The Effect of Ca-Fe Substitution on the Clinopyroxene Crystal Structure

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Abstract

The major structural change resulting from Ca-Fe substitution in four clinopyroxenes of intermediate composition between hedenbergite and ferrosilite, measured at room temperature, is in the size and shape of the M2 polyhedron, whereas the M1 polyhedron remains essentially unchanged. The decrease in the average size of the M2 polyhedron associated with a compositional change from hedenbergite to ferrosilite causes kinking of the tetrahedral chain and consequent increase in the out-of-plane tilting of the basal face of the tetrahedron. As the M2 polyhedron decreases further in size, the space group changes from C2/c to P2_1/c at about Fes,Wo composition. When the composition changes from Fes,Wo to Fes,Wo, the A chain extends and finally reverses its kink direction. The anisotropic temperature factors for these intermediate compositions may be explained as a result of the effects of positional disorder.

Introduction

Most minerals can form solid solutions, either limited or complete, and thus some sites in the unit cells of minerals are occupied statistically by more than one atomic species. If there is a large difference in the ionic radius of the ions occupying the site, the crystal structure may change with a change in occupancy of the site and thus in the apparent size of the coordination polyhedron. One of the best mineralogical examples of multiple occupancy is augite-pigeonite, where substitution of Ca for Fe or Mg is involved.

In the pyroxene quadrilateral (diopside-enstatite-ferrosilite-hedenbergite system) the clinopyroxene space groups are P2_1/c for Ca-poor (pigeonite) compositions and C2/c for Ca-rich (augite) compositions at room temperature. The major differences between the P2_1/c and C2/c structures are that (1) there is only one crystallographically distinct silicate chain in the C2/c structure, whereas two types of the chains exist in the P2_1/c structure, and (2) the M2 site is eight-coordinated in the C2/c end members (diopside: Clark, Appleman, and Pupiko, 1969; hedenbergite: Veblen, 1969, and Cameron et al., 1973) and six-coordinated in the P2_1/c end members (clinofelosilite: Burnham, 1967; clinoprostilite: Morimoto, Appleman, and Evans, 1960).

In clinopyroxenes of intermediate composition, the M2 site is very irregular as a result of multiple occupancy of the large Ca and small Fe or Mg atoms in the site. In a structural refinement of a pigeonite, Mg_2.34 Fe_0.66 Ca_0.06 SiO_3 from Mull, Scotland, Morimoto and Güven (1970) reported a very irregular M2 coordination polyhedron, which they concluded was an average of eight and six coordinations. Güven (1969) studied the relationship between the average size of M2 and kinking of the
tetrahedral chain. Takeda (1972) discussed variation of M2–O bonds in clinopyroxenes as a function of Ca content and showed that the M2 polyhedron becomes very irregular, thus highly unstable, in the middle of the solid solution. He proposed that irregularity of the M2 polyhedron shape provided a structural explanation for the presence of a miscibility gap. In their crystal structural study of six end-member clinopyroxenes at high temperatures, Cameron et al. (1973) explained the increased solid solution between the Ca-poor and Ca-rich clinopyroxenes at high temperature by the change in M2 coordination associated with the P32,3c–P21c phase transition.

The present study is concerned primarily with the effects of chemical substitution on the structure studied at room temperature. To eliminate the structural effects of possible changes in Mg–Fe distribution in the cationic sites, the binary join hedenbergite (CaFe2SiO6)–clinofeldsparlite (Fe2SiO4) was selected. Therefore, these structures reflect solely a difference in structure and Fe content. Furthermore, if the M1 site on the join studied is occupied only by Fe atoms, as expected from its polyhedral size, it is possible to isolate the effects of changes of the M2 site on the other parts of the structure, especially the tetrahedral chain configuration.

