coefficients are incorrect. This is the root cause for the following major discrepancies, observed in Table 5:

1) The $a$ sin $\beta$ value of clinoferrosilite is very high (9.263 - 9.221 = 0.042 Å), and that of clinohypersthene (Mg$\text{Fe}_{50}$) is very low (9.175 - 9.134 = 0.041 Å). The $a$ sin $\beta$ value of hedenbergite also appears to be low.

2) The $\beta$ value of clinohypersthene appears to be low on the basis of the following considerations. Clinoenstatite has a $\beta$ value 71.65° and clinoferrosilite has a $\beta$ value 71.57°. As stated earlier, there are valid reasons to believe that there is a linear variation of cell dimensions in this series. Hence, the $\beta$ value for the intermediate member, clinohypersthene, cannot be lower than 71.57° and 71.65°.

3) The $a$ value of clinoferrosilite is very high (9.754 - 9.720 = 0.034 Å) and that of hedenbergite appears to be low.

The results of Winchell’s (1960) calculations also show similar discrepancies between the calculated and observed $a$ and $\beta$ values of clinoferrosilite. It was thought that these discrepancies can be eliminated, if the regression coefficients are calculated on 15 variables of chemical composition with diopside (Ca$_{50}$Mg$_{50}$) as the origin, as done by Winchell (1961) for optical properties. As there were 12 independent variables in the regression equation in this case, there was some general improvement, noted in the calculated values of $a$ sin $\beta$ of some specimens, in $s_p$ and $R^2$. However, once again the regression coefficients for $a$ sin $\beta$ and $\beta$ were not satisfactory. In fact the calculated $a$ sin $\beta$ value of clinohypersthene (Mg$_{50}$Fe$_{50}$) was found to be unbelievably low (9.107 Å), which is much lower than even that of clinoenstatite. The complete results of this calculation are not given here, as it means an unnecessary addition of three more tables.
Table 4. Regression Coefficients for Clinopyroxenes; Regression Equation

\[ y_p = \sum a_{np} x_i + s_p \]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
<th>( x_4 )</th>
<th>( x_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>constant ( \text{Si}_{cil} )</td>
<td>Al ( \text{Mg}<em>{lb} ) (( \text{Fe}^{3+} )) ( + \text{Ti}</em>{lb} )</td>
<td>( \text{Fe}^{3+} ) ( \text{Ca}_{ja} )</td>
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<td></td>
</tr>
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<td>2</td>
<td>( X )</td>
<td>1.000</td>
<td>1.921</td>
<td>0.054</td>
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</table>

<table>
<thead>
<tr>
<th>( p )</th>
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<th>( \hat{y} )</th>
<th>( b_{lp} )</th>
<th>( s_{lp} )</th>
<th>( s_p )</th>
<th>( R^2 )</th>
<th>( F )-ratio</th>
</tr>
</thead>
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<tr>
<td>2</td>
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<td>+.248</td>
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</table>

* In all these cases it may be noted that \( s_{lp} \) is greater than \( b_{lp} \), thereby indicating that these coefficients may not be significantly different from zero.

** For these two dimensions, 5 variables; 19 degrees of freedom; 25 observations (The two additional specimens are Nos. 6 and 7 in Tables 1 and 2).

Table 5. Estimated Values of Cell Dimensions for Interesting Compositions Not Available in Natural Materials with Their Respective Standard Errors

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell dimensions calculated by regression (using Table 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>( \text{Si}_{cil} )</td>
</tr>
<tr>
<td>Diopside</td>
<td>2</td>
</tr>
<tr>
<td>Hedenbergite</td>
<td>2</td>
</tr>
<tr>
<td>Clinoenstatite</td>
<td>2</td>
</tr>
<tr>
<td>Clinohypersthene</td>
<td>2</td>
</tr>
<tr>
<td>Clinoferrsite</td>
<td>2</td>
</tr>
</tbody>
</table>

* (?) These values seem to show discrepancies.
In Table 4 there are some coefficients, \( b_{ij} \), for which the standard deviations, \( s_{ij} \), are greater than the coefficients themselves, thereby indicating that their values may not be significantly different from zero. A recalculation of regression coefficients after omitting these variables may give slightly improved values. But this slight improvement can never eliminate the major discrepancies noted. These discrepancies arise, because both the above-referred to regression equations (the first with five variables and the second with 12 variables) are based on the assumption that the changes in the lattice constants, when the composition changes from \( \text{Mg}_{56}\text{Ca}_{56} \) to \( \text{Fe}_{63}\text{Ca}_{56} \), are equal to those when the composition changes from \( \text{Mg}_{56}\text{Fe}_{56} \) to \( \text{Fe}_{100} \). In the first case this change is equated to the influence of \( \text{Mg}^{2+} \) in the B position (i.e., \( X_a \)) and in the second case, this change is equated to the influence of \( \text{Fe}^{2+} \) in B position (i.e., variable \( "X_6" \), Winchel's notation, 1961). On the other hand, as stated earlier, a change of composition from \( \text{Ca}_{56}\text{Mg}_{56} \) to \( \text{Ca}_{56}\text{Fe}_{56} \) causes a greater increase in \( a \sin \beta \), \( a, \beta \) values than a change from \( \text{Mg}_{56}\text{Fe}_{56} \) to \( \text{Fe}_{100} \). It was also noted that the increase in \( a \sin \beta \) is approximately three times. Even when all the cations are used as such as independent variables, (without assuming an ordered distribution) as done by Henriques (1958, a, b, c)

