American Mineralogist, Volume 59, pages 549–557, 1974

Structure and Crystal Chemistry of Calcium Tschermak's Pyroxene, $CaAlAlSiO_6$

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, $CaAlAlSiO_6$ (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 $\beta = 106.06°$; 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_8 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, $CaAlAlSiO_6$ (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 $CaAlAlSiO_6$ Single Crystals

The starting material was a mixture of anorthite, gehlenite, and corundum prepared from $CaCO_3$, Al_2O_3, and SiO_2 by solid state reaction in air.

$$3(CaCO_3 + Al_2O_3 + SiO_2) \rightarrow CaAl_2Si_2O_8$$
$$+ Ca_2Al_2SiO_7 + Al_2O_3 \rightarrow 3\ CaAl_2SiO_6.$$

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 $CaAlAlSiO_6$

	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)
O1	.10519(11)	.08210(11)	.12264(19)	.822(13)	.00242(9)	.00259(10)	.00838(29)	.00065(7)	.00122(13)	.00042(14)
O2	.36571(11)	.26707(12)	.30988(21)	.917(14)	.00272(10)	.00222(10)	.01115(32)	-.00020(8)	.00139(14)	-.00009(14)
O3	.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 PtO_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.

TABLE 2. Bond Lengths and Bond Angles of $CaAlAlSiO_6$

Bond Length		Bond Angle	
Atom	Value(Å)	Atom	Value(°)
Octahedron (M1)			
M1-O1A1, B1	2.021 (1)	O-M1-O angles	
-O1A2, B2	1.947 (1)	O1A2, O1B2	175.64 (5)
-O2C1, D1	1.872 (1)	(2)O1A1, O2D1	166.89 (4)
mean of 6	1.947	O1A1, O1B1	84.58 (5)
		O2C1, O2D1	97.79 (6)
O1A1-O1B1	2.719 (2)	(2)O1A1, O2C1	89.93 (5)
O2C1-O2D1	2.822 (2)	(2)O1A1, O1A2	98.03 (5)
(2)O1A1-O2C1	2.753 (2)	(2)O1A1, O1B2	78.70 (4)
(2)O1A1-O1A2	2.995 (2)	(2)O1A2, O2C1	92.54 (5)
(2)O1A2-O2C1	2.709 (2)	(2)O1A2, O2D1	90.33 (5)
(2)O1A2-O2D1	2.760 (2)	T-O1A1-M1	122.51 (5)
(2)O1A1-O1B2	2.516 (2)	T-O1A2-M1	119.39 (7)
mean of 12	2.751	T-O2C1-M1	143.25 (8)
M1-M1 (1)	3.068 (1)		
M1-TA1	3.260 (1)		
M1-TA2	3.145 (1)		
Polyhedron (M2)			
M2-O1A1, O1B1	2.403 (1)	O1A1, O1B1	68.90 (4)
-O2C2, O2D2	2.420 (1)	O2C2, O2D2	147.48 (4)
-O3C1, O3D1	2.469 (1)	O3C1, O3D1	86.65 (4)
-O3C2, O3D2	2.549 (1)	O3C2, O3D2	109.54 (4)
mean of 6	2.431	(2)O1A1, O2C2	83.30 (4)
mean of 8	2.461	(2)O1A1, O3C1	123.22 (4)
		(2)O1A1, O3C2	90.91 (4)
O1A1-O1B1	2.719 (2)	(2)O2C2, O3C1	65.43 (4)
O3C1-O3D1	3.388 (2)	(2)O2C2, O3C2	113.65 (4)
(2)O1A1-O2D2	2.760 (2)	(2)O3C1, O3C2	63.91 (4)
(2)O1A1-O2D2	3.206 (2)	(2)O1A1, O2D2	69.81 (4)
(2)O1A1-O3C2	3.532 (2)	(2)O1A1, O3D1	130.69 (4)
(2)O2C2-O3C1	2.642 (2)	(2)O1A1, O3D2	159.31 (4)
(2)O2C2-O3D2	3.375 (2)	(2)O2C2, O3D2	85.52 (4)
(2)O3C1-O3C2	2.657 (2)	(2)O3C1, O3D2	66.45 (4)
(2)O3C1-O3D2	2.751 (2)	(2)O2C2, O3D1	141 41 (4)
Tetrahedron (Si, Al)			
T-O1	1.693 (1)	O1-T-O2	119.72 (5)
T-O2	1.665 (1)	O1-T-O3A1	109.94 (5)
mean, non-brg.	1.679	O1-T-O3A2	108.43 (6)
		O2-T-O3A1	110.39 (6)
T-O3A1	1.683 (1)	O2-T-O3A2	103.43 (6)
T-O3A2	1.701 (1)	O3A1-T-O3A2	103.49 (6)
mean, brg.	1.692	mean of 6	109.23
mean of 4	1.686	T-O3-TA2	134.94 (7)
O1-O2	2.904 (2)	O3A2-O3A1-O3A2	165.93 (6)
O1-O3A1	2.764 (2)		
O1-O3A2	2.753 (2)		
O2-O3A1	2.749 (2)		
O2-O3A2	2.642 (2)		
O3A1-O3A2	2.657 (2)		
mean of 6	2.745		
T-TA2	3.125 (1)		