**Experimental**

**Unit Cell and Space Group**

Synthetic single crystals of clinopyroxenes on the hedenbergite–clinofeldsparlite join were kindly supplied by Dr. D. H. Lindsey. Synthesis techniques were described by Lindsey and Munoz (1969, Appendix). Crystals of Fs30Wo70, Fs30Wo60, and Fs30Wo50 (all synthesized at 20 kbar and 950°C) and Fs60Wo40 (6 kbar and 1140°C) have been examined using the Buerger precession camera. Class b reflections (h + k = odd) are exhibited by Fs30Wo70 and some crystals of Fs60Wo40, whereas long-exposure photographs of Fs30Wo60, Fs30Wo50, and the other crystals of Fs30Wo50 do not show these b reflections. Thus the (mutually) boundary at room temperature between the space groups P32,3c–P21c is close to the Fs30Wo60 composition on the join hedenbergite–clinopyroxene. At low pressures the clinopyroxene of this composition is not stable relative to the assemblage fayalite–tridymite (Bowen, Schairer, and Pasholak, 1933; Lindsey and Munoz, 1959). No resolved phases are detected on long-exposure precession photographs, and thus the crystals are considered to be homogeneous.

Unit-cell parameters of crystals other than Fs30Wo70 were measured using a back-reflection precision Weissenberg camera. Data for both CuKα and Krβ wavelengths were refined by the least-squares method and included corrections for film shrinkage, camera eccentricity, and specimen absorption (Burnham, 1962). Unit-cell parameters for Fs30Wo60 were determined by a lattice-constant refinement subroutine for a four-circle diffractometer. This subroutine, which is a part of the Geophysical Laboratory diffractometer system, has some new features: auto-centering of reflections and least-squares refinement of the orientation matrix from which the unit-cell parameters (Table 1) are calculated (Finger, unpublished; Gabe, Alexander, and Goodman, 1970). Analysis of the clinopyroxene lattice deformation due to chemical substitution on this join is given elsewhere (Ohashi and Burnham, 1973).

**Measurement and Reduction of X-Ray Intensity Data**

Intensity data were collected using a computer-controlled Picker four-circle diffractometer with Nb-filtered MoKα radiation. Reflections in one quadrant of reciprocal space within the range 0.1 to 0.8 of sin θ/λ were measured employing ω–2θ scans. The observed intensities were corrected for Lorentz and polarization effects and for absorption using the numerical integration techniques of Burnham (1965). In addition, the secondary extinction factor of Zachariasen (1968) was calculated for the Fs30Wo60 and Fs60Wo40 crystals.

The crystal of Fs60Wo40 is twinned on (100). Therefore, the k00 reflections contain superimposed contributions from both twin components. By com-
TABLE 2. Crystal and Refinement Data for Ca-Fe Clinopyroxenes

<table>
<thead>
<tr>
<th></th>
<th>FeSO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>FeSO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>FePO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>FePO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>FePO&lt;sub&gt;4&lt;/sub&gt;</th>
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<tr>
<td>spacer group</td>
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<td>£££</td>
<td>£££</td>
<td>£££</td>
<td>£££</td>
</tr>
<tr>
<td>size of crystal (mm)</td>
<td>0.1-0.20 x 0.25-0.30</td>
<td>0.25-0.50 x 0.50-0.60</td>
<td>0.50-1.00 x 1.00-1.50</td>
<td>0.50-1.00 x 1.00-1.50</td>
<td>0.50-1.00 x 1.00-1.50</td>
</tr>
<tr>
<td>standard deviation (°C)</td>
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<td>0.20</td>
<td>0.30</td>
<td>0.40</td>
<td>0.50</td>
</tr>
<tr>
<td>range of trans. (°C)</td>
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<tr>
<td>number of observations used</td>
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<td>562</td>
<td>563</td>
<td>564</td>
<td>565</td>
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<tr>
<td>residual factor (°C)</td>
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<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Reefinement Procedures

Throughout all refinements, the least-squares program Rine of Finger was used on the IBM 370 and the Univac 1100 computers. Atomic scattering factors were those of Fe<sup>3+</sup>, Ca<sup>2+</sup>, Si<sup>4+</sup>, and O<sup>2-</sup> given by Cromer and Mann (1965) with the anomalous dispersion coefficients of Cromer (1965).