<table>
<thead>
<tr>
<th>Sp. No.</th>
<th>( a ) Å</th>
<th>( b ) Å</th>
<th>( c ) Å</th>
<th>( \delta^0 )</th>
<th>( a \sin \beta ) Å</th>
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</thead>
<tbody>
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</table>
for optical properties, a linear regression equation cannot give a good 
correlation between cell dimensions and composition, because this equa-
tion is also based on the assumption that the effect of any individual ca-
tion (e.g., substitution of $\text{Mg}^{2+}$ by $\text{Fe}^{2+}$) on a particular dimension is 
always equal, i.e., whether $\text{Ca}^{2+} = 0$ or $\text{Ca}^{2+} = 50$.

Thus a linear regression equation fails to give a satisfactory correlation

![Graph](image)

**Fig. 2.** Variation in the $a \sin \beta$ dimension of the clinopyroxene unit cell with $\text{Mg}^{2+}-\text{Fe}^{2+}$ substitution, $\text{Ca}^{2+}$ remaining constant at the value 50.

between the lattice constants and the chemical composition; it means 
that the lattice constants, excepting perhaps the $b$ dimension, of all the 
clinopyroxenes in the common clinopyroxene trapezium cannot be con-
sidered as linear, additive functions of the chemical composition; only in 
the clinoenstatite-clinoferrosilite series there are reasons to expect a 
linear variation. But linear regression equations appear to hold good for 
the refractive indices and specific gravity (Winchell, 1961). Perhaps these 
optical and physical properties are not very sensitive to the slight struc-
tural changes which exist between clinoenstatite-pigeonite-clinoferrosilite series and the diopside-hedenbergite series. But the lattice constants, especially $a$ and $b$ (consequently $a \sin \beta$) seem to be very sensitive to these structural changes and therefore the relation between them cannot be expressed satisfactorily by a linear equation. Recently even for the physical properties, Winchell (1963) has suggested the possibility of a discontinuity of a second order (i.e., slope change) at $\text{Mg}_{50}\text{Fe}_{50}$ which, he attributes, to the ordered substitution of cations in A and B positions.

![Diagram](image)

**Fig. 3.** Variation in $a \sin \beta$ throughout the common clinopyroxene trapezium. The isodimensional lines for values 9.475 Å and 9.500 Å are drawn as dashed lines.

Perhaps if second degree terms are also employed in the regression equations for lattice constants, there may be better agreement between observed and calculated values; but then the equation become so uncomfortably large and complicated (e.g., the equations given byHenriques (1958c) for the refractive indices and $2\nu$) that they cannot be looked upon as an elegant method of expressing the relationship. Perhaps the graphical method (Fig. 3) is simpler, though not very accurate and may satisfy the purposes of petrologists.

On the basis of the above observation that the changes in the lattice constants of the common clinopyroxenes are mainly due to the combined influence of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{Fe}^{2+}$, it was thought that a correlation diagram (Fig. 3) with reference to these three constituents, as suggested by Brown, will be very useful. This diagram is only a modification of that suggested by Brown. Of the five dimensions given in Tables 2 and 3,
a sin β and b were selected because these two can be more accurately determined from a powder photograph than the other three. Further there is an added advantage in using b dimension, because it shows almost a linear variation within the limits of experimental error. As stated earlier, the b values of clinoenstatite and clinoferrosilite, given by Brown, are in very good agreement with those of synthetic ones and hence, the isodimensional lines drawn by him (his Fig. 5) do not appear to need any revision. They can be drawn on this diagram (Fig. 3) for purposes of finding the composition of a pyroxene with the help of these two dimensions. In order to avoid confusion due to overcrowding of lines and to show better the variation in a sin β with the composition, the isodimensional lines for b are not drawn in Fig. 3. The lines for a sin β in this diagram have been drawn on the basis of the following:

1) A linear variation of a sin β with the composition has been assumed for the two component CaMg—Mg, Mg—Fe²⁺, and CaFe—Fe²⁺ series of clinopyroxenes. Therefore these three sides of the trapezium have been divided into equal sections according to linear equations.

2) To get an idea of the variation of a sin β on the fourth side (CaFe-CaMg side), a graph, using the data of six pyroxenes, which have Ca²⁺ equal to or nearly equal to 50 atomic per cent, has been drawn (Fig. 2). In this graph also, a value of 9.530 Å has been assumed for a sin β of hedenbergite, Ca₅₆Fe₅₆.

3) A consideration of the a sin β values of all the pyroxenes plotted in this diagram. The pyroxenes (Table 3), whose compositions have been corrected for exsolution, have also been plotted in this figure.

4) Considering the a sin β values of the three pyroxenes, which lie close to hedenbergite and considering the rapid increase in a sin β values near the hedenbergite-corner of the CaFe—CaMg side of the trapezium (see the steeply rising curve of a sin β in Fig. 2), the a sin β lines for values 9.475 Å and 9.500 Å are drawn as dotted lines. With some more data in this region of the trapezium it is possible to decide, whether they are really straight lines or slightly curved.

It must be noted that this diagram should be applied to only common clinopyroxenes, which contain constituents such as Fe₂O₃, Al₂O₃, MnO, Na₂O, K₂O, Li₂O, TiO₂ and Cr₂O₃ in minor amounts.

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