# Structure and Crystal Chemistry of Calcium Tschermak's Pyroxene, CaAlAlSiO<sub>6</sub>

FUJIO PETER OKAMURA, SUBRATA GHOSE,

Department of Geological Sciences, University of Washington, Seattle, Washington 98195

#### AND HARUO OHASHI

National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki, 300-31, Japan

#### Abstract

The crystal structure of calcium Tschermak's pyroxene, CaAlAlSiO<sub>6</sub> (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 Mo $K\alpha$  radiation. The unweighted R-factor is 0.024. The cell dimensions are:  $a_0 = 9.609$  Å,  $b_0 = 8.652$  Å,  $c_0 = 5.274$  Å 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-O (nbr) = 1.593 + 0.16917 × 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 CaO<sub>8</sub> 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, CaAlAlSiO<sub>6</sub> (hereafter called CaTs). Under high pressure anorthite breaks down to CaTs molecule and silica.

$$CaAl_2Si_2O_8 = CaAlAlSiO_6 + SiO_2$$
.

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 CaAlAlSiO<sub>6</sub> Single Crystals

The starting material was a mixture of anorthite, gehlenite, and corundum prepared from CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> by solid state reaction in air.

$$\begin{aligned} 3(\text{CaCO}_3 \,+\, \text{Al}_2\,\text{O}_3 \,+\, \text{SiO}_2) &\rightarrow \text{CaAl}_2\,\text{Si}_2\text{O}_8 \\ &+\, \text{Ca}_2\text{Al}_2\,\text{SiO}_7 \,+\, \text{Al}_2\text{O}_3 \rightarrow 3\,\,\text{CaAl}_2\,\text{SiO}_8. \end{aligned}$$

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 CaAlAlSiO<sub>6</sub>

	×	У	z	B eq	β11	β 2 2	Взз	β <sub>12</sub>	β13	β23
M1 (A1)	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 (A1 + 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(1
02	.36571(11)	.26707(12)	.30988(21)	.917(14)	.00272(10)	.00222(10)	.01115(32)	00020(8)	.00139(14)	00009(1
03	.35524(11)	.01881(12)	.97977(20)	.843(13)	.00182(9)	.00302(11)	.00947(30)	.00005(8)	.00092(13)	.00004(1

samples were sealed in a platinum capsule 8 mm long and 3 mm in diameter. These capsules in turn were sealed with PtO<sub>2</sub> 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-

TABLE 2. Bond Lengths and Bond Angles of CaAlAlSiO6

Bond Le	ngth	Bond Angle								
Atom	Value(Å)	Atom	Value(°)							
	Octahedr	on (ML)								
MI-OlAl, Bl	2.021 (1)	0-M1-0 angles								
-01A2, B2	1.947 (1)	O1A2, O1B2	175.64 (5)							
-02C1, D1	1.872 (1)	(2)01A1, 02D1	166.89 (4)							
mean of 6	1.947	01A1, 01B1	84.58 (5)							
		02C1, 02D1	97.79 (6							
01A1-01B1	2.719 (2)	(2)01A1, 02C1	89.93 (5							
02C1-02D1	2.822 (2)	(2)01A1, 01A2	98.03 (5							
(2)01A1-02C1	2.753 (2)	(2)01A1, 01B2	78.70 (4							
(2)01A1-01A2	2.995 (2)	(2)01A2, 02C1	92.54 (5							
(2)01A2-02C1	2.709 (2)	(2)01A2, 02D1	90.33 (5							
(2)01A2-02D1	2.760 (2)	T-01A1-M1	122.51 (5							
(2)01A1-01B2	2.516 (2)	T-01A2-M1	119.39 (7 143.25 (8							
mean of 12	2.751	T-02C1-M1	143.25 (0							
M1-M1 (1)	3.068 (1)									
MI-TAL	3.260 (1)									
M1-TA2	3.145 (1)									
ru-inz		(1/2)								
	Polyhedi	on (MZ)								
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							
		(2)01A1, 03C2	90.91 (4							
01A1-01B1	2.719 (2)	(2)02C2, 03C1	65.43 (4							
03C1-03D1	3.388 (2)	(2)02C2, 03C2	113.65 (4							
(2)01A1-02D2	2.760 (2)	(2)03C1, 03C2	63.91 (4							
(2)01A1-02D2	3.206 (2)	(2)01A1, 02D2	69.81 (4							
(2)01A1-03C2	3.532 (2)	(2)01A1, 03D1	130.69 (4							
(2)02C2-03C1	2.642 (2)	(2)01A1, 03D2 (2)02C2, 03D2	159.31 (4							
(2)02C2-03D2	3.375 (2)	(2)0202, 0302	85.52 (4 66.45 (4							
(2)03C1-03C2 (2)03C1-03D2	2.657 (2) 2.751 (2)	(2)03C1, 03D2 (2)02C2, 03D1	14' 31 (4							
(2)0301-0302			2							
	Tetrahedro	n (S1, AI)								
T-01	1.693 (1)	01-T-02	119.72 (5							
T-02	1.665 (1)	01-T-03AL	109.94 (5							
mean, non-brg.	1.679	01-T-03A2	108.43 (6							
		02-T-03A1	110.39 (6							
T-03A1	1.683 (1)	02-T-03A2	103.43 (6							
T-03A2	1.701 (1)	03A1-T-03A2	103.49 (6							
mean, brg.	1.692	mean of 6	109.23							
mean of 4	1.686		124 04 /							
	2.904 (2)	T-03-TA2	134.94 (							
01-02	2.764 (2)	03A2-03A1-03A2	165.93 (							
01-03A1 01-03A2	2.753 (2)									
01-03A2 02-03A1	2.749 (2)									
02-03A1 02-03A2	2.642 (2)									
03A1-03A2	2.657 (2)									
mean of 6	2.745									
T-TA2	3.125 (1)									

