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 $M_2$ polyhedron, whereas the $M_1$ polyhedron remains essentially unchanged. The decrease in the average size of the $M_2$ polyhedron associated with a compositional change from hedenbergite to ferrosilite causes kinking of the tetrahedral chain and consequent increases in the out-of-plane tilting of the basal face of the tetrahedron. As the $M_2$ polyhedron decreases in size, the space group changes from $C2/c$ to $P2_1/c$ at about $Fe_{10}WO_6$ composition. When the composition changes from $Fe_{12}WO_6$ to $Fe_{10}WO_6$, 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 radii of the atoms 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-olivine-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 $M_2$ site\(^1\) 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 $P2_1/c$ and members (clinopyroxene: Burnham, 1967; clinoenstatite: Morimoto, Appleman, and Evans, 1969).

In clinopyroxenes of intermediate composition, the $M_2$ site is very irregular as a result of multiple occupancy of large Ca and small Fe or Mg atoms in the site. In a structural refinement of a pigeonite, $Mg_{29}Fe_{70}Ca_{28}SiO_3$ from Mull, Scotland, Morimoto and Güven (1970) reported a very irregular $M_2$ coordination polyhedron, which they concluded was an average of eight- and six-coordinated. Güven (1969) studied the relationship between the average size of $M_2$ and kinking of the

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\(^1\) Nomenclature for the pyroxenes is that proposed by Burnham et al. (1967).
tetrahedral chain. Takeda (1972) discussed variation of $M_2$-$O$ bonds in clinopyroxenes as a function of $Ca$ content and showed that the $M_2$ polyhedron becomes very irregular, thus highly unstable, in the middle of the solid solution. He proposed that irregularity of the $M_2$ polyhedral 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 $M_2$ coordination associated with the $P3_1/c-P3_2/c$ 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 of Mg-Fe distribution in the cation sites, the binary join hedenbergite ($CaFeSi_2O_6$)-clinofelosilite ($Fe_2SiO_5$) was selected. Therefore, these structures reflect solely a difference between $Ca$ and Fe contents. Furthermore, if the $M_1$ 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 $M_2$ 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-clinofelosilite join were kindly supplied by Dr. D. H. Lindsey. Synthesis techniques were described by Lindsey and Manuz (1969, Appendix). Crystals of $Fe_2Wo_{60}$, $Fe_2W_0$, and $Fe_3Wo_{25}$ (all synthesized at 20 kbar and 950°C), and $Fe_3Wo_{60}$ (6 kbar and 1140°C) have been examined using the Buerger precession camera. Class $b$ reflections ($h + k = \text{odd}$) are exhibited by $Fe_3Wo_{60}$ and some crystals of $Fe_2Wo_{60}$, whereas long-exposure photographs of $Fe_2Wo_{60}$, $Fe_2W_0$, and the other crystals of $Fe_3Wo_{60}$ do not show these $b$ reflections. Thus the (metastable) boundary at room temperature between the space groups $P3_1/c$ and $P3_2/c$ is close to the $Fe_3Wo_{60}$ composition on the join hedenbergite-clinofelosilite. At low pressures the clinopyroxene of this composition is not stable relative to the assemblage fayalite + tridymite (Bowen, Schairer, and Passchier, 1933; Lindsey and Manuz, 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 $Fe_3Wo_{60}$ were measured using a back-reflection precession Weissenberg camera. Data for both $CuK_{\alpha}$ and $K_{\beta}$ 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 $Fe_3Wo_{60}$ were determined by a lattice-constant refinement subroutine for a four-circle diffractometer. This subroutine, which is a part of the Geophysical Laboratory diffracrometer 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 $MoK_{\alpha}$ radiation. Reflections in one quadrant of reciprocal space within the range 0.1 to 0.8 of sin $\theta/\lambda$ were measured employing $\omega$-$2\theta$ scans. The observed intensities were corrected for Lorentz and polarization effects and for absorption using the numerical integration techniques of Burnham (1966).

In addition, the secondary extinction factor of Zachariasen (1968) was calculated for the $Fe_3Wo_{60}$ and $Fe_3Wo_{60}$ crystals. The crystal of $Fe_3Wo_{60}$ was twinned on (100).

