CRYSTAL CHEMISTRY OF KOSMOCHLOR- DIOPSIDE SOLID SOLUTIONS

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Crystal structure parameters have been determined for $\text{Ko}_{75}(\text{NaCrSi}_2\text{O}_6; 75 \text{ mol}\%)$ Di_{25} ($\text{CaMgSi}_2\text{O}_6; 25 \text{ mol}\%$), $\text{Ko}_{50}\text{Di}_{50}$ and $\text{Ko}_{25}\text{Di}_{75}$ synthesized at 1200°C and 20 kb. Refinements in space group C2/c using anisotropic temperature factors and over 600 unrejected reflections for each set of data resulted in weighted R-factors ranging from 0.020 to 0.025. The nearest M1-M1 distances of Ko-Di solid solutions are significantly shorter than those expected from the averaged ionic radii of cations occupying the M1 sites. The longest M1-M1 distances were found for the crystals having the compositions corresponded to the both sides of the miscibility gap at high pressure. It is expected that Cr^{+3} within Ko solid solutions form Cr-O-Cr coupling and Cr^{+3} within Di solid solutions are completely disordered. $\text{Ko}_{75}\text{Di}_{25}$ and $\text{Ko}_{50}\text{Di}_{50}$ being stable only at high pressure have smaller cell volumes than those expected from the values of Ko, $\text{Ko}_{25}\text{Di}_{75}$ and Di. They have shorter M1-O distances than those expected from the averaged ionic radii of cations occupying the M1 sites. Their mean 8 (M2-O) and 6(M2-O) distances are longer than those expected from the values of Ko, $\text{Ko}_{25}\text{Di}_{75}$ and Di. The characteristic structures of $\text{Ko}_{75}\text{Di}_{25}$ and $\text{Ko}_{50}\text{Di}_{50}$ may suggest at least partly those at high pressure.

INTRODUCTION

Phase equilibrium study on the join $\text{CaMgSi}_2\text{O}_6$ (diopside; hereafter called Di)- $\text{NaCrSi}_2\text{O}_6$ (kosmochlor; hereafter called Ko) was investigated by Ikeda and Yagi (1972) at 1 atm. Their result shows that the maximum solubility of Ko molecule in Di is 24 wt% at 1140°C , while Di molecule is not soluble at all in Ko. The solubility of Di molecule in Ko is very much increased with pressure and there is only a narrow immiscibility field. The limits of solubility at 1300°C and 15 kb were found to be 24 mol% of Ko molecule in Di and about 55 mol% of Di molecule in Ko, respectively (Ikeda and Ohashi, 1974). Other Na-Ca pyroxene systems ($\text{NaFeSi}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ and $\text{NaAlSi}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$) can form a complete series of

solid solutions at 1 atm and/or high pressure (Yagi, 1966; Cassie, 1971; Bell and Davis, 1969). Compared to them, the behavior of Ko-Di system is very curious phenomena.

Sodic pyroxenes have some unique relationships in the variations of the nearest M1-M1 distances with the ionic radii of ions occupying M1 sites, the mean Si-O distances with the radii of ions occupying M1 sites and the mean 8 (M2-O) and 6(M2-O) distances with 6(M1-O) distances (Fujita and Ohashi, unpublished data). The crystal structure of Ko is isomorphous with other sodic pyroxenes. However, Ko has a characteristic structure. That is, Ko deviates significantly from these trends. For examples, the nearest M1-M1 distance and the mean Si-O distance in Ko are shorter than the values expected from the ionic radius of Cr^{+3}

occupying the M1 site at room temperature (Clark, Appleman and Papike, 1969).

The characteristic nature recognized in the M1-M1 distance becomes more clearer at high temperature. That is, the increase in the M1-M1 distance with increasing temperature is smallest in Ko. On the other hand, at high temperature (600°C), the correlation of the mean Si-O distance with the radius of ion occupying M1 site and the correlation of the mean 6 (M2-O) distance with 6(M1-O) distance in Ko are same with the trends among sodic pyroxenes (Cameron, Sueno, Prewitt and Papike, 1973).

To study the correlations between the curious behavior in phase diagram and the characteristic structure, crystal structure parameters have been determined at room temperature for three synthesized Ko-Di solid solutions (Ko₇₅Di₂₅, Ko₅₀Di₅₀ and Ko₂₅Di₇₅).