Least-squares refinements of FeSO<sub>4</sub>WO<sub>4</sub> and FeSO<sub>4</sub>WO<sub>4</sub> were initiated with atomic parameters of hedenbergite (Veblen, 1969) and clinoclasesilite (Burnham, 1967), respectively. Refined parameters of FeSO<sub>4</sub>WO<sub>4</sub> and FeSO<sub>4</sub>WO<sub>4</sub>, respectively, were used as initial parameters for FeSO<sub>4</sub>WO<sub>4</sub> and FeSO<sub>4</sub>WO<sub>4</sub>. Reflections were weighted according to \( W = 1/σ^2 \), where \( σ \) is the estimated standard deviation of the observed structure factor. Reflections were rejected from least-squares refinement if the intensity was below two standard deviations of the observed intensity based on counting statistics. At the later stage of least-squares refinement, reflections with \( ΔF = F_o - F_c \) greater than 6 were also rejected.

In each structure the atomic positions, anisotropic temperature factor, and a scale factor were refined. In addition, the isotropic extinction parameter of Zachariasen (1968) was refined for the FeSO<sub>4</sub>WO<sub>4</sub> and FeSO<sub>4</sub>WO<sub>4</sub> data sets. The contraction factors for the twinning in FeSO<sub>4</sub>WO<sub>4</sub> was tested by refining a separate scale factor for \((h00)\). The resulting values were essentially identical, confirming the validity of the prior correction. No strong correlations between parameters were found for the CI/fe structural refinements. However, the A and B chains in the P2<sub>1</sub>fe structure are in general highly correlated: \( -0.75 < B_i < 0.75 \) between \( B_i \)s of SiA and SiB and \( -0.71 < B_i < 0.71 \) between \( B_i \)s of O1A and O1B were found to be the strongest correlations.

From an ionic size consideration, all Ca atoms are assumed to occupy the larger M<sub>2</sub>-site. Thus, for example, the occupancy of cation sites for FeSO<sub>4</sub>WO<sub>4</sub> is 100 percent Fe<sup>3+</sup> in the M<sub>1</sub>-site and 70 percent Fe<sup>4+</sup> and 30 percent Ca in the M<sub>2</sub>-site.

Data for the crystals and refinements are summarized in Table 2. The final positional parameters and temperature factors are given in Tables 3 and 4, respectively. Tables of observed and calculated structure factors may be ordered.*

*To receive a copy of these structure factor tables, order document AM-75-001 from the Business Office, Mineralogical Society of America, suite 1000 lower level, 1009 K Street, N.W., Washington, D.C. 20005. Please remit $1.00 for the microfiche.
of this change are one of the main points of interest in the present study. With increasing Fe content, the M2 polyhedral volume decreases and the M2-O1 and M2-O2 distances also decrease (Fig. 1), as a result of substitution of smaller Fe atoms for larger Ca atoms. On the other hand, all four M2-O3 distances increase when the composition changes from FsgWpg to FsgWot. In the P2_1/c region these bonds split into two groups, one increasing and the other decreasing with further Fe enrichment. In clinohorodolite only six M2-O distances are less than 3 Å, the approximate value of the shortest oxygen-oxygen or metal-metal distance.