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 $CaAlAlSiO_6$. 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 PĪ). For intensity measurements a solid state detection system and Mo$K\alpha$ radiation monochromatized by reflection from a graphite single crystal (2θ = 12.2°) have been used. All $h0l$ reflections with 2θ 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 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) Å^3; Z 4. The calculated density is 3.44 g cm^{-3}.

TABLE 3. Thermal Ellipsoids of $CaAlAlSiO_6$

Atom	Axis	rms amplitude, Å	Angle (°) with a	Angle (°) with b	Angle (°) with c
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 Mo$K\alpha$ 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 × 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 970 Fo values above 3σ(Fo), where σ(Fo) is the standard deviation. The Fo's were weighted as Fo/σ^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

Source of Data		Anorthite $Ca_2Al_2Si_2O_8$ Wainwright and Starkey (1971)	Gehlenite $Ca_2Al_2SiO_7$ Louisnathan (1971)	Ca-Tschermak's $CaAl_2SiO_6$ Present study	Grossular $Ca_3Al_2Si_3O_{12}$ Prandl (1966)
Coordination no. of Ca	000	6	8	8	8
	Z00	7			
	0i0	7			
	Zi0	7			
Volume of Ca-polyhedron Å^3	000	27.835*	23.260	24.508	23.867
	Z00	26.492*			
	0i0	27.226*			
	Zi0	26.791*			
Coordination no. of: Si		4	4	4	4
Al		4	4	4,6	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 $CaAlAlSiO_6$

	$C\,2$	$C\,\bar{1}$	$P\,2/n$	$P\,2_1/n$
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 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) *M*2-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_4 tetrahedron in sillimanite (Burnham, 1963), where it forms a chain alternating with SiO_4 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

