STRUCTURE OF $\text{Ca}_{1.00}\text{Sc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$ PYROXENE

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The crystal structure of $\text{Ca}_{1.00}\text{Sc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$ pyroxene grown by the floating zone method has been refined by the least squares method using 741 reflections measured on an automatic single crystal diffractometer. The unweighted R factor is 0.027 for 670 unrejected reflections. The cell dimensions are; $a_0=9.925\text{\AA}$, $b_0=8.949\text{\AA}$, $c_0=5.460\text{\AA}$, $\beta=105.77^\circ$, and $V=466.75\text{\AA}^3$; space group C2/c. The octahedral (M1) site is occupied by Sc (84 at.%) and Ti (16 at.%). Within the tetrahedral (T) site, Si (36.5 at.%), Al (58 at.%) and Ti (5.5 at.%) ions are completely disordered. These facts mean that Al-O-Al bonds exist in this pyroxene chain and the aluminum avoidance rule has been violated in this structure.

INTRODUCTION

$\text{M}^{+3}\text{-Si}$ order-disorder in pyroxene structure was studied by X-ray structure determinations of $\text{CaAl}_2\text{SiO}_6$, CaFeAlSiO_6 and CaScAlSiO_6 (Okamura, Ghose and Ohashi, 1974; Ghose, Wan, Okamura, Ohashi and Weidner, 1975; Ohashi and Ii, 1978). These pyroxenes belong to a same space group C2/c. These facts mean that Al and Si 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. It is possible to 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. Antiphase domains.

On the other hand, $\text{M}^{+3}\text{-Si}$ order-disorder in pyroxene structure was studied by infrared and Raman spectras of $\text{CaAl}_2\text{SiO}_6$ and $\text{CaGa}_2\text{SiO}_6$ -pyroxenes (Ohashi, 1977). It is difficult to detect that Al-Si order exists or not. But the existence of Ga-Si order is observed clearly.

It is known that $\text{CaTiAl}_2\text{O}_6$ is soluble in CaFeAlSiO_6 and CaScAlSiO_6 at 1 atm (Onuma and Yagi, 1977; Akasaka and Onuma, 1977; Ohashi, unpublished data). If some titanium ions occupy the octahedral sites in these pyroxene solid solutions, there should exist $\text{M}^{+3}\text{-O-M}^{+3}$ bonds in the pyroxene chains, which would lead to the possibility of Al-Si disorder in the chains of pyroxenes synthesized at 1 atm.

The object of the present investigation is to determine whether $\text{M}^{+3}\text{-O-M}^{+3}$ bonds exist or not in the pyroxene chain. The atomic scattering factor of Sc is nearly equal to that of Ti. But it is known that Sc ions occupy only the M1-site in CaScAlSiO_6 pyroxene (Ohashi and Ii, 1978). There-

fore, it is possible to detect the occupancy of Ti ions in tetrahedral sites by X-ray structure analysis.

SYNTHESIS OF SINGLE CRYSTALS

The single crystals were grown by the floating zone method using an apparatus of an infrared radiation convergence type with a 1.5 kw quartz halogen lamp as the heat source. The composition of the starting material was 70 mol% CaScAlSiO_6 -30mol% $\text{CaTiAl}_2\text{O}_6$. The product was a mixture of pyroxenes and other crystals. Electron microprobe analysis of the pyroxene by M. Tsutsumi using CaSiO_3 , TiO_2 , SiO_2 , Al_2O_3 and CaScAlSiO_6 pyroxene as standards indicates a chemical composition,

MEASUREMENT OF INTENSITY DATA AND REFINEMENT OF THE STRUCTURE

From x-ray Weissenberg photographs, the space group was determined to be $C2/c$ by M. Isobe. For the intensity measurements, which were carried out at room temperature, several spherical specimens were prepared. A single crystal sphere of radius 0.08 mm showing the best crystallinity as judged by a transmission Laue photograph was mounted on a computer controlled single crystal diffractometer (Philips PW 1100). The unit-cell dimensions were obtained by the least squares method based on θ measured on the diffractometer. The cell dimensions are; a_0 9.925 (5), b_0 8.949 (2), c_0 5.460 (2) Å, β 105.77 (4)°; V 466.75 (31) Å³; Z 4. The calculated density is 3.41 g/cm³.