Therefore, the $hK0$ reflections contain superimposed contributions from both twin components. By com-
TABLE 2. Crystal and Refinement Data for Ca-Fe Clinopyroxenes

<table>
<thead>
<tr>
<th>Structure</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
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<tr>
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<td>P3_1/m</td>
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<td>8.535</td>
<td>13.385</td>
<td>89.4</td>
<td>89.4</td>
<td>60.0</td>
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<tr>
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<td>P3_1/m</td>
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<td>8.535</td>
<td>13.385</td>
<td>89.4</td>
<td>89.4</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Reefinement Procedures

Throughout all refinements, the least-squares program REINE of Finger was used on the IAC 370 and the UNIVAC 1108 computers. Atomic scattering factors were those of Fe^{2+}, Ca^{2+}, Si^{4+}, and O^{-} given by Czandri and Mann (1968) with the anomalous dispersion coefficients of Czandri (1965).

Least-squares refinements of F_{1} WO_{3} and F_{2} WO_{3} were initiated with atomic parameters of heedenbergite (Vebeln, 1969) and clinopyroxenate (Burnham, 1967), respectively. Refined parameters of F_{1} WO_{3} and F_{2} WO_{3}, respectively, were used as initial parameters of F_{1} WO_{3} and F_{2} WO_{3}. 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 coefficients, and a scale factor were refined. In addition, the isotropic extinction parameter of Zuckerman (1968) was refined for the F_{1} WO_{3} and F_{2} WO_{3} data sets. The correction for the twinning in F_{1} WO_{3} 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/e structural refinements. However, the A and B chains in the Ez/e structure are in general highly correlated: -0.75 between $β_{4}'$s of SiA and SiB and -0.71 between $ν's of OA_{4}$ and OA_{8} were found to be the strongest correlations.

From an ionic size consideration, all Ca atoms are assumed to occupy the larger M2 site. Thus, for example, the occupancy of chain sites for F_{1} WO_{3} is 100 percent Fe^{2+} in the M1 site and 70 percent Fe^{2+} + 30 percent Ca in the M2 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.2

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1. 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, 1099 K Street, N.W., Washington, D. C. 20006. Please remit $1.00 for the microfiche.
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 clinoferrilitite).

The M2 site changes from eight-coordinated in hedenbergite to six-coordinated in ferrosilite. The changes 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 Fe$_{1.9}$Wo$_{0.1}$ to Fe$_{0.19}$Wo$_{0.81}$. In the P$_2$O$_5$ region these bonds split into two groups, one increasing and the other decreasing with further Fe enrichment. In clinoferrilitite 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 Fig. 2. The changes of the M2-O distances occur as a consequence of a rotation of the O3A1-O3A2 and O3B1-O3B2 vectors in...
EFFECT OF Ca-Fe SUBSTITUTION ON THE CLINOPYROXENE STRUCTURE

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 clinoferroilite are after Cameron et al. (1973) and Burnham (1967), 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 O3B1-O3B2 vector, for example, result in an increase of M2-O3B2 and decrease of M2-O3B1.

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 clinoferroilite, 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 Fs10-W03 and Fs25-W07 (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 clinoferroilite are after Cameron et al. (1973) and Burnham (1967), respectively. (b) Relation between the M2 site and the tetrahedral chains in Fs25-W07. 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 tetrahedron distorts, (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 oxygen, 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-poor) side, however, is not simple because there are two crystallographically distinct silicate chains. As the composition changes from Fs02WoO to Fs05WoO, expansions of the Si-O1 and Si-O2 bonds are accompanied by contractions of M2-O1 and M2-O2, respectively. For the O3 atoms, contractions of the Si-O3 bonds are coupled with expansions of the M2-O3 bonds. The M1-O distances remain essentially constant with composition.

Qualitative discussions on bond distances can be developed by introducing a bond strength, defined by Zachariasen (1963). He assumes (1) that the bond strength is empirically related to the bond distance and (2) that the sum of bond strengths for each atom is set to its valence. Coupled changes in the Si-O and M2-O bond distances for the same oxygen atom are a natural consequence of the constant sum of the bond strengths that of the O1-O2-O3-O1 constant (i.e., the bond angle to the M1-O2-O1 bond length). O1 and O3 have longer distances.

Tetrahedral angle, or bond angle, refers to the chemistry, structural, and also to the relationship (Papke et al., 1967). It is not only related to the bond angle but also to the rotation of the tetrahedron with the bond angle being the apparent staggered bond angle is 155°-167° for M2-O3, whereas O1-O3, O2-O3, O1-O2 (Papke et al., 1967). The values of these changes are discussed below.

The values of Si-O bond distances and angles for the composition with nonbridging oxygen, 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°.

