Structure and Crystal Chemistry of Calcium Tschermak's Pyroxene, CaAlAlSiO₆

FUJIO PETER OKAMURA, SUBRATA GOSEH,
Department of Geological Sciences, University of Washington,
Seattle, Washington 98195

AND HARUO OHASHI
National Institute for Researches in Inorganic Materials,
Kurakake, Sakakura-mura, Niihari-gun, Ibaraki, 300-31, Japan

Abstract

The crystal structure of calcium Tschermak's pyroxene, CaAlAlSiO₆ (CaTs) synthesized at 1300°C and 18 kbar has been determined and refined by the least squares method using 1165 reflections measured on a computer controlled automatic single crystal diffractometer, using monochromatic MoKα radiation. The unweighted R-factor is 0.024. The cell dimensions are: a₀ = 9.609 Å, b₀ = 8.652 Å, c₀ = 5.274 Å and β = 106.05°; space group C2/c. Al–Si are completely disordered at the tetrahedral site. The average T-O distance is 1.686 Å. A linear relationship exists between T-O (nbr) and Al(Al + Si) ratio, namely, T-O (nbr) = 1.593 + 0.16917 X Al(Al + Si). The average octahedral Al-O distance of 1.947 Å, which is larger than that in either spodumene (1.919 Å) or jadeite (1.928 Å), reflects the larger cation (Ca) occupying the M2 site. A remarkable feature of the structure of CaTs is the CaO₆ coordination polyhedron, which is smaller (average C:π-O 2.46 Å) and more regular than that in diopside. This feature probably explains the stability of CaTs under high pressure. Possible schemes of Al–Si order within tetrahedral chains have been derived.

Introduction

It seems highly probable that pyroxene is an important constituent of the earth's upper mantle. The pyroxene would be a complex crystalline solution with a considerable amount of the Ca-Tschermak's molecule, CaAlAlSiO₆ (hereafter called CaTs). Under high pressure anorthite breaks down to CaTs molecule and silica.

CaAl₂Si₅O₁₈ = CaAlAlSiO₆ + SiO₂.

CaTs component is increasingly dissolved in a clinopyroxene of the diopside type as a function of pressure (Clark, Scharer, and de Neufville, 1962). Thus clinopyroxenes from eclogites, from granulites, and from ultramafic inclusions in basaltic rocks and kimberlites contain a considerable amount of the CaTs molecule. However, CaTs is also an important component of the lunar clinopyroxenes formed at high temperature, but relatively low pressures. Hence, the solubility of CaTs in clinopyroxenes must be a function of both high pressure and temperature. CaTs has been synthesized and its solubility in diopside has been determined (Clark et al, 1962; Sakata, 1957).

However, despite great interest in the crystal chemistry of this pyroxene, little has been known except cell dimensions (Clark et al, 1962), because no one could synthesize single crystals large enough for structure determination by single-crystal X-ray diffraction methods. One of us (H. O.) now has successfully grown single crystals under high pressure large enough for X-ray studies. We report here the details of the crystal chemistry of CaTs pyroxene based on a structure refinement.

Synthesis of CaAlAlSiO₆ Single Crystals

The starting material was a mixture of anorthite, gehlenite, and corundum prepared from CaCO₃, Al₂O₃, and SiO₂ by solid state reaction in air.

3(CaCO₃ + Al₂O₃ + SiO₂) → CaAl₂Si₅O₁₈

+ Ca₂Al₂SiO₇ + Al₂O₃ → 3 CaAl₂SiO₈.

The mixture was heated at 1300°C under 18 kbar for 24 hours in a piston-cylinder type apparatus similar to that described by Boyd and England (1960). The
samples were sealed in a platinum capsule 8 mm long and 3 mm in diameter. These capsules in turn were sealed with PtO\textsubscript{2} in another platinum capsule 12 mm long and 4 mm in diameter. At the end of the run, the capsule was quenched from 1300°C to room temperature within 10 seconds. The product was a mixture of CaTs and gehlenite.

Electron microprobe analysis of CaTs by Edmond A. Mathez using anorthite glass and pure diopside as standards indicates a chemical composition,

$$\text{Ca}_{1.002}\text{Al}_{0.934}\text{Si}_{1.008}\text{O}_{5.825}$$

(assuming six oxygen atoms). These results indicate a slight deficiency in aluminum and slight excesses for silicon and calcium with respect to the ideal composition. These deviations are beyond the error limits. One possible explanation of the analytical results is coupled aluminum and oxygen deficiency. The chemical composition can then be expressed as

$$\text{Ca}_{1.002}\text{Al}_{0.878}\text{Si}_{1.008}\text{O}_{5.825}$$

For the purposes of structure determination, however, we have assumed the ideal composition CaAl\textsubscript{1.0}Si\textsubscript{1.0}O\textsubscript{5.5}. This assumption does not result in any significant errors in the structure determination.