The intensities were collected on the same diffractometer, scan speed being 3°/min. In the range of $2\theta \leq 60^\circ$, 741 reflec-

tions were measured. The data collection using the computer controlled single crystal diffractometer was done by T. Mizota.

The observed intensities were corrected for Lorentz polarization and monochromator polarization factors. The linear absorption coefficients μ was 32.2 cm⁻¹. Absorption corrections were made. The least squares refinement was based on 678 F_o values above $2\sigma(F_o)$, where $\sigma(F_o)$ was the standard deviation. The structure refinement was made on a HITAC 8800/8700 computer, employing the MINIPAC system (Miyamoto, Takeda and Takano, 1974). Initial positional parameters, with isotropic temperature factors, were taken from those of CaScAlSiO_6 (Ohashi and Ii, 1978). The atomic scattering factors were those given by Cromer and Mann (1968) for ionized cations and O⁻¹. Anomalous dispersion corrections were made by using the coefficients of Cromer and Liberman (1970). The chemical composition has been constrained to $\text{Ca}_{1.00}\text{Sc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$.

At the earlier stage of the refinement, isotropic temperature factors were used, while the site occupancies of Ti and Al were varied. After convergence was reached in the refinement with isotropic temperature factors, refinements using anisotropic temperature factors were employed, where the site occupancies of Ti and Al were varied. At the last of this stage, reflections with $F_o < 25.0$ and $\frac{\Delta F}{\sigma F} > 5.0$ were rejected from the refinement. Furthermore, at the last stage of the refinement, the site occupancies of Ti and Al were checked without any chemical constraint, where the occupancies of Ca, Sc and Si, the positional parameters and the thermal parameters were fixed simultaneously. The unweighted R-factor is 0.028 and the weighted R-factor is 0.050

Table 1. Atomic Parameters of $\text{Ca}_{1.00}\text{Sc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$

	x	y	z	B eq	B ₁₁
M1(Sc _{0.84} Ti _{0.16})	0	.90426(4)	.25	.458(11)	.00122(5)
M2(Ca)	0	.31386(5)	.25	.698(11)	.00245(5)
T(Ti _{0.11} Al _{1.16} Si _{0.73})	.29032(4)	.09244(4)	.22933(9)	.423(12)	.00101(5)
O1	.11100(12)	.08993(11)	.13522(23)	.678(19)	.00185(11)
O2	.36604(12)	.25816(12)	.33001(23)	.824(19)	.00249(11)
O3	.35394(11)	.02182(13)	.99056(21)	.753(20)	.00164(11)

Table 2. Bond Lengths and Bond Angles of $\text{CaSc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$

Bond Length(Å)				Bond Angle(°)			
Octahedron(M1)		Polyhedron(M2)		Tetrahedron(T)			
M1-O1A1, B1	2.178(1)	M2-O1A1, O1B1	2.449(1)	T-O1	1.713(2)	T-O3-T	135.82(7)
-O1A2, B2	2.093(2)	-O2C2, O2D2	2.405(2)	-O2	1.686(1)	O3A2-O3A1-O3A2	163.72(10)
-O2C1, D1	1.996(1)	-O3C1, O3D1	2.541(1)	-O3A1	1.716(1)		
		-O3C2, O3D2	2.650(1)	-O3A2	1.729(1)		
mean of 6	2.089	mean of 6	2.465	mean of 4	1.711		
M1-M1	3.223(1)	mean of 8	2.511				

