

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

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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 MoK α radiation. The unweighted *R*-factor is 0.024. The cell dimensions are: $a_0 = 9.609 \text{ \AA}$, $b_0 = 8.652 \text{ \AA}$, $c_0 = 5.274 \text{ \AA}$ and $\beta = 106.06^\circ$; 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, $T\text{-O (nbr)} = 1.593 + 0.16917 \times \text{Al}/(\text{Al} + \text{Si})$. 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 CaO₃ coordination polyhedron, which is smaller (average Ca-O 2.460 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.



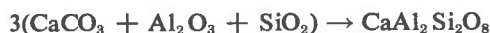
CaTs component is increasingly dissolved in a clinopyroxene of the diopside type as a function of pressure (Clark, Schairer, and de Neufville, 1962). Thus clinopyroxenes from eclogites, from granulites, and from ultramafic inclusions in basaltic rocks and kimberlites contain a considerable amount of 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.



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

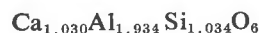
TABLE 1. Atomic Parameters of CaAlAlSiO₆

	x	y	z	B eq	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
M1 (Al)	0	.90934 (7)	1/4	.613 (8)	.00156 (5)	.00168 (6)	.00704 (17)	0	.00022 (7)	0
M2 (Ca)	0	.31117 (4)	1/4	.733 (6)	.00228 (3)	.00180 (4)	.00784 (11)	0	.00050 (5)	0
T (Al + Si)	.28802 (4)	.09693 (4)	.21337 (7)	.529 (6)	.00132 (4)	.00148 (4)	.00652 (12)	-.00004 (3)	.00065 (5)	-.00020 (5)
01	.10519 (11)	.08210 (11)	.12264 (19)	.822 (13)	.00242 (9)	.00259 (10)	.00838 (29)	.00065 (7)	.00122 (13)	.00042 (14)
02	.36571 (11)	.26707 (12)	.30988 (21)	.917 (14)	.00272 (10)	.00222 (10)	.01115 (32)	-.00020 (8)	.00139 (14)	-.00009 (14)
03	.35524 (11)	.01881 (12)	.97977 (20)	.843 (13)	.00182 (9)	.00302 (11)	.00947 (30)	.00005 (8)	.00092 (13)	.00004 (14)

samples were sealed in a platinum capsule 8 mm long and 3 mm in diameter. These capsules in turn were sealed with PtO₂ 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 tempera-

ture 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,



(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



For the purposes of structure determination, however, we have assumed the ideal composition CaAlAlSiO₆. 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 P1). For intensity measurements a solid state detection system and MoK α radiation monochromatized by reflection from a graphite single crystal ($2\theta = 12.2^\circ$) have been used. All *h0l* reflections with 2θ less than 60° were measured using a very slow scan rate ($0.25^\circ/\text{min}$). No reflection violating the *C2/c* space group was detected.

The cell dimensions, refined by the least squares method using 15 reflections with 2θ between 35° and 50° measured on the diffractometer, are: a 9.609(3), b 8.652(2), c 5.274(2) Å, β 106.06(2)°; V 421.35(21) Å³; Z 4. The calculated density is 3.44 g cm⁻³.