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,

$$Ca_{1,030}Al_{1,934}Si_{1,034}O_6$$

(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

$$Ca_{1.0}Al_{1.878}Si_{1.003}O_{5.825}$$
.

For the purposes of structure determination, however, we have assumed the ideal composition CaAlAlSiO<sub>6</sub>. 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 PI). For intensity measurements a solid state detection system and  $MoK\alpha$  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  $60^{\circ}$  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  $2\theta$  between  $35^{\circ}$  and  $50^{\circ}$  measured on the diffractometer, are: a 9.609(3), b 8.652(2), c 5.274(2) Å,  $\beta$  106.06(2)°; V 421.35(21) Å<sup>3</sup>; Z 4. The calculated density is 3.44 g cm<sup>-3</sup>.

TABLE 3. Thermal Ellipsoids of CaAlAlSiO6

Atom	Axis	rms ampli- tude, A	Angle with		Angle with 1	Angle (			
MI	I	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		
	1 2 3	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)	
	1 2 3	0.076	145	(21)	57	(23)	86	(3)	
	3	0.094	107	(2)	98	(2)	8	(2)	
01	1	0.086	51	(7)	138	(7)	87	(5)	
	1 2 3	0.105	69	(9)	89	(7)	175	(9)	
	3	0.113	46	(12)	48	(12)	86	(10)	
02	1	0.091	77	(5)	13	(5)	90	(3)	
	1 2 3	0.109	160	(7)	77	(6)	89	(7)	
	3	0.121	105	(6)	90	(3)	1	(6)	
03	1	0.089	16	(4)	93	(5)	90	(4)	
	1 2 3	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  $MoK\alpha$  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  $(0.06 \times 0.12 \times 0.20 \text{ mm})$  and the linear absorption coefficient  $\mu$  (= 22 cm<sup>-1</sup>) were both small, no absorption corrections were made. The least squares refinement is based on 970 Fo values above  $3\sigma(Fo)$ , where  $\sigma(Fo)$  is the standard deviation. The Fo's were weighted as  $Fo/\sigma^2(Fo)$ . 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

	Anort	hite	Gehlenite	Ca-Tschermak's	Grossular				
Source of Data	Wainwrigh	2 <sup>S1</sup> 2 <sup>0</sup> 8 t and Starkey 971)	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> Louisnathan (1971)	CaAl <sub>2</sub> SiO <sub>6</sub> Present study	Ca 3 <sup>Al</sup> 2 <sup>Si</sup> 3 <sup>0</sup> 12 Prandl (1966)				
Coordina-	000	6	8	8	8				
tion no.	Z00	7			-				
of Ca	010	7			•				
	210	7							
Volume of	000	27.835*	23,260	24.508	23.867				
Ca-poly-	Z00	26.492*							
hedron A	010	27.226*							
	Z10	26.791*							
Coordina-									
tion no.					4				
of: Si	4		4	4	6				
Al	4		4	4,6	2/3				
M/O ratio	3/4		5/7	2/3					

<sup>\*</sup> These values are calculated based on 8-coordination for the comparison with other minerals.

TABLE 5. Possible Space Groups for Ordered CaAlAlSiO6

	C 2	CI	P 2/n	$P_{1/n}$
Centricity	acentric	centric	centric	centric
Type of equipoint	0, y, 1/4*	x,y,z	0, y, 1/4*	x <b>\</b> 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)	Y ~ MgSiOg (Lindemann, 1961)

<sup>\*</sup> Origin chosen such that 2-fold (or  $2_1$ -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 AlO<sub>4</sub> tetrahedron in sillimanite (Burnham, 1963), where it forms a chain alternating with SiO<sub>4</sub> 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

$$T - O(nbr) = 1.593 + 0.16917 \times \frac{A1}{(A1 + Si)}$$

or inversely

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

In spite of the differences in the size of the T-O tetrahedra, the puckering of the chains as defined by the  $O_3$ - $O_3$ '- $O_3$ " angle is comparable in CaTs (165.9°) and diopside (166.4°). The T-T separation is 3.125 Å,

TABLE 6. Observed and Calculated Structure Factors in Calcium-Tschermak's Pyroxene CaAlAlSiO<sub>6</sub>