### Measurement of Intensity Data and Refinement of the Structure

From single crystal X-ray precession photographs, the space group was determined to be C2/c. A single crystal fragment showing good crystallinity as judged by a transmission Laue photograph was mounted on a computer-controlled single-crystal diffractometer (Syntex P\textsubscript{l}). For intensity measurements a solid state detection system and MoK\textalpha radiation monochromatized by reflection from a graphite single crystal ($2\theta = 12.2^\circ$) have been used. All h0l reflections with $2\theta$ less than 60° were measured using a very slow scan rate (0.25°/min). No reflection violating the C2/c space group was detected.

The cell dimensions, refined by the least squares method using 15 reflections with 20 between 35° and 50° measured on the diffractometer, are: 

- $a = 9.609(3)$, $b = 8.652(2)$, $c = 5.274(2)$ Å, \( \beta = 106.06(2)^\circ \);
- $V = 421.35(21)$ Å\textsuperscript{3}; $Z = 4$. The calculated density is 3.44 g cm\textsuperscript{-3}.

#### Table 1. Atomic Parameters of CaAl\textsubscript{1.0}Si\textsubscript{1.0}O\textsubscript{5.5}

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{eq}$</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
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<td>M1 (Al)</td>
<td>0</td>
<td>0.9036(7)</td>
<td>1/4</td>
<td>0.613(8)</td>
<td>0.00156(5)</td>
<td>0.00169(6)</td>
<td>0.00704(17)</td>
<td>0</td>
<td>0.00022(7)</td>
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<td>3.3137(4)</td>
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<td>0.733(6)</td>
<td>0.00228(3)</td>
<td>0.00180(6)</td>
<td>0.00784(11)</td>
<td>0</td>
<td>0.00050(5)</td>
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<td>T (Al + Si)</td>
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<td>0.09693(4)</td>
<td>1/4</td>
<td>0.529(6)</td>
<td>0.00332(4)</td>
<td>0.00148(6)</td>
<td>0.00652(12)</td>
<td>0</td>
<td>0.00004(3)</td>
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#### Table 2. Bond Lengths and Bond Angles of CaAl\textsubscript{1.0}Si\textsubscript{1.0}O\textsubscript{5.5}

<table>
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<tr>
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<th>Value (Å)</th>
<th>Atom</th>
<th>Value (º)</th>
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<td>Tetrahedron (Si1, Al1)</td>
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<td>T-01</td>
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<td>T-02</td>
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<td>104.43 (5)</td>
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<td>T-03A1</td>
<td>1.683 (1)</td>
<td>01-02-03</td>
<td>110.39 (6)</td>
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<td>01-02-03</td>
<td>103.43 (9)</td>
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<td>mean, brg.</td>
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<td>T-03A2</td>
<td>3.125 (1)</td>
<td>03A2-01A2</td>
<td>165.93 (6)</td>
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</table>
The intensities of 1165 reflections have been measured using monochromatic MoKα radiation (50kV, 20mA) and a variable scan rate, the minimum scan rate being 0.5°/min. The observed intensities were corrected for Lorentz, polarization, and monochromator polarization factors. Since the size of the crystal (0.06 × 0.12 × 0.20 mm) and the linear absorption coefficient μ (22 cm⁻¹) were both small, no absorption corrections were made. The least squares refinement is based on 970Fo values above 3σ(Fo), where σ(Fo) is the standard deviation. The Fo's were weighted as Fo/σ²(Fo). The full matrix least squares program Rfime (Finger, 1969) was employed using the atomic coordinates and isotropic temperature factors of diopside (Clark, Appleman, and Papke, 1969) as input parameters. The atomic scattering factors for Ca, Al, Si, and O were taken from Cromer (1965). Anomalous dispersion corrections have been made (Cromer and Waber, 1965).

After 3 cycles of isotropic refinement, the R-factor (unweighted) decreased from 0.424 to 0.048. Two cycles of refinement using anisotropic temperature factors reduced the R-factor to 0.024 (unweighted) and 0.029 (weighted). The atomic parameters are listed in Table 1. Bond lengths and angles as well as ellipsoids of thermal vibration with the standard deviations were calculated using the program Ennon (Finger, 1969) and are listed in Tables 2 and 3 respectively. Observed and calculated structure factors are listed in Table 6.