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

or inversely

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

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 $CaAlAlSiO_6$

k	l	F_{obs}	F_{calc}
		h = 0	
0	2	154.244	149.776
0	4	* 93.349	90.776
0	6	32.165	31.091
0	8	25.622	24.426
2	0	32.371	29.955
2	1	15.969	14.791
2	2	71.068	59.125
2	3	31.639	32.055
2	5	31.947	31.298
2	6	9.502	9.659
2	7	15.531	15.597
2	8	6.191	3.991
4	0	23.749	21.938
4	1	139.833	105.047
4	2	56.319	66.356
4	3	36.143	38.116
4	4	11.921	11.099
4	5	13.113	9.811
4	6	26.363	25.175
4	7	16.624	15.833
4	8	7.132	5.537
6	0	82.965	73.793
6	1	67.404	65.356
6	2	69.093	69.752
6	3	35.419	36.611
6	5	21.746	22.258
8	0	16.851	15.954
8	1	20.973	23.212
8	2	27.533	27.439
8	3	6.579	7.024
8	4	11.139	10.853
8	5	25.691	26.774
8	7	6.573	5.370
10	1	75.835	75.258
10	2	54.429	54.150
10	3	24.535	24.504
10	4	40.551	41.006
10	5	19.491	18.129
10	6	23.284	23.123
12	0	37.600	37.821
12	2	21.125	21.099
12	4	5.983	5.850
12	5	18.994	19.326
14	0	22.572	22.676
14	1	16.248	15.914
14	2	23.647	23.202
		h = 1	
1	-8	17.053	15.079
1	-7	11.171	9.827
1	-6	6.644	9.431
1	-5	3.994	4.875
1	-4	69.337	69.220
1	-3	9.125	4.416
1	-2	19.759	21.922
1	-1	6.387	4.725
1	1	21.194	22.036
1	2	66.193	52.965
1	3	6.417	6.778
1	4	19.165	16.836
1	5	21.421	21.018
1	6	21.675	21.639
1	7	27.965	27.039
1	8	25.339	25.301
3	-8	13.415	12.541
3	-7	41.171	40.723
3	-6	41.497	41.153
3	-5	82.977	83.660
3	-4	25.453	25.135
3	-3	123.397	123.476
3	-2	81.753	79.558
3	-1	86.023	84.292
3	0	15.389	15.339
3	1	38.327	31.923
3	2	36.994	38.054
3	3	9.331	9.413
3	4	13.941	10.984
3	6	9.793	9.578
3	7	12.455	11.434
3	8	19.357	17.737
5	-6	7.023	5.299
5	-5	3.290	3.357
5	-4	14.789	15.354
5	-3	20.895	21.654
5	-2	4.473	3.322
5	-1	45.135	46.559
5	0	97.469	95.659
5	1	17.447	17.482
5	2	67.794	67.761
5	3	43.399	45.893
5	4	55.342	57.759
5	5	15.635	15.459
5	6	51.133	52.152
5	7	8.723	8.363
5	8	43.366	41.881
7	-7	32.981	31.358
7	-6	18.193	17.983
7	-5	49.083	50.577
7	-4	21.942	21.861
7	-3	81.384	82.352
7	-2	33.192	33.663
7	-1	66.721	68.427
7	0	29.583	29.582
7	1	69.913	67.421
7	2	21.681	22.254
7	3	24.914	25.893
7	4	7.543	8.222
7	5	24.644	24.431
7	6	6.155	5.956
9	-6	4.725	3.837
9	-5	13.453	13.414
9	-4	17.334	17.339
9	-3	31.721	31.736
9	-1	9.483	9.352
9	0	13.093	13.293
9	1	20.913	20.371
9	2	34.435	34.943
9	3	33.189	33.355
9	4	32.015	32.429
9	5	8.137	8.649
9	6	22.476	22.546
11	-5	3.533	4.733
11	-4	27.535	26.552
11	-3	9.133	9.271
11	-2	27.362	27.214
11	0	14.425	15.232
11	1	17.609	17.534
11	3	11.213	11.597
11	4	5.862	4.459
11	5	25.912	25.701
13	-4	14.573	10.886
13	-3	19.965	19.913
13	-2	14.435	14.191
13	-1	23.913	21.292
13	0	36.584	36.325
13	2	34.997	34.532
13	4	14.311	14.177
		h = 2	
0	-8	45.701	45.852
0	-6	43.328	44.694
0	-4	32.251	32.211
0	-2	31.628	29.773
0	0	25.983	24.742
0	2	94.236	92.448
0	4	12.204	11.710
0	6	24.557	24.414
0	8	17.733	17.248
2	-7	4.817	5.372
2	-5	22.034	21.335
2	-4	5.678	4.850
2	-3	141.359	152.947
2	-2	24.671	79.322
2	-1	144.721	143.770
2	0	94.432	93.478
2	1	113.446	123.989
2	2	29.738	30.901
2	3	92.954	92.831
2	4	56.715	63.383