This change of the M2 coordination can be visualized with the aid of Figure 2. The changes of the M2-O distances occur as a consequence of a rotation of the O3A1-O3A2 and O3B1-O3B2 vectors in

### Table 4. Anisotropic Temperature Factors for Ca-Fe Clinopyroxenes

<table>
<thead>
<tr>
<th>Site</th>
<th>Fs2</th>
<th>Fs3</th>
<th>Fs4</th>
<th>Fs5</th>
<th>Fs6</th>
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<tbody>
<tr>
<td>Mg1</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>Mg2</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>Mg3</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>Mg4</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>Mg5</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>Mg6</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
</tbody>
</table>

### Table 5. Interatomic Distances M1-O and M2-O in Ca-Fe Clinopyroxenes

<table>
<thead>
<tr>
<th>Site</th>
<th>Fs2</th>
<th>Fs3</th>
<th>Fs4</th>
<th>Fs5</th>
<th>Fs6</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>M2</td>
<td>0.000(1)</td>
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<td>0.000(1)</td>
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</table>

**Results and Discussion**

**M1 and M2 Sites**

Interatomic distances for the M1 and M2 sites are given in Table 5. The M1-O bond distances (Fig. 1) and the polyhedral volume (Table 5) both show essentially no change for the M1 site with Ca-Fe substitution. This observation seems to verify the assumption that all calcium is restricted to M2 on the join studied. As characterized by the quadratic elongation and the angle variance given in Table 5 (quantities proposed by Robinson, Gibbs, and Ribbe, 1971, as measures of polyhedral distortion), the M1 polyhedron deviates slightly more from an ideal octahedron on the Fe-rich side. It is, however, still much more regular than the M2 polyhedron (quadratic elongation = 1.06 and angle variance = 164° for M2 in clinohorodolite).

The M2 site changes from eight-coordinated in hedenbergite to six-coordinated in ferrosilite. Details

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**Footnotes:**

- Anisotropic temperature factors, T_{ij}, are in the form of

  \[ T_{ij} = B_{ij} + 2 \cdot B_{ii} \cdot T \cdot \cos \theta \]

  \[ B_{ij} \text{ is the estimated standard deviation (ESD) in au} \]
  \[ B_{ii} \text{ is the estimated standard deviation in au} \]

- Quadratic elongation is expressed as the ratio of observed to ideal octahedral volume.

- Angle variance is defined as the ratio of observed to ideal octahedral angle.

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**Figure 1:**

Bond distance (Å) for the clinohorodolite structure. See Fig. 1 for details.

**Figure 2:**

The description geometry of the four polyhedra (Ca or Fe) is given only to clinopyroxene and other in Fig. 2. An interatomic distance would be discussed in terms of the real structure given an atomic model.
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Fig. 1. Variation of M1-O and M2-O interatomic distances with ferrosilite content in Ca-Fe clinopyroxenes. Error bars represent ±1 standard deviation. Data for hedenbergite and clinoferrosilite are after Cameron et al. (1972) and Burnham (1962), respectively. See Figure 2 for details of M2 coordination geometry.

(100) accompanied by relative movements of the O1 and O2 atoms toward M2. Rotations of the O381-O382 vector, for example, result in an increase of M2-O382 and decrease of M2-O381.

The question arises whether the structural changes described above are real changes of polyhedral geometry. If the shape of any given M2 coordination polyhedron is governed only by the species of atom (Ca or Fe) occupying that site (case 1), there will be only two possible types of M2 polyhedra in the pyroxenes studied, one found in hedenbergite and the other in clinoferrosilite, and the crystal structure of an intermediate phase obtained by X-ray diffraction would be an average of the two. In case 1, therefore, discussion of the M2 polyhedral geometry for intermediate compositions would have little physical meaning because the average would not represent the real structure. On the other hand, if the shape of any given M2 polyhedron is determined not only by the atomic species in the site but also by those in the neighboring M2 sites (case 2), then there are various possibilities for the M2 polyhedral shapes. In this case structural refinement of the X-ray data would still yield an average structure, but it would approximate the true structure more closely than in case 1.

Results of a Mössbauer study on these clinopyroxenes (Dowty and Lindsey, 1973) may help to resolve these two cases. The quadrupole splitting can be correlated with the degree of polyhedral distortion and thus it reflects primarily a short-range atomic arrangement around the iron atom. The change of the M2 quadrupole splitting (Fig. 3) indicates that the local configuration around the ferrous ion changes as the bulk chemical composition changes. Thus the M2 polyhedron occupied by the ferrous ion is also affected by the Fe/(Fe + Ca) ratio in the rest of the structure. Therefore, it is concluded that the M2 polyhedron obtained from X-ray refinement is not an artifact but represents the most probable polyhedral geometry for a given chemical composition.