Atom	Axis	rms amplitude, Å	Angle(°) with a	Angle(°) with b	Angle(°) with c
M1	1	0.070	60(6)	90	45(6)
	2	0.078	90	180	90
	3	0.080	150(6)	90	45(6)
M2	1	0.078	74(1)	90	32(1)
	2	0.083	90	180	90
	3	0.116	164(1)	90	58(1)
T	1	0.067	40(9)	75(5)	69(9)
	2	0.074	50(9)	107(12)	150(10)
	3	0.078	89(8)	158(10)	69(12)
O1	1	0.090	58(36)	33(35)	92(27)
	2	0.093	33(38)	121(39)	113(73)
	3	0.095	84(59)	101(39)	24(67)
O2	1	0.094	88(8)	158(13)	70(11)
	2	0.103	109(15)	111(13)	139(19)
	3	0.110	160(15)	84(9)	56(14)
O3	1	0.086	31(18)	83(16)	76(14)
	2	0.092	66(20)	140(17)	126(9)
	3	0.113	108(5)	129(6)	40(6)

Table 3. Thermal Ellipsoids of $\text{CaSc}_{0.84}\text{Ti}_{0.27}\text{Al}_{1.16}\text{Si}_{0.73}\text{O}_6$

for 678 reflections and 0.027 (weighted R=0.035) for 670 unrejected reflections. The final parameters with standard deviations are listed in Table 1. Bond lengths and angles as well as ellipsoids of thermal vibra-

tion with standard deviations are listed in Table 2 and 3, respectively.

DESCRIPTION AND DISCUSSION

As shown by the results of the refinement, the tetrahedral sites are occupied by Si (36.5at.%), Al (58at.%) and Ti (5.5 at.%). This fact means that Al-O-Al bonds exist in this pyroxene chains and the aluminum avoidance rule has been violated in this structure.

As expected, the presence of Al (58 at.%) and Ti (5.5 at.%) in the tetrahedral sites causes an expansion of the T-O tetrahedron. There are two kinds of bonds in the clinopyroxene tetrahedron; one is a bridging (brg) bond connecting the tetrahedra into the chain and the other is a non-bridging (nbrg) bond. Each tetrahedron has two brg (T-O3Al and T-O3A2) and two nbrg (T-O1 and T-O2) bonds.

The variation of the T-O (brg) and T-O

Table 1 .Continued

β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
.00150(5)	.00376(17)	0	.00030(6)	0
.00172(6)	.00481(16)	0	-.00003(7)	0
.00147(6)	.00374(18)	-.00007(3)	.00038(7)	-.00016(6)
.00204(12)	.00643(41)	-.00007(8)	.00096(18)	-.00005(16)
.00223(12)	.00747(37)	.00002(9)	.00094(16)	.00027(18)
.00250(14)	.00738(42)	.00004(8)	.00059(17)	-.00082(16)

Fig. 1 T-O distances plotted against the averaged ionic radii of cations occupying T-sites in several C2/c pyroxenes. Open circles represent the mean T-O (brg) and the mean T-O (nbrg) distances, and the associated vertical line connects the individual values. Solid circles represent the mean T-O distances.

(nbrg) bond distances with the averaged ionic radii of ions occupying the T-sites in Ca-Al-bearing clinopyroxenes is shown in Fig. 1. The each bond distance is listed in table 4. As indicated by Takeda (1972b), the mean nbrg bond distance is a good

indicator of the averaged ionic radii of ions occupying the T-sites. On the other hand, the T-O (brg) distances are scattered, affected by other factors.

The variation of the T-O bond distances with the radii of ions occupying the M1-sites in Na-pyroxenes is shown in Fig. 2. The each bond distance is listed in table 5. With enlarging the sizes of ions occupying the M1-sites, the T-O(brg) bond distances increase the lengths. Furthermore, there is an unique relationship between the mean T-O bond distances and the radii of ions occupying the M1-sites in Na-pyroxenes. The mean T-O bond distances of $\text{NaCrSi}_2\text{O}_6$ and NaVSi_2O_6 having characteristic M^{+3} ions in the M1-sites (Fujita and Ohashi, unpublished data) are shorter than the expected value respectively. However, as shown in Fig. 2, the anomalous shortness of the mean T-O bond distance of $\text{NaCrSi}_2\text{O}_6$ disappears at 600°C. That is, at high temperature, the correlation of the mean T-O distance with the radius of ion occupying the M1-site in $\text{NaCrSi}_2\text{O}_6$ is same with the trend among Na-pyroxenes. This phenomenon is also expected in NaVSi_2O_6 .