2	5	76.927	77.663
2	6	21.115	21.857
2	7	35.222	34.725
2	8	19.633	19.685
4	-8	11.631	11.555
4	-7	21.289	22.042
4	-6	32.921	32.327
4	-5	22.433	22.137
4	-4	17.968	18.172
4	-3	33.959	34.661
4	-2	3.833	2.622
4	-1	15.817	15.619
4	0	9.442	11.433
4	2	41.349	41.299
4	3	7.188	7.801
4	4	23.334	23.391
4	5	13.929	14.638
4	6	24.359	23.967
4	8	4.469	4.654
6	-8	5.569	5.516
6	-7	18.491	17.962
6	-6	13.707	13.532
6	-4	23.951	24.234
6	-3	12.862	12.902
6	-2	51.575	52.891
6	-1	22.094	21.689
6	0	35.864	35.921
6	1	11.073	11.472
6	2	22.832	22.016
6	3	6.299	4.821
6	4	17.219	17.343
6	5	12.199	12.182
6	6	24.113	24.013
6	7	5.910	5.995
8	-7	13.032	11.122
8	-6	29.333	29.349
8	-5	9.492	8.931
8	-4	31.092	32.075
8	-3	23.441	24.115
8	-2	35.475	35.157
8	-1	72.925	72.796
8	0	44.221	47.975
8	1	46.269	45.147
8	2	33.132	35.981
8	3	64.272	65.954
8	4	23.669	24.757
8	5	42.271	42.931
8	6	9.442	9.109
10	-6	23.631	23.507
10	-5	27.048	27.031
10	-4	25.908	25.476
10	-3	32.619	33.339
10	-2	12.598	11.360
10	-1	92.193	93.349
10	1	9.132	9.576
10	3	22.585	21.632
10	4	5.048	4.932
10	5	15.624	15.693
12	-5	12.759	12.871
12	-3	47.648	48.371
12	-2	11.457	11.111
12	-1	41.139	41.940
12	1	56.454	55.945
12	2	9.794	9.259
12	3	19.364	11.753
14	-3	9.647	6.453
14	-2	3.311	5.147
14	1	14.571	14.419
		h = 3	
1	-8	9.305	9.315
1	-7	22.449	21.652
1	-6	35.379	34.612
1	-5	53.763	50.739
1	-4	69.292	71.855
1	-3	80.697	84.357
1	-2	3.135	4.853
1	-1	93.060	93.184
1	0	79.411	75.299
1	1	84.664	83.212
1	2	15.792	15.467
1	3	27.306	28.487
1	4	21.640	22.456
1	5	7.899	7.409
1	6	28.993	29.043
1	7	4.710	3.359
1	8	7.147	7.911
3	-8	9.915	9.867
3	-7	8.548	9.158
3	-6	8.375	7.563
3	-5	14.391	14.306
3	-4	28.514	30.357
3	-3	12.133	12.752
3	-2	7.250	9.921
3	-1	86.453	79.293
3	0	78.326	76.180
3	1	23.964	23.399
3	2	8.119	8.046
3	3	16.410	15.085
3	4	37.494	38.449
3	5	37.482	37.818
3	6	10.598	10.197
3	7	32.208	32.152
5	-8	26.139	26.027
5	-7	70.005	73.047
5	-6	5.575	5.244
5	-4	94.771	95.399
5	-3	4.634	5.925
5	-2	125.432	124.765
5	-1	16.652	15.658
5	0	87.568	88.136
5	2	104.720	107.757
5	3	10.987	11.156
5	4	23.746	24.293
5	5	24.153	24.322
5	6	13.443	9.470
5	7	17.871	16.502
7	-7	15.309	14.450
7	-6	19.315	19.375
7	-5	13.573	10.411
7	-4	11.431	11.246
7	0	14.217	14.883
7	1	28.539	20.138
7	2	27.305	27.700
7	3	32.475	32.715
7	5	43.775	43.879
7	7	42.486	41.021
9	-7	15.652	14.690
9	-6	28.758	21.030
9	-5	40.669	40.399
9	-4	30.785	31.393
9	-3	16.115	15.323
9	-2	24.583	24.973
9	-1	17.365	17.469
9	0	30.788	30.772
9	1	20.177	19.755
9	2	12.120	11.706
9	3	23.873	23.950
9	4	16.037	16.040
11	-5	11.670	12.658
11	-4	25.970	26.077
11	-3	25.903	25.812
11	-2	19.347	19.277
11	-1	17.640	17.742
11	0	19.625	19.955
11	1	14.319	14.235
11	2	6.104	7.247
11	4	9.359	9.118
11	5	6.492	5.935
13	-4	15.729	15.733
13	-3	22.600	22.869
13	-2	6.372	5.837
13	-1	8.219	9.434
13	0	11.729	12.979
13	1	13.725	10.450
13	2	26.333	25.207
		h = 4	
0	-6	41.473	41.433
0	-4	43.377	45.081
0	-2	85.447	93.263
0	0	13.412	14.332
0	2	133.499	135.039
0	4	90.373	92.591
0	6	58.973	59.051
2	-8	32.493	33.881
2	-7	51.534	51.409
2	-6	13.596	13.446
2	-5	44.713	45.759
2	-4	31.325	33.321
2	-3	45.359	49.422