TABLE 2. Bond Lengths and Bond Angles of CaAlAlSiO₆

Bond Length		Bond Angle	
Atom	Value(Å)	Atom	Value(°)
Octahedron (M1)			
M1-01A1, B1	2.021 (1)	0-M1-O angles	
-01A2, B2	1.947 (1)	01A2, 01B2	175.64 (5)
-02C1, D1	1.872 (1)	(2)01A1, 02D1	166.89 (4)
mean of 6	1.947	01A1, 01B1	84.58 (5)
01A1-01B1	2.719 (2)	02C1, 02D1	97.79 (6)
02C1-02D1	2.822 (2)	(2)01A1, 02C1	89.93 (5)
(2)01A1-02C1	2.753 (2)	(2)01A1, 01A2	98.03 (5)
(2)01A1-01A2	2.995 (2)	(2)01A1, 01B2	78.70 (4)
(2)01A2-02C1	2.709 (2)	(2)01A2, 02C1	92.54 (5)
(2)01A2-02D1	2.760 (2)	(2)01A2, 02D1	90.33 (5)
(2)01A1-01B2	2.516 (2)	T-01A1-M1	122.51 (5)
mean of 12	2.751	T-01A2-M1	119.39 (7)
M1-M1 (1)	3.068 (1)	T-02C1-M1	143.25 (8)
M1-TA1	3.260 (1)		
M1-TA2	3.145 (1)		
Polyhedron (M2)			
M2-01A1, 01B1	2.403 (1)	01A1, 01B1	68.90 (4)
-02C2, 02D2	2.420 (1)	02C2, 02D2	147.48 (4)
-03C1, 03D1	2.469 (1)	03C1, 03D1	86.65 (4)
-03C2, 03D2	2.549 (1)	03C2, 03D2	109.54 (4)
mean of 6	2.431	(2)01A1, 02C2	83.30 (4)
mean of 8	2.461	(2)01A1, 03C1	123.22 (4)
01A1-01B1	2.719 (2)	(2)01A1, 03C2	90.91 (4)
03C1-03D1	3.388 (2)	(2)02C2, 03C1	65.43 (4)
(2)01A1-02D2	2.760 (2)	(2)02C2, 03C2	113.65 (4)
(2)01A1-02D2	3.206 (2)	(2)03C1, 03C2	63.91 (4)
(2)01A1-03C2	3.532 (2)	(2)01A1, 02D2	69.81 (4)
(2)02C2-03C1	2.642 (2)	(2)01A1, 03D1	130.69 (4)
(2)02C2-03D2	3.375 (2)	(2)01A1, 03D2	159.31 (4)
(2)03C1-03C2	2.657 (2)	(2)02C2, 03D2	85.52 (4)
(2)03C1-03D2	2.751 (2)	(2)03C1, 03D2	66.45 (4)
		(2)02C2, 03D1	14° '1 (4)
Tetrahedron (Si, Al)			
T-01	1.693 (1)	01-T-02	119.72 (5)
T-02	1.665 (1)	01-T-03A1	109.94 (5)
mean, non-brg.	1.679	01-T-03A2	108.43 (6)
T-03A1	1.683 (1)	02-T-03A1	110.39 (6)
T-03A2	1.701 (1)	02-T-03A2	103.43 (6)
mean, brg.	1.692	03A1-T-03A2	103.49 (6)
mean of 4	1.686	mean of 6	109.23
01-02	2.904 (2)	T-03-TA2	134.94 (7)
01-03A1	2.764 (2)	03A2-03A1-03A2	165.93 (6)
01-03A2	2.753 (2)		
02-03A1	2.749 (2)		
02-03A2	2.642 (2)		
03A1-03A2	2.657 (2)		
mean of 6	2.745		
T-TA2	3.125 (1)		

TABLE 3. Thermal Ellipsoids of CaAlAlSiO₆

Atom	Axis	rms amplitude, Å	Angle (°) with <i>a</i>	Angle (°) with <i>b</i>	Angle (°) with <i>c</i>
M1	1	0.079	36 (68)	90	71 (68)
	2	0.080	90	180	90
	3	0.103	126 (3)	90	19 (3)
M2	1	0.083	90	0	90
	2	0.094	130 (7)	90	124 (7)
	3	0.111	140 (3)	90	34 (3)
T	1	0.074	61 (23)	34 (23)	83 (3)
	2	0.076	145 (21)	57 (23)	86 (3)
	3	0.094	107 (2)	98 (2)	8 (2)
O1	1	0.086	51 (7)	138 (7)	87 (5)
	2	0.105	69 (9)	89 (7)	175 (9)
	3	0.113	46 (12)	48 (12)	86 (10)
O2	1	0.091	77 (5)	13 (5)	90 (3)
	2	0.109	160 (7)	77 (6)	89 (7)
	3	0.121	105 (6)	90 (3)	1 (6)
O3	1	0.089	16 (4)	93 (5)	90 (4)
	2	0.107	93 (7)	177 (7)	86 (14)
	3	0.113	106 (9)	86 (12)	1 (9)

The intensities of 1165 reflections have been measured using monochromatic MoK α 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 ($= 22 \text{ cm}^{-1}$) were both small, no absorption corrections were made. The least squares refinement is based on 970 Fo values above $3\sigma(\text{Fo})$, where $\sigma(\text{Fo})$ is the standard deviation. The Fo's were weighted as $\text{Fo}/\sigma^2(\text{Fo})$. The full matrix least squares program RFINE (Finger, 1969) was employed using the atomic coordinates and isotropic temperature factors of diopside (Clark, Appleman, and Papike, 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).