From the trend observed in the T-O bond distances in Na-pyroxenes, it is concluded that the size of M^{+3} ion occupying the M1-site varies the length of the T-O (brg) bond distance. So, from this fact, it

Table 4. The T-O distances (Å) in Ca-Al-bearing clinopyroxenes

Crystal	ionic radius of T site ion	T-O1	T-O2	mean, non-brg.	T-O3A1	T-O3A2	mean, mean of brg.	mean of 4	Source
CaMgSi ₂ O ₆	0.26	1.602(2)	1.585(1)	1.594	1.664(2)	1.687(2)	1.676	1.634	1
KaKaniui	0.272	1.621(2)	1.604(3)	1.612	1.662(2)	1.674(2)	1.668	1.640	1
12052	0.274	1.616(2)	1.596(3)	1.606	1.660(3)	1.670(3)	1.665	1.636	2
Takashima	0.277	1.624(1)	1.605(2)	1.6145	1.666(2)	1.680(2)	1.673	1.644	3
Oka	0.292	1.640(5)	1.629(4)	1.6345	1.697(5)	1.685(5)	1.691	1.663	4
Allende ^a	0.308	1.666	1.642	1.654	1.690	1.709	1.700	1.677	5
CaAl ₂ SiO ₆	0.325	1.693(1)	1.665(1)	1.679	1.683(1)	1.701(1)	1.692	1.686	6
CaScAlSiO ₆	0.325	1.690(1)	1.663(1)	1.677	1.707(1)	1.721(1)	1.714	1.695	7
CaFeAlSiO ₆	0.334	1.695(1)	1.671(1)	1.683	1.703(1)	1.722(1)	1.713	1.698	8
CaSc _{0.84} Ti _{0.27} Al _{1.16} Si _{1.73} O ₆	0.344	1.713(2)	1.686(1)	1.700	1.716(1)	1.729(1)	1.723	1.711	9

^aOne standard deviation, ± 0.002 Å. 1)Clark, Appleman and Papike(1969) 2) Takeda(1972a)
3)Takeda(1972b) 4)Peacor(1967) 5)Dowty and Clark(1973) 6)Okamura, Ghose and Ohashi(1974)
7)Ohashi and Ii(1978) 8)Okamura, Ghose and Ohashi, unpublished data. 9)Present study

Table 5. The Si-O distances (Å) in Na-pyroxenes

Crystal	Temperature (°C)	Si-O1	Si-O2	mean, non-brg.	Si-O3A1	Si-O3A2	mean, mean of brg.	mean of 4	Source
NaAlSi ₂ O ₆	R.T.	1.637(2)	1.590(2)	1.613	1.628(2)	1.636(2)	1.632	1.623	1
	600	1.637(2)	1.594(2)	1.616	1.629(2)	1.643(2)	1.636	1.626	2
NaCrSi ₂ O ₆	R.T.	1.626(4)	1.586(3)	1.606	1.640(4)	1.645(4)	1.642	1.624	3
	600	1.638(4)	1.598(4)	1.618	1.631(5)	1.650(5)	1.641	1.629	2
NaVSi ₂ O ₆	R.T.	1.624(2)	1.593(2)	1.609	1.630(2)	1.648(2)	1.639	1.624	4
NaFeSi ₂ O ₆	R.T.	1.629(2)	1.598(2)	1.614	1.637(2)	1.646(2)	1.642	1.628	3
	600	1.633(2)	1.598(2)	1.616	1.641(2)	1.647(2)	1.644	1.630	2
NaScSi ₂ O ₆	R.T.	1.630(3)	1.592(2)	1.611	1.653(2)	1.653(3)	1.653	1.632	5
NaInSi ₂ O ₆	R.T.	1.641(7)	1.595(8)	1.618	1.633(8)	1.664(7)	1.648	1.633	6