2	-2	25.958	25.051
2	-1	72.799	70.538
2	0	23.774	23.059
2	1	12.235	12.504
2	2	47.363	47.840
2	3	14.904	15.327
2	4	4.868	5.098
2	5	5.102	4.679
2	6	5.103	4.511
2	7	14.393	14.019
4	-8	13.030	12.820
4	-7	5.352	4.941
4	-6	23.115	23.830
4	-5	14.360	15.358
4	-4	22.625	23.348
4	-3	21.389	20.415
4	-2	9.613	8.395
4	-1	4.114	4.064
4	0	51.270	52.126
4	1	34.559	37.841
4	2	55.650	58.115
4	3	45.079	47.254
4	4	54.534	55.806
4	5	37.793	37.871
4	6	15.944	16.357
4	7	11.441	11.855
6	-8	14.537	14.400
6	-7	7.281	6.979
6	-6	15.472	15.503
6	-5	5.449	5.425
6	-4	19.272	15.438
6	-3	11.372	11.720
6	-2	24.563	25.870
6	-1	25.573	24.977
6	0	7.104	4.855
6	1	19.459	17.491
6	2	21.563	22.539
6	3	34.783	35.133
6	4	40.094	40.673
6	5	19.492	20.412
6	6	12.713	12.034
6	7	23.164	22.539
8	-8	31.547	31.649
8	-7	13.419	15.977
8	-6	25.355	25.707
8	-5	39.020	39.159
8	-4	17.264	17.259
8	-3	17.455	17.250
8	-2	23.471	23.473
8	-1	4.593	3.997
8	0	34.591	37.035
8	1	13.356	13.139
8	2	29.191	29.734
8	3	36.612	35.619
8	4	27.643	27.894
8	5	5.614	5.546
8	6	9.439	9.173
10	-6	7.234	6.953
10	-5	9.319	9.724
10	-4	17.139	17.393
10	-3	22.420	22.136
10	-2	41.255	40.811
10	-1	36.939	37.036
10	0	48.327	49.489
10	1	37.183	37.454
10	2	53.492	63.812
10	3	9.492	5.998
10	4	49.745	48.950
10	5	16.375	15.083
12	-5	24.255	24.732
12	-4	9.825	9.351
12	-3	26.729	25.803
12	-2	5.132	5.691
12	-1	27.443	27.736
12	1	13.529	13.928
12	2	21.693	20.908
12	3	16.236	15.964
12	4	23.404	20.274
14	-2	15.186	15.401
14	-1	8.786	9.950
14	0	21.319	21.542
14	1	25.212	25.139
		h = 5	
1	-9	7.240	5.954
1	-8	6.277	5.774
1	-6	21.433	21.760
1	-5	11.267	11.291
1	-4	15.729	16.031
1	-2	47.984	59.145
1	-1	12.458	11.660
1	0	59.935	66.759
1	2	24.352	24.699
1	3	27.919	29.314
1	5	22.190	22.412
1	6	11.247	11.539
1	7	13.367	13.011
3	-8	16.746	18.153
3	-7	33.341	33.242
3	-6	13.591	13.851
3	-5	32.176	32.298
3	-4	41.377	42.055
3	-3	53.676	54.122
3	-2	36.924	39.626
3	-1	123.183	115.846
3	0	57.939	57.990
3	1	136.466	137.552
3	2	44.713	45.693
3	3	52.373	53.552
3	4	22.476	23.234
3	5	25.358	25.852
3	6	19.416	19.388
3	7	11.151	10.452
5	-8	6.421	5.855
5	-7	22.084	21.894
5	-6	15.962	15.819
5	-5	17.453	17.485
5	-4	7.275	7.373
5	-3	31.527	31.916
5	-2	13.210	13.092
5	-1	19.195	18.153
5	0	7.135	7.153
5	1	28.229	29.377
5	2	24.231	24.129
5	3	7.251	7.817
5	4	43.923	46.834
5	5	7.393	7.100
5	6	24.437	23.938
7	-7	32.223	32.076
7	-5	59.694	60.099
7	-3	63.256	64.956
7	-2	4.492	4.426
7	-1	99.166	99.511
7	0	38.594	39.377
7	1	59.662	59.116
7	2	21.653	22.099
7	3	45.534	45.979
7	5	13.149	13.382
9	-5	5.454	4.353
9	-3	7.563	7.233
9	-2	9.362	9.698
9	-1	35.613	36.345
9	0	11.735	11.903
9	1	16.531	15.952
9	2	11.794	10.259
9	3	8.925	9.464
9	5	15.293	15.197
11	-5	6.753	7.153
11	-4	21.277	23.217
11	-3	9.565	9.848
11	-2	33.167	33.314
11	-1	11.403	10.330
11	0	33.555	33.815
11	1	7.796	5.798
11	2	14.791	15.134
11	3	3.123	3.484
13	-4	31.297	31.352
13	-3	26.459	26.544
13	-2	25.693	25.674
13	-1	19.319	20.019
13	0	12.086	12.237
13	1	29.914	33.005
13	2	13.545	13.373
		h = 6	
0	-8	37.432	37.343
0	-6	53.533	55.336
0	-4	109.504	122.711
0	-2	112.245	121.544
0	0	73.252	73.986