SYNTHETIC AND CHEMICAL DATA

All of the crystals used in the structural studies presented herein were synthesized by Ohashi (1977) at about 1200°C and 20 kb for 40–48 hours. Electron microprobe analysis of the crystals by A. Ono using CaSiO₃, SiO₂, Cr₂O₃, MgO and NaAlSi₃O₈ as standards indicates chemical compositions,

(assuming six oxygen atoms).

For the purposes of structure determination, we have assumed the ideal compositions,

This assumption does not result in any significant errors in the structure determination.

MEASUREMENT OF INTENSITY DATA AND REFINEMENT OF THE STRUCTURE

From the X-ray weissenberg photographs the space groups were determined to be C2/c for the three specimens. For the intensity measurements, which were carried out at room temperature, 'as grown single crystals' with the best crystallinity as judged by oscillation and weissenberg photographs were used. The unit cell dimensions were determined by the least squares method based on $\sin \theta$ measured on a computer controlled single-crystal diffractometer (Rigaku-AFC-III). The cell dimensions, the

Table 1. Unit cell parameters and data reduction information for Ko-Di solid solutions.

	Di*	Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅	Ko*
a(Å)	9.746(4)	9.691(3)	9.633(4)	9.594(3)	9.550(16)
b(Å)	8.899(5)	8.868(2)	8.808(2)	8.748(3)	8.712(7)
c(Å)	5.251(6)	5.249(1)	5.254(2)	5.256(2)	5.273(8)
β(°)	105.63(6)	106.13(2)	106.45(4)	106.94(2)	107.44(16)
V(Å ³)	438.6(3)	433.37(21)	427.54(25)	422.00(25)	418.6(1.4)
Calc. density, g/cm ⁻³	3.278	3.361	3.448	3.535	3.603
Size of crystal(μm)		35×80×80	35×60×80	30×30×80	
linear absorption coefficient (cm ⁻¹)		20.3	27.2	34.2	

Table 2. Data collection information for three pyroxenes

Crystal	Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
Number of reflections			
measured	762	750	742
observed	659	626	614
used in refinement	655	618	608
Conditions of rejections	X:ΔF	20.0	20.0
ΔF>X	Y:ΔF/σF	5.0	7.0
or	Z:Fo	30.0	30.0
ΔF/σF>Y and Fo<Z			
Anisotropic	R	0.026	0.024
wt'd. R		0.025	0.020

calculated densities, the sizes of crystals and the linear absorption coefficients are given in Table 1. Intensity measurements were made with the same diffractometer using monochromatic MoK_{α1} radiations, scan rate being 2°/min. In the range of $2\theta \leq 63^\circ$, 742–762 independent reflections were measured. The unobserved limits were set at 2σ with σ determined by counting statistics and 128–103 reflections were considered unobserved. Since the sizes of the crystals and the linear absorption coefficients μ (34.2–20.3 cm⁻¹) were both small, no absorption corrections were made. The structure refinements were made on a HITAC 8800/8700 computer, employing the MINEPAC system (Miyamoto, Takeda and Takano, 1974). Initial positional parameters with isotropic temperature factors, were calculated from those of NaCrSi₂O₆ and CaMgSi₂O₆ (Clark, Appleman and Papike, 1969). The atomic scattering factors were those given by Cromer and Mann (1968) for ionized cations and O⁻. Anomalous dispersion corrections were made by using the coefficients of Cromer and Liberman (1970). The chemical compositions have been constrained to Ko₇₅Di₂₅, Ko₅₀Di₅₀, and Ko₂₅Di₇₅. At the earlier stage of the refinement, isotropic temperature factors were used. After convergences were reached in the refinement with isotropic temperature factors, refine-