	*	Fobs  h = 0  154,24, 9 93,349 32,165 25,522 32,771 15,969	h = 0  154.244 149.776  9 93.349 90.776  32.165 31.091  55.622 24.426  32.771 29.955  15.969 44.791	h = 0 33 33 34 35 35 36 37 37 37 37 37 37 37 37 37 37 37 37 37	h = 0 3 - 6	\$ -0 \$ 7.021 \$ 13-024	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	h = 0	h = 0	h = 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	h = 0	h = 0	h = 0	h = 0	\$ -6	h = 0	\$ -6	h = 0	\$ -6	008	7 OSS CUIC N 7 OSS
******	*	9 93.349 32.165 25.622 32.771 15.969 71.368 31.947 3.502 15.531 6.191 23.749 139.833	9 91,349 99.776 32,185 31,091 25,622 24,426 32,771 24,955 15,959 14,791 71,488 59,125 31,439 32,655 15,591 15,591 15,591 15,591 15,591 15,591 21,792 21,938 21,793 21,938	# 9 1,149 9 9.776 5. 32,165 31,091 5. 55,622 24,425 5. 32,171 24,955 8. 11,459 14,731 9. 71,458 59,125 8. 31,439 32,455 8. 31,439 32,455 8. 31,439 12,455 8. 31,439 12,455 8. 31,439 12,455 9. 4,931 15,597 8. 6,191 3,941 7. 22,749 21,938 129,833 115,047 7.	13-24-1 149-776 1 2-2 93.34-5 39-776 1 2-1 93.74-6 39-776 1 2-1 15.062 39-776 2 1 2 15.071 2-145 2 1 2 15.071	1524x 1.49.776 5 -2 24x.992 93.13.9 32.776 5 -2 4x.712 93.13.9 31.776 5 -2 4x.712 93.13.9 31.76 93.10.9 31.76 93.10.9 31.76 93.10.9 31.76 93.10.9 31.76 93.10.9 31.76	12-24	1524 1.49.776 5 -2 12.493 7.485 4 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1524x 1.43.776 5 -2 24.495 21.4516 4 -2 23.277 2 24.455 31.276 5 -2 4.471 2 24.455 4 -2 24.276 2 24.456 2 24.	13-24	1524x 1247.76x 5 -2 52.895 21.454 -5 72.413 22.117 23.117 31.515 31.75	15-2-14   1-6-776   5 -2   15-892   21-854   4 -5   22-872   22-177   3   3   3   3   3   3   3   3   3	1524x 1.43,776 5 -2 24.497 34.494 4 -9 22.497 2 -4 3.494 3 3.247 3 -2 3.247	15-22+   10-776   1 -2   12-892   21-894   4 -5   22-872   22-172   2 -172   2 -8   22-872	13.24 143.776 5 -2 26.995 14.636 4 -5 22.439 22.437 1 -4 25.514 31.387 2 3.387 3 3.387	15.24 148,776 5 -2 56.995 14.616 4 -5 22.418 22.417 1 -8 25.514 37.357 2 2 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	13.24x 149.776 5 -2 4.413 14.544 4 -5 22.413 22.413 1 -2 25.514 32.357 2 3 3 3.57 3 3 3 3.57 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	15.24 148,776 5 -2 5.895 21.618 4-5 22.418 22.418 1 -4 26.518 12.775 2 5 5 4.488 23.189 31.518 31.576 5 -2 4.477 3.227 -4 17.595 31.518 1 -2 17.528 2 5 5 4.488 23.189 31.518 31.	13.24 143.76 1 -2 144.76 1 -2 144.84 1 -2 22.43 22.43 22.43 1 -2 14.24 1 12.23 1 12.73 2 1 14.776 1 -2 14.24 1 14.776 1 -2 14.24 1 14.276 1 -2 14.24 1 14.276 1 -2 14.24 1 14.276 1 -2 14.24 1 14.276 1 -2 14.24 1 14.	