Both the X-ray and the Mössbauer results indicate that a great change in the M2 polyhedral shape occurs at compositions between Fs45 Wo55 and Fs80 Wo20 (Fig. 3). The fact that the most rapid change occurs near the Fe-rich end of the solid solution is explained by the more severe effect expected for substitution of large Ca atoms into the small M2 polyhedron.

Fig. 2. (a) Variation of the oxygen positions around the M2 site in Ca-Fe clinopyroxenes. Arrows indicate shifts of the oxygen atoms relative to the M2 atom with Ca-Fe substitution; these may not represent actual shifts in the structure (see text, section on temperature factors, for discussion). Data for hedenbergite and clinoferrosilite are after Cameron et al. (1972) and Burnham (1962), respectively. (b) Relation between the M2 site and the tetrahedral chains in Fs80 Wo20. Note that positional changes of the O3 atoms shown in (a) result in rotations of the tetrahedral chains.
Silicate Chains

Octahedral expansion affects the tetrahedral chains in three ways: (1) The silicate tetrahedra distort, (2) the tetrahedral chain angles change, and (3) the degree of out-of-plane tilting of the basal faces of the tetrahedra vary (Cameron et al., 1973). Details of these changes associated with Ca-Fe substitution are discussed below.

Tetrahedron. Interatomic distances and angles for the silicate tetrahedra are given in Table 6. The Si-O3 (bridging oxygen) bond is the longest of the Si-O bonds, and of the two nonbridging oxygens, the Si-O2 distance is shorter than the Si-O1. The angle O1-Si-O2, 114°-119°, is larger than the ideal tetrahedral angle, 109.46°.

The Si-O3 (bridging) bond distances (Fig. 4) decrease with replacement of Fe for Ca on the augite (Ca-rich) side, whereas the Si-O (nonbridging) bond distances increase. Variation on the pigeonite (Ca-

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**Table 6. Interatomic Distances and Angles for Si Tetrahedra in Ca-Fe Clinopyroxenes**

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>Si-O1</th>
<th>Si-O2</th>
<th>Si-O3</th>
<th>O1-Si-O2</th>
<th>O1-Si-O3</th>
<th>O1-Si-O1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe±0.5%</td>
<td>1.620(2)</td>
<td>1.610(2)</td>
<td>1.617(3)</td>
<td>1.058(2)</td>
<td>1.059(2)</td>
<td>1.061(2)</td>
</tr>
<tr>
<td>Fe±0.3%</td>
<td>1.618(2)</td>
<td>1.610(2)</td>
<td>1.617(3)</td>
<td>1.058(2)</td>
<td>1.059(2)</td>
<td>1.061(2)</td>
</tr>
</tbody>
</table>

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**Fig. 3. Comparison of variations of the M2 quadrapole splitting (Dowty and Lindley, 1973) and the M2-O3 interatomic distance (Dowty and Lindley, 1973) with Fe/Om content in Ca-Fe clinopyroxenes. See Figure 1 for M2-O1 and M2-O3 distance variations. Note that both X-ray and Mössbauer studies indicate a sharp change in M2 polyhedral shape between the compositions Fe±0.5% and Fe±0.3%.

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**Fig. 4. Si-O bond distance (Å) vs. Fe/Om content in Ca-Fe clinopyroxenes. Fe±0.5% denotes the Ca-poor end member, while Fe±0.3% denotes the Ca-rich end member.**
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strengths. When the strength of one bond increases, that of another must decrease to maintain the sum constant. Because only three cations are coordinated to the O2 atom, the bond strengths for Si-O2, M1-O2, and M2-O2 are larger (thus shorter in length) than any other corresponding bonds for the O1 and O3 oxygens.