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 *M*2-O1, *M*2-O2, *M*2-O3, and *M*2-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 *M*2-O1 and *M*2-O2 bonds are lengthened in CaTs, while *M*2-O3 and *M*2-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, $LiAlSi_2O_6$ (Clark *et al*, 1969) and jadeite, $NaAlSi_2O_6$ (Prewitt and Burnham, 1966). Apparently, the size of the Al-O octahedra increases with the size of the cation occupying the *M*2 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 *M*2-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 *M*2-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 *M*1-O2 and *T*-O2 bonds and longer *M*1-O1 and *T*-O1 bonds. The *M*2-O1 and *M*2-O2 distances (2.403 and 2.420 Å) are similar in spite of this charge imbalance on O1 and O2.

Crystal Chemistry of the $CaMgSi_2O_6$-$CaAlAlSiO_6$ 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 Mg^{2+} by Al^{3+} at the *M*1 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 *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

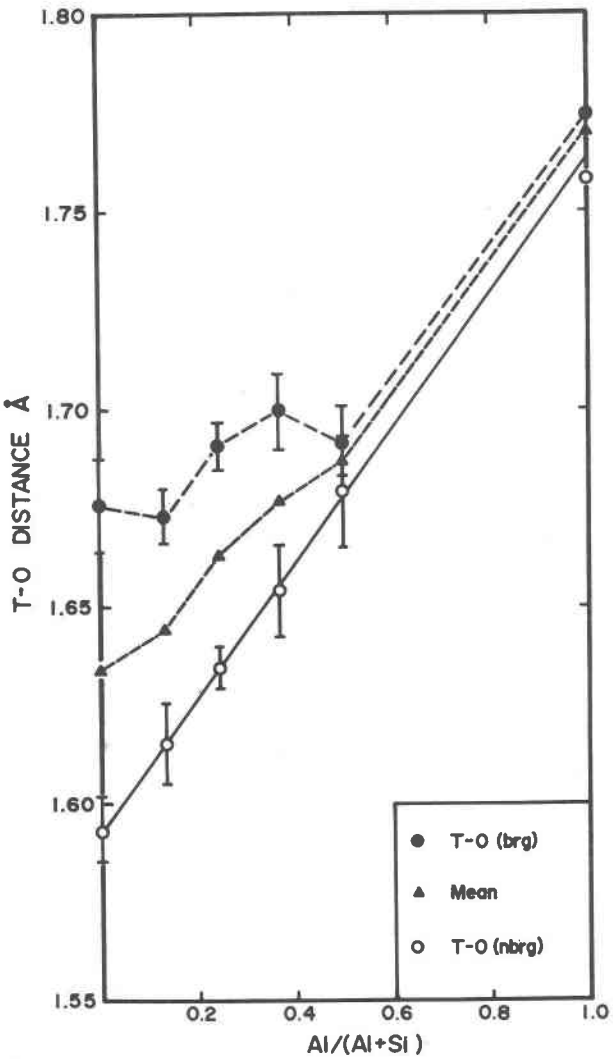

FIG. 1. *T*-O distances plotted against Al/(Al + Si) ratio in tetrahedral site in several *C*2/*c* pyroxenes and sillimanite. Data from Clark *et al* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), present study, and Burnham (1963) for sillimanite.

can be used as a measure of the thickness of the cation layer (Fig. 3). On the other hand, the distance from *M*2 to the nearest chain equals $b \times (0.5\text{-}y_{M2})$, where y_{M2} is the *y*-coordinate of the *M*2 cation (Ca), and yields a fourth curve (Fig. 3). Comparing these third and fourth curves to those showing changes in the *M*2-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 *M*2 site) forms with oxygen, two pairs involve O1 and O2 which are bonded to *M*1 as well; two other pairs involve the tetrahedral-chain-forming oxygens O3 and O3′, which are also bonded to a second *M*2 site. *M*2-O1 and *M*2-O2 bonds are much shorter than *M*2-O3 and *M*2-O3′ bonds (Table 2). As the Al^{3+} content (replacing Mg^{2+}) increases, the *M*2-O1 and *M*2-O2 bonds become weaker, because O1 and O2 are more strongly bonded to Al^{3+} at the *M*1 site. Simultaneously, as Al-Si substitution proceeds at the tetrahedral site, Ca^{2+} at the *M*2 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 *M*1 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 $CaAl_2SiO_6$ 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°C and 1420°C the following reactions proceed from the left to the right with increasing pressure:

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{gehlenite}}{Ca_2Al_2SiO_7} + \underset{\text{corundum}}{Al_2O_3} = 3\ \underset{\text{CaTs}}{CaAl_2SiO_6} \qquad \langle 1 \rangle$$

$$3\ \underset{\text{CaTs}}{CaAl_2SiO_6} = \underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + 2\ \underset{\text{corundum}}{Al_2O_3} \qquad \langle 2 \rangle$$

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

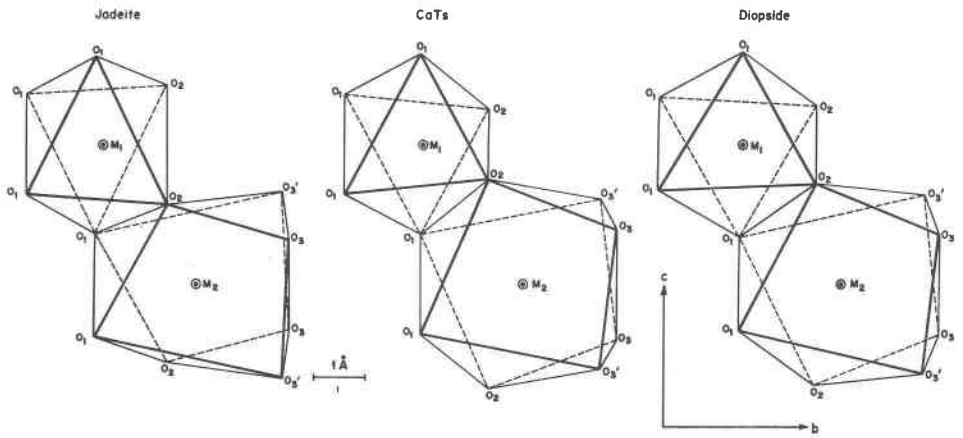

FIG. 2. $M1$ and $M2$ polyhedra in jadeite (Prewitt and Burnham, 1966), $CaAlAlSiO_6$ (present study), and diopside (Clark *et al*, 1969) viewed along [100].

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" ($h + k$ = odd) reflections to become

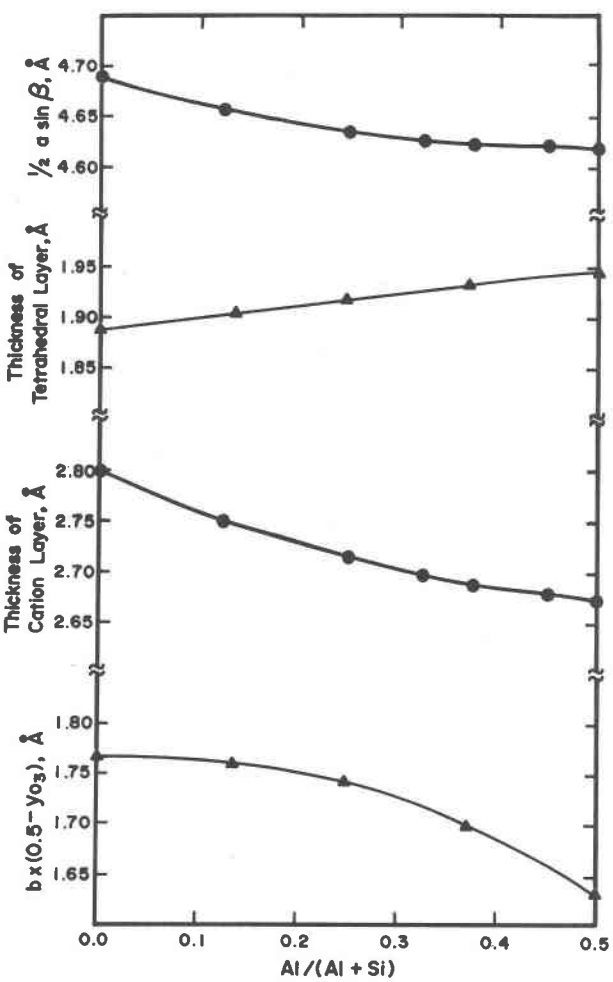

FIG. 3. Estimated metrical changes in structures in the $CaMgSi_2O_6$–$CaAlAlSiO_6$ join (see text). ● Data from Clark *et al* (1962); ▲ Data from Clark *et al* (1969), Takeda (1972), Peacor (1967), Dowty and Clark (1973), and present study.