10   10   10   10   10   10   10   10	15.24 1.05,776 5 -2 5.59	12-24   13-776   3 -3   18-995   11-616   4 -5   22-139   22-131   1 -8   26-516   33-357   2   1 -6   15-997   1 -7   12-519   13-139   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   12-519   13-376   1 -7   13
2 · · · · · · · · · · · · · · · · · · ·		32.771 15.969 71.468 31.937 4.592 45.531 6.191 23.793 129.833 56.319 36.443 11.921	32.771 29.955 15.969 16.791 71.458 59.129 31.433 32.555 31.947 31.293 4.502 1.659 16.511 1.599 21.749 21.938 129.834 125.047 56.319 56.356 35.143 38.116	32,771 29,995 11,731 15,959 14,731 15,959 14,731 17,1458 59,125 11,1458 59,125 11,1458	32.27t 29.995 8 2 13.959 14.771 9 8 7 13.959 27.55 8 8 7 13.939 27.055 8 8 7 13.939 27.055 8 8 6 1.502 1.599 8 7 8 1.502 1.599 8 7 8 22.749 21.935 7 8 55.310 85.356 7 8 55.310 85.356 7 8 55.310 85.356 7 8 13.947 21.199 7 8	32.271 29.955 8 2 87.794 13.955 11.751 9 1 4.532 13.955 12.555 8 4 5.532 13.957 31.293 5 5 5 7.521 15.927 15.557 9 7 6.721 15.921 15.557 9 7 6.721 15.921 15.557 9 7 7 6.721 12.774 22.935 7 6 10.555 15.557 7 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 10.555 15.557 7 7 7 7 10.555 15.557 7 7 7 7 10.555 15.557 7 7 7 7 10.555 15.557 7 7 7 7 7 10.555 15.557 7 7 7 7 7 7 10.555 15.557 7 7 7 7 7 7 10.555 15.557 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32.77	32.271 23.955 5 2 67.795 67.792 1.15.959 1.15.95	32-271 29-695 8 2 87-796 27-791 4 2 14-82 15-995 15	32-271 29.655 5 2 37.794 67.795 4 5.442 11.433 13.955 14.795 5 2 41.234 11.335 13.955 14.795 67.795 4 5.442 11.433 13.955 14.795 67.795	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	\$2.77\$\text{2.9.655}\$\text{ \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$, \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$, \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$, \$\frac{1}{2}\$} \text{ \$\frac{1}{2}\$}	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	\$2.77\$	\$2.77\$	\$2.97t	32.271 23.955 5 2 57.756 2 3 67.756 67.755 4 5.412 11.413 1 1 23.956 23.339 6 7 15.555 15.956	\$2.77\$\begin{array}{cccccccccccccccccccccccccccccccccccc	\$2.27\$\text{1.29}\$\$\text{5.55}\$\$\tau	\$2.27\$ \$2.965\$ \$1\$ \$2.965\$ \$1\$ \$2.96\$ \$1.765\$ \$2.96\$	\$2.27\$\text{1.0}\$\text{2.0}\$\text{55}\$\text{5}\$\text{2}\$\text{5}\$\text{5}\$\text{7.76}\$\text{5}\$5
	1.502 15.531 6.191 23.749 129.833 56.319 36.143		1.659 15.597 3.991 21.938 183.047 66.356 38.116 11.899 9.811 25.175 15.833	1.659 15.597 3.991 21.938 185.047 65.356 38.116 11.099 9.811 25.175	1.659 5 1 2.597 5 4 3.991 7 -7 21.938 7 -8 195.947 7 -5 36.356 7 -1 31.099 7 -7 11.099 7 -	15.597	1.659 9 7 6.723 6.381 15.597 7 7 1.753 1.853 21.293 7 7 1.853 1.753 1.753 22.293 7 7 1.853 1.753 1.753 35.355 7 1.853 1.753 1.753 35.355 7 1.853 1.753 1.753 35.355 7 1.853 1.753 1.753 35.355 7 1.853 1.753 1.753 1.753 35.353 7 1.853 1.753 1.753 1.753 35.353 7 1.853 1.753 1.753 1.753 1.753 35.353 7 1.853 1.753 1.753 1.753 1.753 35.353 7 1.853 1.753 1.753 1.753 1.753 1.753 35.353 7 1.753 1.	