Tetrahedral Chain Angle. The tetrahedral chain angle, O3-O3-O3, has been shown to vary with chemical composition, particularly with Ca content, and also with temperature (Clark et al. 1969; Brown et al., 1972; Smyth and Burnham, 1972; Cameron et al., 1973). Proper attention must be given, however, not only to angles but also to the rotation direction with respect to the octahedra (Thompson, 1970; Papke et al., 1973). Overlooking the difference in the rotation sense, the chain in augites is often compared with the A chain in pigeonites on the basis of the apparent similarity of the tetrahedral chain angle, which is 165° for hedenbergite (Cameron et al., 1973) and 167° for the A chain in clinopyroxene (Burnham, 1967). The sense of rotation is, however, reversed in these chains.

The variation of the tetrahedral chain angles with composition is plotted in Figure 5. As the effective size of M2 decreases by substitution of Fe for Ca, the chain becomes more kinked, from 165° in Fs4Wo8 to 159° in Fs8Wo6. The relation between the M2 site and the tetrahedral chains can be visualized using Figure 2: a vector connecting O3H1 and O3H2 can be seen to rotate clockwise when the composition changes from Fs4Wo8 to Fs8Wo6, and this rotation results in a decrease in the O3-O3-O3 angle. As the size of M2 decreases further from Fs8Wo6, the chains on opposite sides of each M2 polyhedron become crystallographically distinct. The B chain becomes increasingly kinked, whereas the A chain becomes extended and reverses its rotation direction between Fs4Wo8 and Fs8Wo6. Thus in Fs8Wo6, the A chain is "S-rotated" (Thompson, 1970) and the B chain is "O-rotated."

Out-of-Plane Tilting of the Basal Face of the Tetrahedron. The out-of-plane tilting of the basal face of the tetrahedron, which is defined as the angle between (100) and the basal face,
very little effect on the O1-O1 distance, which varies only from 3.038 Å in Fe$_{0.89}$Si$_{0.11}$O$_{1.96}$ to 3.040 Å in Fe$_{0.88}$W$_{0.12}$O$_{1.96}$ as the chain angle decreases from 164.5° to 142°; therefore, the relative position of O1 is very nearly fixed. The only means of kinking the chain without moving O1 results in the movement of the O2 atom in such a manner that the out-of-plane tilting increases (Fig. 6).

**Temperature Factors**

The variation of isotropic temperature factors with composition (Fig. 7) falls into two groups: one (M2, O2, and O3) has a marked peak in the middle of the solid solution, whereas the other (M1, Si, and O1) is relatively flat. These differences in behavior can be explained by the effects of positional disorder due to multiple occupancy of the M2 site. Because the ionic radii of the Ca and Fe atoms are considerably different, which would be expected from shortening of the M2-O2 bonds.

O2-O1-O3', of the tetrahedron, provides another measure to describe the silicate tetrahedral chain configuration. The direction of the observed tilting is such that the O1 and O2 atoms in the same tetrahedron are on opposite sides of the (100) plane containing the O3 atoms (Fig. 6). As exhibited in Figure 5 and Table 5, the out-of-plane tilting generally tends to increase when the composition changes from hedenbergite to ferrosilite. This increased tilting is a direct response of the tetrahedral chain to the changes in the M2 polyhedron. When the composition changes from Fe$_{0.89}$W$_{0.11}$O$_{1.96}$ to Fe$_{0.88}$W$_{0.12}$O$_{1.96}$ (Fig. 1), the M2-O2 distances decrease but M2-O3 distances increase. These changes in the M2-O distances will result in an increase in the out-of-plane tilting angle (Fig. 6). In the pigeonite region the tilting is larger for the B chain than for the A chain, reflecting the fact that M2-O2B < M2-O2A and M2-O3B1 > M2-O3A1 (Fig. 1).