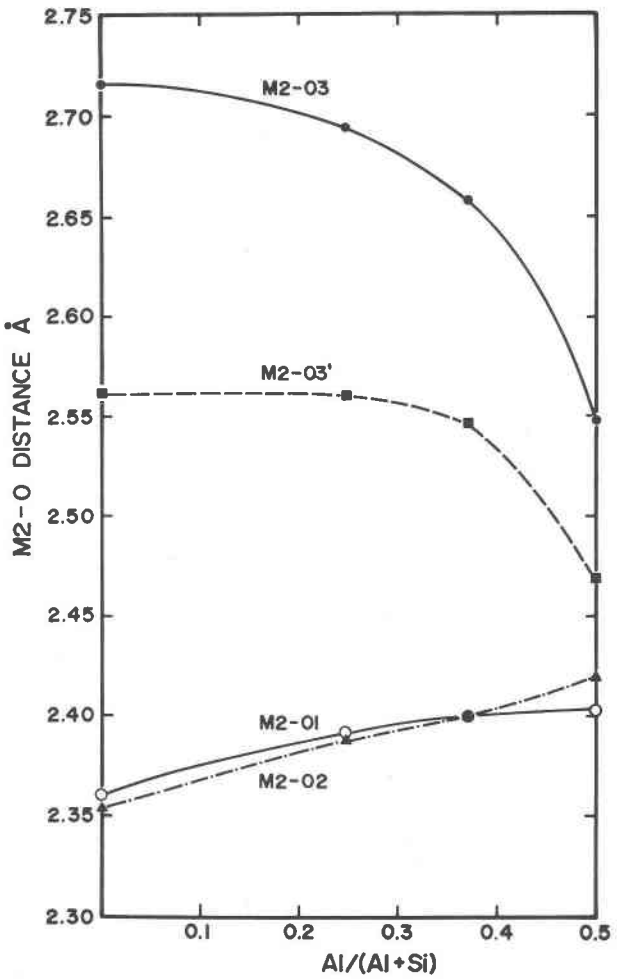

FIG. 4. Changes in $M2$-O distances in some $C2/c$ pyroxenes plotted against Al/(Al + Si) ratio. Data from Clark *et al* (1969), Peacor (1967), Dowty and Clark (1973), and present study.

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, $P2/n$ or $C2$ are the more plausible models.

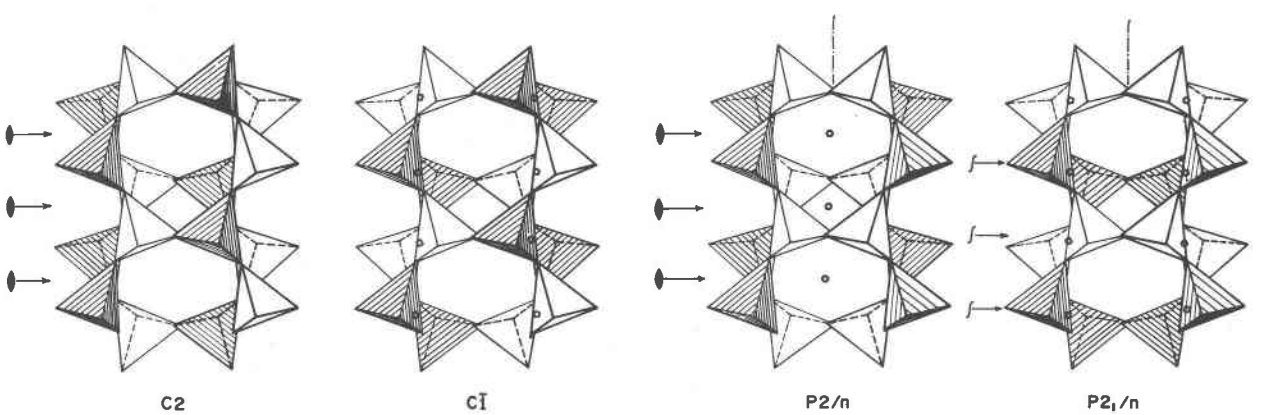

FIG. 5. Possible Al–Si ordering schemes in TO_3 chains of CaTs. Shadowed (likewise, white) tetrahedra are crystallographically equivalent.

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^{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 $CaMgSi_2O_6$-$CaAl_2SiO_6$ join can be successfully explained in terms of the relative shifts of atoms required to attain the local charge balance.
5) $C2$, $P2/n$, $C\bar{1}$ 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.