1.659 9 7 8.721 6.551 1 1.559 1 1.559 1 2 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1 1.559 1 1.559 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1.659 9 7 1.731 1.321 1.56 15.597 7 1 4 1.735 1.56 1.56 1.56 1.56 1.56 1.56 1.56 1.5	1.659 9 7 8.731 8.581 4 6 24.989 15.597 5 6 12.598 1 8.581 4 6 24.989 15.597 6 12.698 17.597 6 12.698 17.69	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.659 9 7 8.731 9.561 4 6 24.355 23.967 1 15.537 2 6 4.7355 41.651 6 6 24.355 23.967 3 3.991 7 -7 24.961 24.556 5 -8 5.999 3.996 5 15.938 7 -6 12.199 17.969 6 -7 15.491 17.969 9 15.940 7 -5 4.405 3.86.977 5 -6 13.727 13.532 8 15.940 7 -2 12.494 24.895 6 -2 13.491 17.969 9 15.940 7 -2 2 12.494 24.895 6 -2 13.491 12.4	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.659 9 7 8.723 0.361 0 2.558 22.967 1 8 13.598 12.1012 - 1 15.597 2 8 1.7.158 1.1.001 8 1.558 22.967 1 8 13.598 12.1012 - 1 15.991 7 7 8 1.558 1.001 8 1.558 1.001 8 1.558 1 7 32.228 32.152 - 1 15.937 7 8 1.1.158 1.1.001 8 1.558 1 8 1.558 1 7 32.228 32.152 - 1 15.336 7 8 1.1.159 17.001 8 1.578 1 17.982 1 8 5.557 1 1 15.336 7 8 1.1.384 12.38 8 1.577 1 1.578 1 1.578 1 8 1.577 1 1.572 1 8 1.578 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1.659 9 7 6.731 6.381 6 24.385 23.967 1 6 13.598 13.197 -	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.659 9 7 6.721 6.351 6 22.985 22.967 1 6 10.199 10.197 - 6.655 23.086 3 - 6.555 23.086 3 -	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
11.9; 12.1; 26.30 16.5; 7.1; 52.90 57.4; 59.3; 35.4; 21.7;	21 13 63 24 32 65 65 84 93 19	11.099 9.811 25.179 15.833 5.537 73.793 65.356 69.752 35.611 22.296		7777777777	/ -2 / -1 / 1 / 1 / 2 / 2 / 3 / 4 / 5	7 -2 33.192 7 -1 56.791 7 1 29.581 7 1 59.913 7 2 11.081 7 2 24.916 7 5 24.916 7 7 8.655	7 -2 33.192 33.681 7 -1 50.761 50.427 7 1 20.561 20.562 7 2 20.561 20.562 7 2 20.561 20.224 7 3 20.661 20.224 7 4 7.642 20.224 7 7 8.642 70.421 7 7 8.652 70.431	7 -2 33-122 33-68-1 5 7 -1 56-701 66-422 6 7 1 29-68-1 29-68-1 5 7 2 29-68-1 29-68-1 5 7 2 29-68-1 29-68-1 5 7 3 29-68-1 29-68-1 5 7 3 29-68-1 29-68-3 7 7 2-88-3 8-222 6 7 5 29-68-4 29-48-1 5 7 5 29-68-4 29-48-1 5 7 5 29-68-4 39-48-1 5	7 -2 33.132 35.613 5 -2 7 -1 56.731 69.427 6 -1 7 1 29.531 29.532 6 5 7 2 29.531 29.522 6 5 7 3 29.531 29.522 6 5 7 3 29.531 29.522 6 5 7 4 7.543 6 22.26 6 4 7 5 29.654 79.431 5 5 7 5 29.654 79.431 5 5	7 - 2	7 -2 35.432 35.651 5 -2 51.575 52.581 7 -1 56.755 52.581 5 -2 51.575 52.581	7 -2 33.132 33.601 5 -2 51.575 62.551 9 7 -1 6.60.231 6 -2 51.575 62.551 9 7 -1 6.60.231 6 -1 6.60.9 51.60.9 5	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	7 -2 33.432 33.693	7 -2 35.122 35.612 5 -2 11.575 92.956 9 -2 125.612 124.755 17 -1 15.612	7 = 2 33.432 33.693	7 = 2 33.432 33.682 8 = 2 51.575 92.831 9 = 2 123.622 124.755 8 4 1.518 95.886 17 - 1 15.682 124.755 8 4 1.518 95.886 17 - 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	7	7 = 2 33.432 33.693 5 = 2 81.975 92.951 9 = 2 125.432 124.755 4 81.334 35.006 3 2 2 125.432 124.755 4 81.334 35.006 3 2 2 125.432 124.755 125.	7 = 2 33.432