### Description of the Structure

Though the crystal structure of CaTs is similar to that of diopside (Clark, Appleman, and Papke, 1969), there are two important differences with respect to (a) T-O tetrahedron and (b) M2-O polyhedron geometries.

#### T-O Tetrahedron

Since the tetrahedral chain is composed of half Al and half Si, the size of the T-O tetrahedron is considerably larger (T-O av. 1.686 Å) in CaTs than that in diopside (T-O av. 1.634 Å). In Figure 1 the T-O distances in pyroxenes with various tetrahedral Al/(Al + Si) ratios are plotted, together with those in AlO₄ tetrahedron in sillimanite (Burnham, 1963), where it forms a chain alternating with SiO₄ tetrahedron. It can be seen that the Al/(Al + Si) ratio shows a good linear relationship with the T-O (nbr) distance, but not with the T-O (br) distance. The linear relationship can be expressed as

\[ T - O(\text{nbr}) = 1.593 + 0.16917 \times \frac{\text{Al}}{\text{(Al + Si)}} \]

or inversely

\[ \frac{\text{Al}}{\text{(Al + Si)}} = 5.9113 \times (T - O(\text{nbr}) - 1.593). \]

In spite of the differences in the size of the T-O tetrahedra, the puckering of the chains as defined by the O₃-O₄′-O₅″ angle is comparable in CaTs (165.9°) and diopside (166.4°). The T-T separation is 3.125 Å,
which is considerably larger than the Si-Si separation in jadeite (3.061 Å) and diopside (3.107 Å). The T-O3-T angle in CaTs is 134.94°.

The M2-O Polyhedron

One of the surprising results of this study is the discovery that in CaTs the size of the Ca-O polyhedron is much smaller and more regular than that in diopside. The average Ca-O bond lengths are 2.461 Å and 2.498 Å in CaTs and diopside respectively. Thus while in diopside M2-O1, M2-O2, M2-O3, and M2-O3' are 2.360, 2.353, 2.561, and 2.717 Å respectively, in CaTs they are 2.403, 2.420, 2.469, and 2.549 respectively. Compared to diopside, the M2-O1 and M2-O2 bonds are lengthened in CaTs, while M2-O3 and M2-O3' are considerably shortened (Fig. 2).

The M1-O Octahedron

The distortion of the Al-O octahedron in CaTs is similar to those found in spodumene, LiAlSi2O6 (Clark et al, 1969) and jadeite, NaAlSi2O6 (Prewitt and Burnham, 1966). Apparently, the size of the Al-O octahedra increases with the size of the cation occupying the M2 site. Thus, in spodumene the average Al-O distance is 1.919 Å, in jadeite 1.928 Å, and in CaTs 1.974 Å. The Al-O octahedra share a common edge (O1-O1') to form chains parallel to the c-axis. This shared edge is longer in CaTs (2.516 Å) than in jadeite (2.458 Å). On the other hand, two octahedral edges shared with the M2-O polyhedra (O1-O2) are shorter in CaTs (2.760 Å) than those in jadeite (2.818 Å). The Al-Al distances within the octahedral chain in CaTs (3.068 Å) and jadeite are virtually the same.

Charge Balance

Bridging oxygen O3, in the tetrahedral chain, is coordinated to two (Al + Si) at distances 1.683 and 1.701 Å and to two Ca atoms at 2.469 and 2.549 Å. It receives a charge contribution of +7/8 each from

Table 6. Observed and Calculated Structure Factors in Calcium-Tschermak's Pyroxene CaAlAlSiO₄
two (Al + Si) atoms. The remaining charge of +1/4 is balanced by its bonding to Ca³⁺. Hence, the M2-O3' bonds in CaTs are much shorter than in diopside (2.549 versus 2.717 Å), where O3 oxygens are completely charge compensated.

Oxygen O2 is charge deficient (−3/8), while O1 is overbonded by +1/8. This explains the shorter M1-O2 and T-O2 bonds and longer M1-O1 and T-O1 bonds. The M2-O1 and M2-O2 distances (2.403 and 2.420 Å) are similar in spite of this charge imbalance on O1 and O2.