1) Prewitt and Burnham(1966) 2) Cameron, Sueno, Prewitt and Papike(1973) 3) Clark,
Appleman and Papike(1969) 4) Fujita and Ohashi, unpublished data. 5) Hawthorne and
Grundy(1973) 6) Christensen and Hazell(1967)

Fig. 2. T-O distances at room temperature and 600°C plotted against the ionic radius of the cation occupying the M1-site for the NaM³Si₂O₆ pyroxenes. Solid circles represent the mean T-O distances at room temperature, and the associated vertical line connects the mean T-O (brg) and the mean T-O (nbrg) distances. Open circles represent the mean T-O distances at 600°C.

is possible to consider that the anomalous shortness of the T-O (brg) bond distances of CaAl₂SiO₆ can be caused by the smallness of Al³⁺ ion in the M1-site. The difference between the mean T-O (brg) distances of NaAlSi₂O₆ and NaScSi₂O₆ is 0.021 Å. While, the difference between CaAl₂SiO₆ and CaScAlSiO₆ is 0.022 Å. Therefore, the variation of the mean T-O (brg) distance caused by the Al-Sc substitution in the M1-site was found to be exactly same in the two groups.

The T-O (brg) distances of Kakanui, 12052 and Takashima are anomalously short as well as CaAl₂SiO₆. The M2-sites of

these pyroxenes are occupied by Ca(+Na) and Mg ions. The Ca(+Na) content (in at.%) in the M2-sites are 71, 61 and 80, respectively (Takeda, 1972b). It is possible to consider that the shortness of the T-O (brg) distances of these pyroxenes is caused by the substitution of the small (Mg^{+2} and Fe^{+2}) ions in the M2-sites.

$\text{CaAl}_2\text{SiO}_6$ including Al^{+3} ions in the M1-sites is not stable at 1 atm and changes to anorthite+gehlenite+corundum at high temperature (Hays, 1966). On the other hand, Ca-Al-poor pyroxene including Mg^{+2} and Fe^{+2} ions in the M2-sites is stable at 1 atm. Although the smallness of each ion occupying M-site causes the shortness of the T-O (brg) distances at room temperature, there must be some differences between them. If Mg^{+2} and Fe^{+2} ions can behave as larger ions, affected by thermal vibration at high temperature, the T-O (brg) bonds can elongate the distances. Although details can not be discussed until a series of experimental studies on Ca-Al bearing pyroxenes using high temperature X-ray single crystal diffractometer, it is expected that there are more simple relationships between the T-O bond distances and the averaged ionic radii occupying the T-sites at high temperature.

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$Ca_{1.00}Sc_{0.84}Ti_{0.27}Al_{1.16}Si_{0.73}O_6$ 輝石の構造

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帯域熔融法によってつくった $Ca_{1.00}Sc_{0.84}Ti_{0.27}Al_{1.16}Si_{0.73}O_6$ 輝石の結晶構造をリファインした。格子常数は $a_0=9.925\text{\AA}$, $b_0=8.949\text{\AA}$, $c_0=5.460\text{\AA}$, $\beta=105.77^\circ$, $V=466.75\text{\AA}^3$ で、空間群は $C2/c$ である。M1 サイトは Sc (84at. %) と Ti (16at. %) で占められている。T サイトには Si (36.5at. %), Al (58at. %) 及び Ti (5.5at. %) が完全に無秩序に分布している。これらの事実、この輝石中の鎖内に Al-O-Al 結合が存在し、アルミニウム・アボイダンス・ルールがこの構造中ではやぶれていることを意味している。