35.419 21.746 16.851 23.973 27.535 6.579 11.139 25.691 6.573		22.296 15.954 23.212 27.439 7.024 19.853 25.774 5.373			7 -6 9 -6 9 -3 9 -1 9 -1 9 -1	7	7	7 h 5.55 5 9.95 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	7 6 5.55 5.95 5 5 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	7 A 5.555 5.995 5 B 57-113 9 -6 5.755 1.657 5 7 5.916 9 -6 13.450 11.450 5 -7 5.916 9 -1 13.450 11.450 5 -6 12.252 9 -1 17.751 5 -7 5.95 9 -1 17.751 5 -7 5.95 9 -1 1.751 5 -7 5 -7 5 -7 5 -7 5 -7 5 -7 5 -7 5	7 h 5.555 9.996 5 5 7.112 22.613 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	7 h 5.555 5.956 6 7 5.113 25.413 5 7 6 7 6 7 6 7 6 7 6 7 6 7 6 7 6 7 6 7	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	7 h 5.155 5.996 5 E F.111 2.014 5 7 17.971 15.592 5 3 4.49 5.40 5 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	7 + 5.55	7 + 5.55
	75.815 54.629 24.535 61.551 11.491 23.286 37.600	75.2 54.1 24.5 41.0 18.1 23.1	58 50 84 06 29 23	59 04 06 29 23	73 3 2 568 4 3 64 9 5 06 9 7 9 9 223 11 9 221 11 9	70 5 2 14.955 50 4 3 11.155 50 9 6 52.015 50 9 5 0.107 20 20 11 -5 2.474 21 11 -5 2.535 21 11 -5 2.535	71	71	71	79	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
	37.509 21.125 5.983 18.994 22.572 16.245 23.647	37.821 21.699 5.850 19.326 22.676 15.914 23.232		11 11 11 11 11 11		11 -3 9.33 11 -2 77.352 11 1 1-428 11 1 1.7.509 11 1 1.7.509 11 2 25.912 13 3 25.912 13 4 1.573	11 -3 9.13 9.272 11 -2 77.352 27.214 11 -3 14.425 17.534 11 1 14.425 17.534 11 1 17.537 17.534 11 1 18.587 11 1 18.587 11 1 25.572 25.773 11 1 25.775 10.685	11 -3	11 -2 013 0.277 3 0 11 -2 77.352 17.252 14 -5 11 1 2 12252 17.522 14 -5 11 1 12252 17.522 14 -5 11 1 17.513 17.533 15 -4 11 1 17.513 17.535 15 -5 11 2 15.512 17.537 14 -5 11 2 25.512 25.751 13 -1 13 -4 16.572 15.685 13 1	11 -2 0.131 0.272 0 0 5.442 11 -2 7.562 7.725 10 -5 5.442 11 1 1 1.745 17.563 12 -5 2.661 11 1 1 1.745 17.563 12 -5 2.661 11 1 1 1.745 17.565 12 -5 2.661 11 1 1 1.745 17.565 14 -7 21.7461 11 1 1.745 17.565 1.446 14 -7 21.7461 11 1 1 1.745 17.565 1.446 14 -7 21.7461 11 1 1 1.745 17.765 17	11 -3	11 -3 0.133 9.272 3 6 7.442 7.2567 6 11 -2 7.1562 9.7.254 10 -5 21.014 20.01 20.01 1 11 -1 7.156 11 7.256 12 -5 21.01 20.01 20.01 1 11 1 1.7.156 11 7.256 12 -5 21.01 20.01 20.01 1 11 1 1.121 11.1257 12 -5 21.01 20.01 20.01 20.01 1 11 1 1 1.017 12 1.017 12 -5 11.017 12 1 11 1 1 1.017 12 1.017 12 1.017 12 1 11 1 1 1.017 12 1.017 12 1.017 12 1 11 1 1 1.017 12 1.01	11 -2 0.112 0.272 3 0 5.442 2.250 0 -2  11 -2 7.152 7.7.254 10 -5 2.501 2.25.077 5 -2  11 1 1 1 1.7.413 17.254 10 -5 2.501 2.25.077 5 -2  11 1 1 1.7.413 17.254 12 -5 2.501 2.25.077 5 -2  11 1 1 1.7.413 17.254 12 -5 2.501 2.25.07 1 -2  11 1 1 1.211 11.257 12 -5 2.501 2.35.07 2 1  11 1 1 1.250 12 -5 2.501 2.2501 11.250 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.250 12 1.2501 11.2501 2 1  11 1 1 1 1.2501 12 1.2501 11.2501 2 1  11 1 1 1 1.2501 12 1.2501 11.2501 2 1  11 1 1 1 1.2501 12 1.2501 11.2501 2 1  11 1 1 1 1.2501 12 1.2501 11.2501 11.2501 2 1  11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	11 -3	11 -2 0.112 0.772 3 6 7.482 7.287 6 -2 15.115 15.223 1 1.225 1	11 -3	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11 -3	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
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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, LiAlSi<sub>2</sub>O<sub>6</sub>