Crystal Chemistry of the CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ Join

Clark et al (1962) has shown that under high pressure and temperature there is a continuous solid solution between diopside and CaTs. Furthermore, the cell dimensions are not linear functions of composition. Thus, the molar volume as well as a and b dimensions show negative deviation, while c and β (obtuse) show pronounced positive deviations from linearity. Hence, the solid solution must be strongly non-ideal. This is expected, since the solid solution involves coupled replacement of ions with different charges and sizes, namely Mg²⁺ by Al³⁺ at the M1 site and Si⁴⁺ by Al³⁺ at the tetrahedral site. We will now examine the nature of the deviation in cell dimensions from linearity as a function of composition in the light of the crystal chemistry of CaTs.

A plot of the distance between the two O3 layers in the same chain slab against Al/(Al + Si) ratio shows a linear relationship. Therefore, this interlayer distance can be used as a standard for discussing the effect of Al/(Al + Si) ratio on the thickness of the tetrahedral layer. By subtracting this value from the 1/2 a sin β curve in the diopside-CaTs join, a third curve is obtained which shows the distance between two O3 layers adjacent to cation layers; this distance

| Table 6, Continued |
can be used as a measure of the thickness of the cation layer (Fig. 3). On the other hand, the distance from $M2$ to the nearest chain equals $b \times (0.5 - \gamma_{M2})$, where $\gamma_{M2}$ is the $y$-coordinate of the $M2$ cation ($Ca$), and yields a fourth curve (Fig. 3). Comparing these third and fourth curves to those showing changes in $M2$-$O$ distances (Fig. 4), we find that the crystalchemical change along diopside-CaTs join proceeds in two stages as follows.

Of the four pairs of bonds that $Ca^{2+}$ (at the $M2$ site) forms with oxygen, two pairs involve $O1$ and $O2$ which are bonded to $M1$ as well; two other pairs involve the tetrahedral-chain-forming oxygens $O3$ and $O3'$, which are also bonded to a second $M2$ site. $M2$-$O1$ and $M2$-$O2$ bonds are much shorter than $M2$-$O3$ and $M2$-$O3'$ bonds (Table 2). As the $Al^{3+}$ content (replacing $Mg^{2+}$) increases, the $M2$-$O1$ and $M2$-$O2$ bonds become weaker, because $O1$ and $O2$ are more strongly bonded to $Al^{3+}$ at the $M1$ site. Simultaneously, as $Al$-$Si$ substitution proceeds at the tetrahedral site, $Ca^{2+}$ at the $M2$ site is more strongly attached towards the pair of $O3$ and $O3'$ atoms, because these atoms become increasingly charge deficient.

In the initial stage, this change in local charge balance will be accomplished most efficiently by the decrease in thickness of the cation layer and mutual shifts between both $O3$ and $O3'$ pairs along the chain direction, which corresponds to an increase in the obtuse angle $\beta$. This adjustment, however, has a limit, because it requires extreme approach of an $O3$ pair.

In the next stage, when $Mg^{2+}$ has been replaced further by $Al^{3+}$ at the $M1$ site, neither $O1$ nor $O2$ can keep $Ca^{2+}$ close, $Ca^{2+}$ moving along the 2-fold axis towards $O3$ and $O3'$ pairs until local charge balance is attained. At this stage the obtuse angle $\beta$ must decrease again, so that $O3$ and $O3'$ pairs can be more evenly bonded to $Ca^{2+}$. This is achieved by puckering the tetrahedral chain, which decreases the $c$ dimensions.

**Characteristics of Ca-Tschermak's Pyroxene as a High Pressure Phase**

Zvetkov (1945), Segnit (1953), Sakata (1957), and Neufville and Schairer (1962) have shown that the maximum content of $CaAl_2SiO_6$ that can be dissolved in diopside is less than 40 mole percent at 1 atm. This is close to the maximum value of the CaTs content in terrestrial fassaite. On the other hand, Kushiro (1969) has shown that the mole fraction of CaTs in diopside in equilibrium with anorthite + quartz increases with both temperature and pressure.

Hays (1966) showed that between about $1160^\circ C$ and $1420^\circ C$ the following reactions proceed from the left to the right with increasing pressure:

$$CaAl_2SiO_6 + Ca_2Al_2SiO_7 + Al_2O_3 = 3 CaAl_2SiO_6$$

$$3 CaAl_2SiO_6 = CaAl_2SiO_3 + 2 Al_2O_3$$

Hijikata and Yagi (1967) independently synthesized CaTs using reaction (2).
It is worthwhile to compare the volumes of coordination polyhedra around Ca atoms in anorthite, gehlenite, CaTs, and grossular. As shown in Table 4, the polyhedral volumes can successfully explain the relative stability relationships among these phases except for gehlenite, which has a Ca-polyhedron smaller than that in CaTs. But considering the facts that in gehlenite two Ca-O distances are much longer (2.815 Å) and all the Al atoms occupy tetrahedral sites, together with the higher thermal expansion, we conclude that gehlenite is stable at lower pressure than CaTs.