TABLE 4. Volumes of Ca-Polyhedra in Some Aluminosilicates

Source of Data	Anorthite		Gehlenite	Ca-Tschermak's	Grossular
	Ca ₂ Al ₂ Si ₂ O ₈	Ca ₂ Al ₂ Si ₂ O ₈	Ca ₂ Al ₂ Si ₂ O ₇	CaAl ₂ Si ₂ O ₆	Ca ₃ Al ₂ Si ₃ O ₁₂
	Wainwright and Starkey (1971)	Louisnathan (1971)	Louisnathan (1971)	Present study	Prandl (1966)
Coordination no. of Ca	000 200 010 210	6 7 7 7	8	8	8
Volume of Ca-polyhedron Å ³	000 200 010 210	27.835* 26.492* 27.226* 26.791*	23.260	24.508	23.867
Coordination no. of: Si	4 4	4 4	4	4 4,6	4 6
M/O ratio	3/4		5/7	2/3	2/3

* These values are calculated based on 8-coordination for the comparison with other minerals.

TABLE 5. Possible Space Groups for Ordered CaAlAlSiO₆

	C 2	C $\bar{1}$	P 2/n	P 2 ₁ /n
Centricity	acentric	centric	centric	centric
Type of equipoint	0, y, 1/4*	x, y, z	0, y, 1/4*	x/y, z*
Number of M sites	4	2	4	2
Reported example of pyroxene structure	spodumene (Appleman and Stewart, 1966)	none	Bessi omphacite (Matsumoto and Banno, 1970)	γ -MgSiO ₃ (Lindemann, 1961)

* Origin chosen such that 2-fold (or 2₁-screw) axis is at the same level for all pyroxenes.

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 ERROR (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 Papike, 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

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

or inversely

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

In spite of the differences in the size of the *T*-O tetrahedra, the puckering of the chains as defined by the O₃-O₃'-O₃'' angle is comparable in CaTs (165.9°) and diopside (166.4°). The *T*-*T* separation is 3.125 Å,

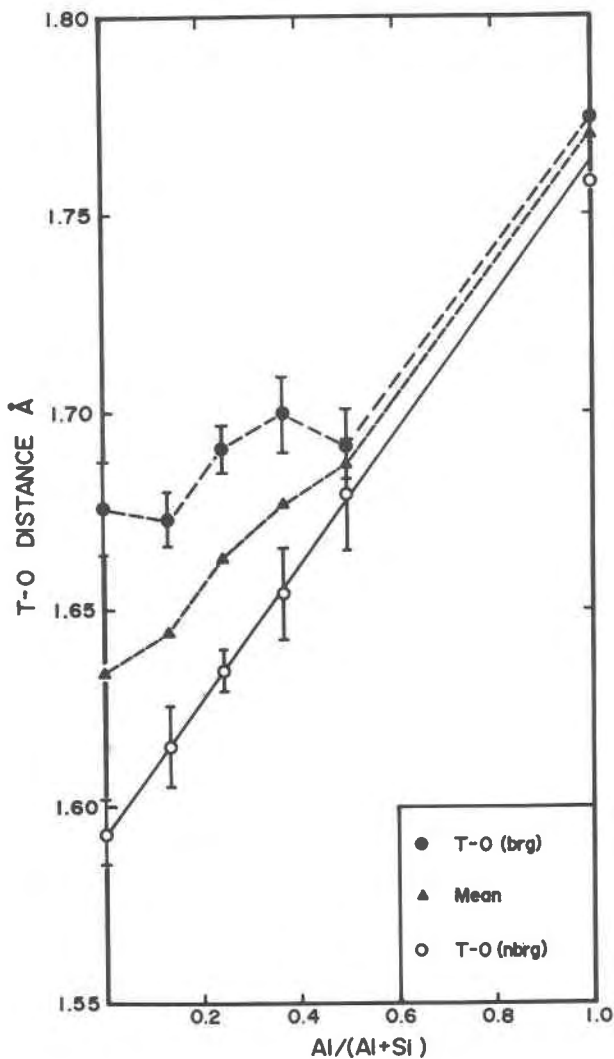


FIG. 1. T-O distances plotted against Al/(Al + Si) ratio in tetrahedral site in several C2/c pyroxenes and sillimanite. Data from Clark *et al* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), present study, and Burnham (1963) for sillimanite.

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 $b \times (0.5 - y_{M2})$, where y_{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 the $M2$ -O distances (Fig. 4), we find that the crystal-chemical 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.