(Clark et al, 1969) and jadeite, NaAlSi<sub>2</sub>O<sub>6</sub> (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

two (Al + Si) atoms. The remaining charge of +1/4 is balanced by its bonding to  $Ca^{2+}$ . 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<sub>2</sub>O<sub>6</sub>-CaAlAlSiO<sub>6</sub> 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  $\beta$  (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  $Mg^{2+}$  by  $Al^{3+}$  at the Ml site and  $Si^{4+}$  by  $Al^{3+}$  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  $\beta$  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

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	×.	Fobs	Fcalc	7	6 X	Fobs	Fcalc		1	Fobs	Feale		1	Fobs	Fcalc	*	1	Fobs	Fodic	N	1	Fobs	Foalc
1	2	7,257	9.726	- 3		12.092	12.159	2	4.7	8.295	8,996	- 3	- 3	44.199	41.859 7.653	1	ä	35.319	34.774	1	+6	23.927	26.292
1	7	4.454	5.059	- 1	-6	24.557	24.997	- 3	19	21.945	27.732	- 5	~ 2 ~ 1	7.403	234.921	1	7	35.935	25.734	L	- 1	22.564	23.611
2	-6	9,000	9.957	- 1	1	10.617	21.041		11	12.861	12.921	- 3	1	65.769	55.424	- 5	3	27.585	25,639	3.	-3	11./91	11.646
2	-3	7+471	7 - 90 3	- 1	-1	33-282	33.969		- 3	14.933	15.278	- 9	2	7.532	51.137	2	- 7	18.587	15.657	1	-2	13.033	13.726 7.319
ž	-1	47.563	35,545 57,858	1	1 1	11.564	11.757	-	1	5.998	5 · 150 17 · 677	- 3	- 6	15.021	14.675	2	-6 -5	8.395	9.257	1	2	10.587	17.32 w
2	3	23,537	21.726	1		13.412	13.673		1	12.393	11.958	3	- 5	14.70+	30.001	3	-4	33.123	12,451	1	1.	9.441	5.776
Z	ž	17.746	39.127	- 3	1	4.25.4	7.077	-	- 26	19,393	19.415	3	-1	9.863	9,627	1	-2	13.199	9.944	1	.7	11.255	11.327
2	3	55.47+	5.495	1		19,153	5.994	- 0	+5	30.177	3.956	- 0	3	5.935	9 - 32 8	4	-1	25.433	27.064	3	+6	5,789	5.614
2	5	14.742	41.884	- 9	-11	24.354	19.854	4	119	46.148	45,955	11	-3	5.92d 11.244	11.433	1	2	5.221	5.991 3.179	1	-5	22,255	25,942
2	- 1	35.955	33.539	1	-1	11.092	13.854		2	27.523 5.296	28.028	11	-2	9.703	3.754	4	3	11.267	11.244	1	-1	19.183	10.355
1	-8	21.982	21.934	1		12.210	12.278	- 1	2	15.26)	8.271	11	1	15.051	17.420		-7 -6	8.852 17.466	17.127	3	1	24.137	25.616
2	-6	23,676	21.120	- 1	-1	13.292	18.226	- 5	.5	22.144	21.643	11	2	31.443	39.617		-5	6.579	7.275	1	- 5	24.500 24.683	25.254
*	-4	22.957	22.957	- 3	-1	22.59.	79.959	- 3	-6	25.312	25.757						- 3	13.437	13.271	3	+14	39.541	53.861 No.232
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6.2	-2	34.773	5.458 35.134	11	38	13.75.	13.298	T.	2	11,911	11.333	- 6	-2	7.635	7.244		1	39.914	29.623	-		12.611	11.633
12	-1	22.015	23,243	33	+2	32.125	9,129	1	3	21.419	35.251	- 2	-1	17.401	15.813	+	+7	13.234	12+316	5	-1	29.364	24.854
4.7	1	7.021	33,150 5,652	13	-1	23.751	17.323	1	1.6	18+199	15.842		*	19.532	19.975		* to	5.415	4.551	-	-1	20.151	23.121
1.	3	22.367	22 = 72 1					3	+6	14.590	19.746	- 9	- 6	15.22.	14.155		+1	1.294	7 - 81 4	-9	*	2.792	5 - 55 7
12 11 12	-2	20.371 14.632 23.125	10.727 20.129 10.600 22.957			h = 8		1	15	33.535 31.535 32.514	61,633 21,623 31,649	- 1	-:	5.741 iu.314 19.31;	5.975 19.155 15.123		-1 -1	27.251 22.454 7.574	21.433 22.701 7.624				
12 12	2	7.711	7.624	9	-6	12,993	12.590	1	12	20.75+ 52.289 10.389	39.035 59.113 39.605	- 1	4	18:525 16:555 32:919	17.492 15.655 32.186		+5	5.347 11.493	5.223 9.893 1.965	1	4	h = 15 15,735	15.432
8.6		+2.292	41.227	2	-1	5.155 25.518	28.692	3	-	10.000	19,455	- 2	1	12-919	11.123	6	-1	5,728	35.773	1	1 5	13+753	14.218
				2	1	78.532	79.404	- 3	1	34.551	55, 469		- 5	22.70	12.399	ā.	a.	63.454	29.469	3	*5	32.773	32.597
		h = 7		6		51.205	52,507	- 1	9	29.495	29.855	1.1	- 4	33.452	37.801	7	2	13,959	11.013	- 2	- 4	23,341	22.593
1	15	12.239	9.132	2	-7	46.575	47.826	3	**	37.417	15.412	11	- 5	23.522	29.215		-5	19.451	19.131	3	-2	21-125	25.759
1	+8	15.354	9.933 15.850	2	+6	24.451	24.858 72.452	5	-5	12.402	12.393	11	-1	23,115	19.865		+3	+3.591	42.024	1	-44	9.443	3.678
1	-1	11,555	33,629	1.5	-4	9.513	13.738	5	-2	29.645	29.44 3	24	1	4. +4.	7.949	- 8	-2	10-127	15.00 1	- 2	-1	19.793	15.823
1	-Z	99.121	92.452 35.321	2	-1	74.196 36.795	37.819	5	*1	10.020	16.325	12	-	29,555	29.545	9	1	25.955	25.03%				
1	1	31+119	29.693	2	5	23.913	52.040 19.811	5	1.	14.352	15.952					1.4	-1	14-937	13 4 91 7				
1	2	\$0.000 00.723	25.691	2	1 2	54.491 32.717	55.171 33.631		2	7+435	11,138			h = 11								h = 16	
1	3	26.453	27.448	5	3	28.713	29.542	9	+7	1.229	7.676	1	-6	14.475	14.556			(40 - 0.24)		- 3	+2	20.155	19.935
1	1	29+922	29.613	3		7.263	7.119	7	+5	11.368	11.971	- 8	-1	5.635 15.313	9.258			h = 13		-	+3	16-56+	15.273
		14.505	17.911		-9	5.317	5 + 351			15.490	15.160	1	+1	33.325	3).111	1	• ?	11,111	14.251	1	13	25.575	24.743