There is a correlation between the tilting and the tetrahedral B chain angle (Fig. 5)—the more kinked the chain angle, the greater the out-of-plane tilting. This relationship may be explained by simple geometrical arguments. The kinking of the chain results in an increase in the offset of O3 atom pairs parallel to b (Fig. 2b). However, these changes have

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**Fig. 6.** A portion of the Fe$_{0.89}$W$_{0.11}$O$_{1.96}$ structure showing the relation between the M2 site and the out-of-plane tilting of the basal face of the tetrahedron. The O2 atoms shift slightly toward M2 and away from the (100) plane, passing through the O3 atoms. As a result, the basal face of the tetrahedron tilts a few degrees with respect to (100). Out-of-plane tilting increases when the effective ionic size of M2 decreases, as would be expected from shortening of M2-O2 bonds.

**Fig. 7.** Variation of equivalent isotropic temperature factors with ferrosilite content in Ca-Fe clinopyroxenes. Error bars represent ±1 standard deviation (if not shown, the standard deviation is smaller than the radius of circles). Data for hedenbergite and ferrosilite are after Cameron et al. (1973) and Burnham (1967), respectively.
different, one might expect a positional fluctuation, which results from variation of the atomic positions (in terms of fractional coordinates of the unit-cell translations) from one unit cell to another. The effects of positional disorder may be significant, especially for the multiple occupancy sites.

In the clinopyroxenes under study, the M2 site shows its largest apparent temperature factor in the middle of the solid solution (Fig. 7), as is expected from its multiple occupancy by Ca and Fe atoms. The O2 and O3 atoms also exhibit large apparent temperature factors for intermediate compositions. This effect can be related to disorder of the tetrahedral chain rotation, as will be discussed below. In contrast M1 and Si, which are not directly linked to M2, show less significant effects of positional disorder. Interestingly, the positional disorder of the apical oxygen O1, although it is coordinated to M2, is the smallest among the oxygen atoms, indicating that the position of O1 is relatively well localized in the unit cell.

Some of the thermal vibration ellipsoids given in Table 7 show abnormally large anisotropy, which may be explained by positional disorder. The apparent thermal vibration ellipsoids for the atoms in the M2 polyhedron are shown in Figure 8. M2, for example, has the longest ellipsoid axis parallel to the b axis, except in hedenbergite, in which the longest axis is normal to the b axis. The thermal vibration ellipsoid in hedenbergite presumably represents

| Table 7. Magnitudes and Orientations of the Principal Axes of Thermal Vibration Ellipsoids in Ca-Fe Clinopyroxenes |
|------------------|------------------|------------------|------------------|
|                  | r.m.s. major axis (Å) | Angle (deg.) of 45° with 010  | r.m.s. major axis (Å) | Angle (deg.) of 45° with 010 |
|                  | a                | b                | c                | a                | b                |
| a                 | b               | c                | a                | b                | c                |
| FeMG005 1        | 0.002(2)        | 0.002(2)         | 0.002(2)        | 0.002(2)        | 0.002(2)         | 0.002(2)         |
| 2                 | 0.002(3)        | 0.002(3)         | 0.002(3)        | 0.002(3)        | 0.002(3)         | 0.002(3)         |
| 3                 | 0.002(4)        | 0.002(4)         | 0.002(4)        | 0.002(4)        | 0.002(4)         | 0.002(4)         |
| FeMG105 1        | 0.004(2)        | 0.004(2)         | 0.004(2)        | 0.004(2)        | 0.004(2)         | 0.004(2)         |
| 2                 | 0.004(3)        | 0.004(3)         | 0.004(3)        | 0.004(3)        | 0.004(3)         | 0.004(3)         |
| 3                 | 0.004(4)        | 0.004(4)         | 0.004(4)        | 0.004(4)        | 0.004(4)         | 0.004(4)         |
| FeMG15 1         | 0.006(2)        | 0.006(2)         | 0.006(2)        | 0.006(2)        | 0.006(2)         | 0.006(2)         |
| 2                 | 0.006(3)        | 0.006(3)         | 0.006(3)        | 0.006(3)        | 0.006(3)         | 0.006(3)         |
| 3                 | 0.006(4)        | 0.006(4)         | 0.006(4)        | 0.006(4)        | 0.006(4)         | 0.006(4)         |

*Parenthesized figures represent the estimated standard deviation (SD) in terms of least units cited for the value to their immediate left, thus for 0.004(3) read 0.004 ± 0.003.