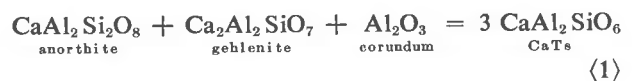
In the initial stage, this change in local charge balance will be accomplished most efficiently by the decrease in thickness of the cation layer and mutual shifts between both O3 and O3' pairs along the chain direction, which corresponds to an increase in the obtuse angle β . This adjustment, however, 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 β 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 $\text{CaAl}_2\text{SiO}_6$ 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°C and 1420°C the following reactions proceed from the left to the right with increasing pressure:



Hijikata and Yagi (1967) independently synthesized CaTs using reaction (2).

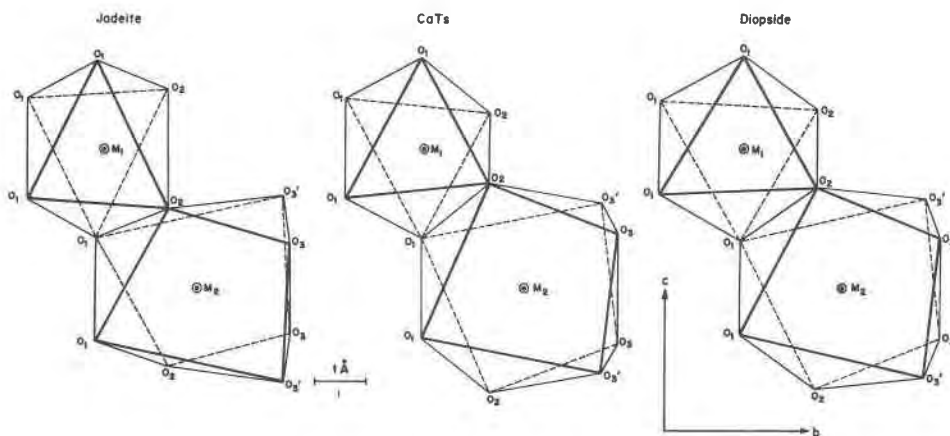


FIG. 2. M_1 and M_2 polyhedra in jadeite (Prewitt and Burnham, 1966), CaAlAlSiO_6 (present study), and diopside (Clark *et al.*, 1969) viewed along [100].

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 TO_3 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 TO_3 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 ($P2_1/c$) with fine and well-sorted domain size can cause the "b" ($h+k = \text{odd}$) reflections to become

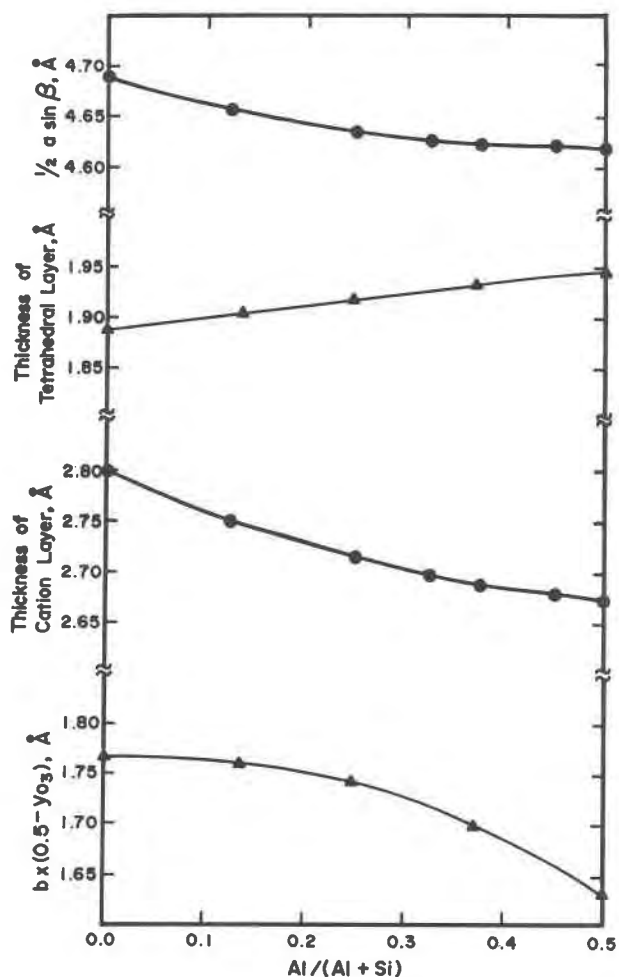


FIG. 3. Estimated metrical changes in structures in the $\text{CaMgSi}_2\text{O}_6$ - CaAlAlSiO_6 join (see text). ● Data from Clark *et al.* (1962); ▲ Data from Clark *et al.* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), and present study.