![Figure 3](image-url) Comparison of variations of the M2 quadropole splitting (Davy and Lindsey, 1973) and the M2-O3 interatomic distances with formula content in Ca-Fe clinopyroxenes. See Figure 1 for M2-O1 and M2-O3 distance variations. Note that both X-ray and electron diffraction studies indicate a sharp change in M2 polyhedral shape with the compositions Fs02WoO and Fs05WoO.

![Figure 4](image-url) Si-O bond distances (Å) for the oxygens in Ca-Fe clinopyroxenes: O1 (1.60 Å), O2 (1.40 Å), O3 (1.80 Å) with respective bond angles of 155°, 167°, and 155°. The bond angles are calculated from the ideal tetrahedral angle, 109.46°, with the formula content in Fig. 2 (Davy and Lindsey, 1973) and the data of Figs. 3 and 4. The bond distances are evaluated from the ideal tetrahedral angle, 109.46°, with the formula content in Fig. 2 (Davy and Lindsey, 1973) and the data of Figs. 3 and 4.
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 clinoferrosilite (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 Fs80Wo20 to 159° in Fs20Wo80. 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 Fs80Wo20 to Fs20Wo80, and this rotation results in a decrease in the O3-O3-O3 angle. As the size of M2 decreases further from Fs20Wo80, 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 Fs80Wo20 and Fs20Wo80. Thus in Fs80Wo20 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,
Fig. 6. A portion of the Fe₂₋₈₋₋₉₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋个百分·。 The O₂ atoms shift slightly toward O₁ 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.

O₂-O₃-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 ferrobasalt. This increased tilting is a direct response of the tetrahedral chain to the changes in the M₂ polyhedron. When the composition changes from Fe₂₋₈₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋ಠ ratified, 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 very little effect on the O₁-O₁ distance, which varies only from 3.038 Å in Fe₂₋₈₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋₋₀₋ಠ ratified, 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, in turn, translates into distinct effects on positional disorder especially for the M₂ site.

In the pigeonite region, the middle of the solid solution from iron basalt to ferrobasalt shows a peak in (M₂, O₂, and O₃) that is not present in temperature. This effect on the tetrahedral tilt in Ca Ferron is depicted in Figures 7 and 8.
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 Sι, 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 hedbergite, in which the longest axis is normal to the b axis. The thermal vibration ellipsoid in hedbergite presumably represents

### Table 7. Magnitudes and Orientations of the Principal Axes of Thermal Vibration Ellipsoids in Ca-Fe Clinopyroxenes

<table>
<thead>
<tr>
<th>Ellipsoid axes (Å)</th>
<th>r.m.s. magnitude (Å²)</th>
<th>Angle (deg.) of b with</th>
<th>r.m.s. magnitude (Å²)</th>
<th>Angle (deg.) of b with</th>
<th>r.m.s. magnitude (Å²)</th>
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*Parenthesized figures represent the estimated standard deviation (e.s.d.) in terms of least units cited for the value followed by a plus or minus.**

**Denotes an axis which is indeterminate because the ellipsoid is essentially planar.***

***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.

As composing the ferrobasalts, the results of the CaO-FeO-MgO-Fe$_2$O$_3$-(Ca,Fe)$_2$O$_4$ compositions except for a lack of chemical end members indicates that all the O2 atoms can be considered as difference studies.

In the Fe$_2$O$_3$-Fe$_3$O$_4$-FeO compositions, the Fe$_2$O$_3$ decreases with increasing temperature, and the cationic positions in the M2 polyhedron seem to exhibit a shift toward the Fe$_3$O$_4$ orientation, i.e., in the direction of Fe$_3$O$_4$.

The decrease in the Fe$_2$O$_3$ content is accompanied by a decrease in the relative content of the Fe$_3$O$_4$ orientation. The decrease in the Fe$_2$O$_3$ content is accompanied by a decrease in the Fe$_3$O$_4$ orientation.

The large difference in the Fe$_2$O$_3$ content of the M2, O2, and O3 compositions implies that the Ca-Fe ratio is the major effect of atomic occupancy in the olivine.

Together these results suggest that the major difference in the Ca-Fe ratio is the major effect of atomic occupancy in the olivine.
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 bleating 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-ferrosilite 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 clinopyroxenes 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 ferrosilite. The M2-O3 distances exhibit a sharp change between the compositions Fe8W06 and Fe8W08.

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 Fe8W06 and Fe8W08. 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 clinopyroxenes can be explained by the effect of atomic positional disorder due to multiple occupancy in M2.

Together with the crystal structures of the end-member 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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