Considering all these facts, it seems likely that Al prefers the tetrahedral site at higher temperatures and the octahedral site at higher pressures.

Al-Si Order-Disorder in the TO₃ Chain

In the CaTs sample investigated, Si and Al are randomly distributed among tetrahedral sites. However, this does not necessarily mean that the aluminum avoidance rule has been violated in this structure and short-range Al-Si order is ruled out. We may consider two models which can statistically give the C2/c space group by X-ray diffraction in spite of the presence of domains with short-range Al-Si order:

A. The structure is composed of ordered TO₃ chains, but without any order among different chains.

B. Anti-phase domains.

It is clear that model A gives an average structure by X-ray diffraction. Ghose et al (in preparation) have shown theoretically that anti-phase domains in pigeonite (P2₁/c) with fine and well-sorted domain size can cause the “b” (h + k = odd) reflections to become
diffuse and virtually undetectable. It is worthwhile to consider the possible space groups for CaTs with a three-dimensionally ordered arrangement of Si and Al. In that case, we may restrict the models to those with only one kind of $TO_3$ chain, since a large $M2$ cation such as $Ca^{2+}$ will rule out the existence of the extremely kinked chains found in Ca-poor pyroxene structures. Then, the principles for derivation of possible structures can be simplified as follows:

I. Symmetrical relationship between two chains adjacent to a cation layer.
   a. 2-fold axis
   b. I

II. Symmetrical relationship between two chains which are on the same side in neighboring chain slabs.
   a. C-center
   b. n-glide plane

From combinations among these symmetry elements, four space groups can be derived (Table 5 and Fig. 5). All of these space groups can give an apparent space group $C2/c$ as determined by X-ray diffraction through the formation of small anti-phase domains, in the same way discussed by Ghose et al (in preparation). There are no physical criteria to distinguish among those models in terms of relative stability. On the other hand, we know that jadeite has diopside-like $M2$-polyhedron with longer $M2$-$O3$ and $M2$-$O3'$ distances, whereas CaTs shows rather regularly coordinated $M2$ sites. In the structure of pyroxenes on the NaAlSi$_2$O$_6$-CaAl$_2$SiO$_6$ join, we expect two kinds of $M2$ sites, namely, a jadeite-type $M2$ site for Na$^+$ and CaTs-type $M2$ site for Ca$^{2+}$. In such a case, $P2/n$ or $C2$ are the more plausible models.

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**Fig. 4.** Changes in $M2$-$O$ distances in some $C2/c$ pyroxenes plotted against $Al/(Al + Si)$ ratio. Data from Clark et al (1969), Peacor (1967), Dowty and Clark (1973), and present study.

**Fig. 5.** Possible Al-Si ordering schemes in $TO_3$ chains of CaTs. Shadowed (likewise, white) tetrahedra are crystallographically equivalent.
STRUCTURE OF CALCIUM TSCHERMAK'S PYROXENE

Conclusion

1) There is a precise linear relationship between non-bridging T-O distance and the Al/(Al+Si) ratio.
2) Ca-Tschermak’s pyroxene has a compact M2 site coordinated by 8 oxygen atoms more evenly bonded to Ca$^{2+}$ than in diopside.
3) The Al content in the octahedral site is a potential geobarometer whereas that in the tetrahedral site is a potential geothermometer.
4) Significant changes in all parameters of pyroxenes from the CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ join can be successfully explained in terms of the relative shifts of atoms required to attain the local charge balance.
5) $C2$, $P2/n$, $C1$ and $P2_1/n$ are possible space groups for calcium Tschermak’s pyroxene with one kind of TO$_3$ chain showing perfect Al-Si order.

Addendum

Since this paper has been submitted for publication, we have discovered extra reflections in a different sample of CaTs, indicating space group $C2$, rather than $C2/c$. The extra reflections clearly indicate Si-Al ordering in the tetrahedral chain. Similar observations have also been made by T. Grove and Professor C. W. Burnham, Harvard University. Si-Al ordering in CaTs is currently under investigation in our laboratory.

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