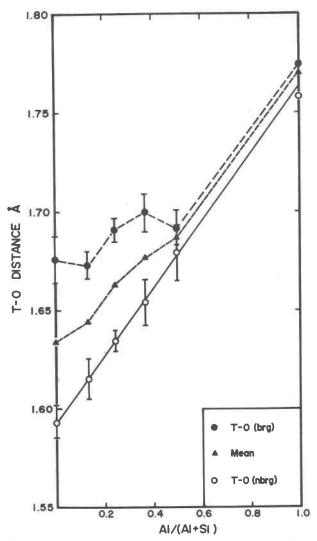


Fig. 1. T-O distances plotted against Al/(Al + Si) ratio in tetrahedral site in several C2/c pyroxenes and sillimanite. Data from Clark *et al* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), present study, and Burnham (1963) for sillimanite.

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  $b \times (0.5 \cdot y_{M2})$ , 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<sup>3+</sup> content (replacing Mg<sup>2+</sup>) increases, the M2-O1 and M2-O2 bonds become weaker, because O1 and O2 are more strongly bonded to Al<sup>3+</sup> at the M1 site. Simultaneously, as Al-Si substitution proceeds at the tetrahedral site, Ca<sup>2+</sup> 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 Ml site, neither OI 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<sub>2</sub>SiO<sub>6</sub> 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:

$$\begin{array}{l} \operatorname{CaAl_2Si_2O_8} + \operatorname{Ca_2Al_2SiO_7} + \operatorname{Al_2O_3}_{\text{corundum}} = 3 \operatorname{CaAl_2SiO_6}_{\text{CaTs}} \\ & & & & & & & & & & & & \\ \end{array}$$

$$3 \operatorname{CaAl}_{2} \operatorname{SiO}_{6} = \operatorname{Ca}_{3} \operatorname{Al}_{2} \operatorname{Si}_{3} \operatorname{O}_{12} + 2 \operatorname{Al}_{2} \operatorname{O}_{3} \qquad \langle 2 \rangle$$
CaTs grossular corundum

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

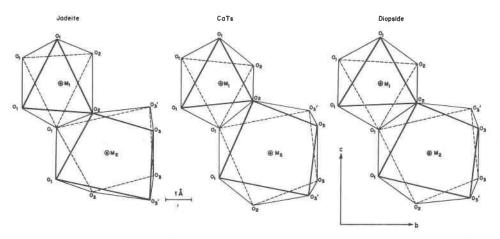


Fig. 2. M1 and M2 polyhedra in jadeite (Prewitt and Burnham, 1966), CaAlAlSiO<sub>6</sub> (present study), and diopside (Clark et al, 1969) viewed along [100].

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<sub>3</sub> 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<sub>3</sub> 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 = odd) reflections to become

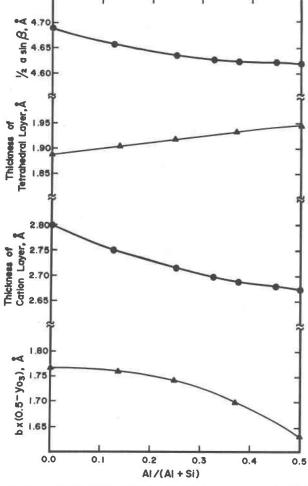


Fig. 3. Estimated metrical changes in structures in the CaMgSi<sub>2</sub>O<sub>6</sub>-CaAlAlSiO<sub>6</sub> join (see text). ● Data from Clark *et al* (1962); ▲ Data from Clark *et al* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), and present study.

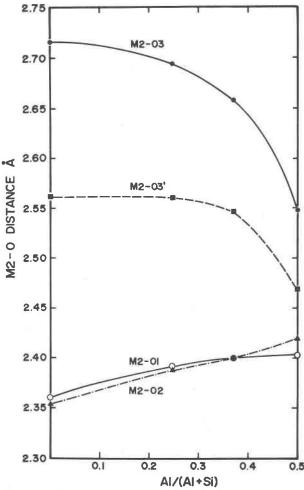


Fig. 4. Changes in M2-O distances in some C2/c pyroxenes plotted against Al/(Al + Si) ratio. Data from Clark *et al* (1969), Peacor (1967), Dowty and Clark (1973), and present study.

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. Ī
- 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<sub>2</sub>O<sub>6</sub>-CaAl<sub>2</sub>SiO<sub>6</sub> join, we expect two kinds of M2 sites, namely, a jadeite-type M2 site for Na<sup>+</sup> and CaTs-type M2 site for Ca<sup>2+</sup>. In such a case, P2/n or C2 are the more plausible models.

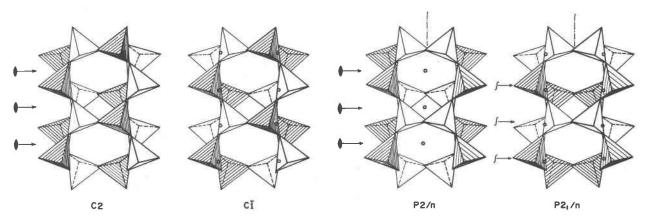


Fig. 5. Possible Al-Si ordering schemes in TO<sub>3</sub> chains of CaTs. Shadowed (likewise, white) tetrahedra are crystallographically equivalent.

#### 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 Ca<sup>2+</sup> 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<sub>2</sub>O<sub>6</sub>-CaAl<sub>2</sub>SiO<sub>6</sub> join can be successfully explained in terms of the relative shifts of atoms required to attain the local charge balance.
- 5) C2, P2/n,  $C\bar{1}$  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.

#### Acknowledgments

This research has been supported by NASA grant NGR 48-002-149. We are indebted to Professors B. W. Evans and I. S. McCallum for discussions and a review of the manuscript, to Edmond A. Mathez for the microprobe analysis, and to Professor C. W. Burnham, Harvard University, for informing us of their X-ray and microprobe studies on CaTs.

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Manuscript received, October 8, 1973; accepted for publication, December 26, 1973.