Table 3. Atomic parameters of three pyroxenes

		Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
M1	X	0.	0.	0.
	Y	0.90693 (11)	0.90664 (9)	0.90704 (7)
	Z	0.25	0.25	0.25
	B	0.452 (15)	0.402 (11)	0.328 (9)
	B ₁₁	0.00122 (9)	0.00090 (7)	0.00077 (6)
	B ₁₂	0.00151 (11)	0.00173 (8)	0.00123 (6)
	B ₁₃	0.00413 (31)	0.00354 (24)	0.00311 (19)
	B ₂₂	0.	0.	0.
	B ₂₃	0.00026 (14)	0.00044 (11)	0.00017 (8)
	B ₃₃	0.	0.	0.
M2	X	0.	0.	0.
	Y	0.30159 (10)	0.30189 (11)	0.30164 (13)
	Z	0.25	0.25	0.25
	B	0.744 (14)	0.920 (16)	0.949 (18)
	B ₁₁	0.00261 (9)	0.00308 (11)	0.00335 (13)
	B ₁₂	0.00174 (9)	0.00254 (11)	0.00232 (13)
	B ₁₃	0.00595 (29)	0.00698 (34)	0.00742 (37)
	B ₂₂	0.	0.	0.
	B ₂₃	-0.00051 (13)	-0.00052 (15)	-0.00070 (18)
	B ₃₃	0.	0.	0.
T	X	0.28745 (7)	0.28894 (7)	0.29069 (7)
	Y	0.09274 (8)	0.09221 (8)	0.09182 (7)
	Z	0.22989 (13)	0.23032 (12)	0.23192 (12)
	B	0.352 (11)	0.435 (10)	0.360 (9)
	B ₁₁	0.00094 (6)	0.00092 (6)	0.00083 (6)
	B ₁₂	0.00128 (7)	0.00194 (7)	0.00144 (6)
	B ₁₃	0.00317 (22)	0.00391 (21)	0.00358 (19)
	B ₂₂	-0.00008 (6)	-0.00002 (6)	-0.00013 (6)
	B ₂₃	0.00041 (9)	0.00061 (8)	0.00052 (9)
	B ₃₃	-0.00005 (11)	-0.00015 (11)	0.00001 (9)

Table 3. Continued

		Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
O1	X	0.11508 (19)	0.11421 (17)	0.11362 (16)
	Y	0.08460 (21)	0.08192 (21)	0.07986 (19)
	Z	0.14047 (31)	0.13879 (29)	0.13684 (28)
	B	0.539 (27)	0.589 (26)	0.493 (24)
	B ₁₁	0.00114 (17)	0.00096 (17)	0.00090 (16)
	B ₁₂	0.00223 (21)	0.00291 (21)	0.00212 (19)
	B ₁₃	0.00468 (58)	0.00459 (55)	0.00472 (54)
	B ₂₂	0.00014 (16)	0.00007 (16)	0.00015 (14)
	B ₂₃	0.00022 (26)	-0.00000 (26)	0.00020 (25)
	B ₃₃	0.00008 (29)	-0.00044 (29)	0.00039 (25)
O2	X	0.36057 (20)	0.35967 (18)	0.35987 (18)
	Y	0.25109 (20)	0.25409 (19)	0.25677 (19)
	Z	0.31450 (34)	0.30991 (31)	0.30614 (30)
	B	0.662 (29)	0.742 (28)	0.653 (26)
	B ₁₁	0.00244 (20)	0.00216 (19)	0.00210 (18)
	B ₁₂	0.00180 (21)	0.00270 (21)	0.00206 (19)
	B ₁₃	0.00595 (65)	0.00605 (63)	0.00612 (60)
	B ₂₂	-0.00054 (17)	-0.00087 (17)	-0.00066 (15)
	B ₂₃	0.00132 (31)	0.00073 (28)	0.00100 (28)
	B ₃₃	-0.00015 (29)	-0.00047 (28)	-0.00026 (26)
O3	X	0.35083 (19)	0.35103 (18)	0.35195 (17)
	Y	0.01558 (20)	0.01370 (19)	0.01205 (19)
	Z	-0.00287 (35)	-0.00010 (33)	0.00383 (32)
	B	0.545 (26)	0.550 (24)	0.506 (23)
	B ₁₁	0.00122 (18)	0.00107 (16)	0.00117 (16)
	B ₁₂	0.00228 (21)	0.00272 (20)	0.00258 (19)
	B ₁₃	0.00467 (55)	0.00422 (52)	0.00306 (49)
	B ₂₂	0.00013 (16)	-0.00002 (16)	0.00012 (15)
	B ₂₃	0.00048 (27)	0.00052 (24)	0.00038 (25)
	B ₃₃	-0.00057 (29)	-0.00055 (28)	-0.00095 (24)

ment using anisotropic temperature factors were employed. At this stage some reflections were rejected from the refinements. The conditions of the rejections, the number of reflections used in refinements and the unweighted and weighted R-factors for the anisotropic refinements are listed in Table 2. The final atomic parameters with standard deviations are listed in Table 3. Bond lengths and angles as well as ellipsoids of thermal vibration with standard deviations are listed in Tables 4 and 5, respectively.