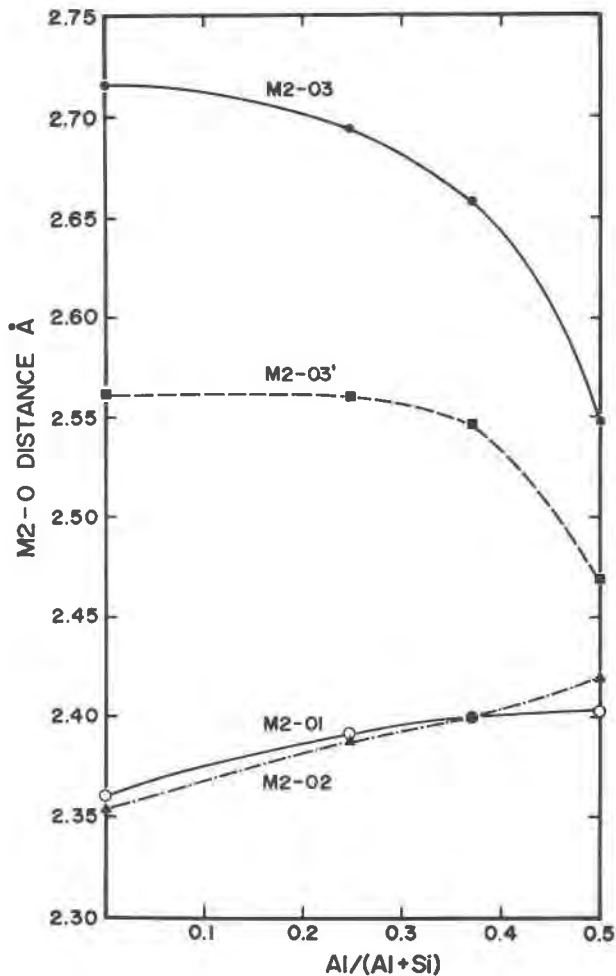


FIG. 4. Changes in $M2-O$ distances in some $C2/c$ pyroxenes plotted against $Al/(Al + Si)$ ratio. Data from Clark *et al* (1969), Peacor (1967), Dowty and Clark (1973), and present study.

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. $\bar{1}$
- 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 $NaAlSi_2O_6$ - $CaAl_2SiO_6$ 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, $P2_1/n$ or $C2$ are the more plausible models.

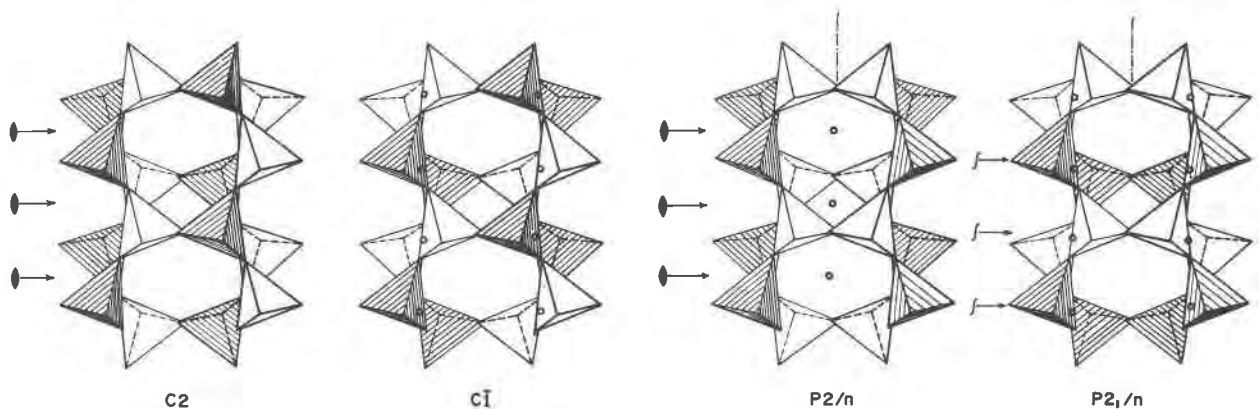


FIG. 5. Possible Al-Si ordering schemes in TO_3 chains of CaTs. Shaded (likewise, white) tetrahedra are crystallographically equivalent.

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 Ca²⁺ 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 CaMgSi₂O₆-CaAl₂SiO₆ join can be successfully explained in terms of the relative shifts of atoms required to attain the local charge balance.
- 5) C₂, P_{2/n}, C₁ and P_{2₁/n} are possible space groups for calcium Tschermak's pyroxene with one kind of TO₃ 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 C_{2/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.

Acknowledgments

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