*Orientation of axis is indeterminate because the ellipsoid is essentially uniaxial.

**The corresponding eigen value is close to zero but negative.
primarily intrinsic vibrations, whereas those in intermediate compositions include significant effects of positional disorder. As for the M2 displacement, this study suggests the same interpretation reached by Takeda (1972). Since O1 shows relatively small changes in ellipsoid shape throughout the solid solution, it seems reasonable to conclude that as the composition becomes more iron-rich, the mean position of M2 shifts toward O1 rather than the other way.

In intermediate compositions the longest ellipsoid axis for the O2 atom tends to orient parallel to the bond direction of M2–O2 (Fig. 9a). Since M2–O2 is the shortest bond in the M2 polyhedron, the multiple occupancy of the Ca and Fe atoms in M2 may produce significant disorder of O2 along the bond direction.

Together, O2, and O3 could provide a clue to the Ca–Fe occupancy.

The large apparent thermal vibration ellipsoids for M2 and O3 atoms in Ca–Fe diopsides could be due to a lack of chemical order or to a lack of chemical order, giving the appearance of a mixture of both Ca and Fe atoms in the Ca–Fe diopsides.
The large apparent thermal vibration ellipsoid for the O3 atoms in the intermediate compositions can be interpreted as positional disorder associated with tetrahedral chain rotation (Fig. 9b). As previously shown (Fig. 2) the change in size of the M2 cation causes a rotation of the tetrahedral chains. The rotation angle of the individual chains may be slightly different from the average chain angle, and the resulting positional fluctuation will appear as large apparent vibrations of O3 in (100), the approximate plane of the rotation, and along a bleeding direction of the basal faces of the two tetrahedra bridged by O3, O1 and Si, however, are close to the rotation axis and thus are not affected by this rotation.

Conclusions

As composition changes on the hedenbergite-ferroolite join, the polyhedral volume and bond distances of the M1 site do not change appreciably, except for a slight distortion of the polyhedron. Such lack of change in M1 confirms that few, if any, Ca atoms can occupy M1 sites in the Ca-Fe clinopyroxenites studied.

In the M2 coordination polyhedron the M2-O1 and M2-O2 distances and the polyhedral volume decrease when the composition changes from hedenbergite to ferroolite. The M2-O3 distances exhibit a sharp change between the compositions Fe$_3$Mg$_2$Si$_2$O$_6$ and Fe$_3$Mg$_2$Si$_2$O$_6$.

The decrease in the average size of the M2 atom causes kinking of the tetrahedral B chain. Extension and reversal of rotation sense of the A chain occur between the compositions Fe$_3$Mg$_2$Si$_2$O$_6$ and Fe$_3$Mg$_2$Si$_2$O$_6$. The decrease in M2 cation size causes an increase in the out-of-plane tilting of the basal face of the tetrahedron.

The large temperature factors found for the M2, O2, and O3 atoms in intermediate compositions of the Ca-Fe clinopyroxenites can be explained by the effect of atomic positional disorder due to multiple occupancy in M2.

Together with the crystal structures of the endmember clinopyroxenes at high temperatures (Cameron et al., 1973), the results of the present study could provide a basis for future studies of the crystal structures of intermediate clinopyroxenes at high temperature. These studies, which will undoubtedly have mineralogical significance for a better understanding of crystallization and exsolution in natural pyroxenes, are also necessary for relating the crystal structures to the experimentally determined phase diagram.

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