DESCRIPTION OF THE STRUCTURE

O3-O3'-O3'' angle: The variation of the O3-O3'-O3'' angle with the composition for the refined Ko-Di solid solutions (Ko and Di, Clark, Appleman and Papike, 1969) is shown in Fig. 1. A smooth curve can be drawn

Fig. 1. O3A2-O3A1-O3A2 bond angle (°) plotted against the compositions in Ko-Di solid solutions.

Fig. 2. Si-O3-Si bond angle (°) plotted against the compositions in Ko-Di solid solutions.

through those points representing the composition and angle.

Si-O3-Si angle: The variation of the Si-O3-Si angle with the composition for the refined Ko-Di solid solutions is shown in Fig. 2. Si-O3-Si angles of $Ko_{75}Di_{25}$ and $Ko_{50}Di_{50}$ being stable only at high pressure are larger than those expected from the values of Ko, $Ko_{25}Di_{75}$ and Di (hereafter called KD-group).

T-O₄ tetrahedron: The variation of the Si-O distances with the compositions in Ko-Di solid solutions are shown in Fig. 3. Solid circles represent the mean distances, and the associated vertical line connects the diindividual values. Open circles are the mean of the four Si-O distances. There is a discontinuity in the variation of the mean of the four Si-O distances with the compositions. The region of the discontinuity corresponds to the region of the immiscibility. However, this discontinuity may disappear at high temperature as recognized in Ko end member.

It seems that Si-O bond has some flexibility in sodic pyroxene and changes slightly the bond distance under the influence of non-tetrahedral cation. There is an unique relationship in the variation of the mean Si-O distances with the radii of ions occupying M1 sites in sodic pyroxenes (Fujita and Ohashi, unpublished data). The mean Si-O distance of Ko at room temperature is shorter than the one expected from the ionic radius of Cr^{+3} (Clark, Appleman and Papike, 1969). However, the distance at high temperature (600°C) is same with the one expected by the unique relationship among sodic pyroxenes at 600°C (Cameron, Sueno, Prewitt and Papike, 1973).

M1-O₆ octahedron: There is a linear relationship between the M1-O distances and

Table 4-A. Bond lengths (Å) and angles (Å) for the M1 octahedra in three pyroxenes

	Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
M1-O1A1, B1	2.101 (2)	2.073 (2)	2.051 (2)
-O1A2, B2	2.045 (2)	2.030 (2)	2.011 (2)
-O2C1, D1	2.026 (2)	1.993 (2)	1.963 (2)
mean of 6	2.057	2.032	2.008
O1A1-O1B1	2.779 (4)	2.768 (3)	2.771 (3)
O2C1-O2D1	2.963 (4)	2.944 (4)	2.916 (3)
(2)O1A1-O2C1	2.971 (3)	2.904 (2)	2.846 (2)
(2)O1A1-O1A2	3.023 (2)	2.997 (2)	2.976 (2)
(2)O1A2-O2C1	2.863 (3)	2.836 (3)	2.806 (2)
(2)O1A2-O2D1	2.965 (3)	2.947 (3)	2.920 (2)
(2)O1A2-O1B2	2.752 (4)	2.689 (3)	2.636 (3)
mean of 12	2.908	2.872	2.838
M1-M1	3.101 (1)	3.099 (1)	3.091 (1)
M1-TA1	3.263 (1)	3.254 (1)	3.249 (1)
M1-TA2	3.195 (1)	3.184 (2)	3.174 (1)
O-M1-O angles (°)			
O1A2, O1B2	175.79 (12)	174.31 (11)	173.45 (10)
(2)O1A1, O2D1	170.68 (7)	169.78 (7)	169.25 (6)
O1A1, O1B1	82.82 (10)	83.76 (10)	85.01 (9)
O2C1, O2D1	93.98 (11)	95.23 (11)	95.92 (10)
(2)O1A1, O2C1	92.09 (7)	91.13 (7)	90.28 (7)
(2)O1A1, O1A2	93.65 (7)	93.85 (7)	94.24 (6)
(2)O1A1, O1B2	83.18 (8)	81.90 (7)	80.91 (7)
(2)O1A2, O2C1	89.38 (7)	89.65 (7)	89.83 (7)
(2)O1A2, O2D1	93.49 (8)	94.19 (7)	94.55 (7)
T-O1A1-M1	122.80 (10)	123.27 (10)	123.61 (9)
T-O1A2-M1	121.64 (10)	121.23 (9)	121.09 (9)
T-O2C1-M1	145.80 (11)	145.60 (11)	145.76 (10)

Table 4-B. Bond lengths (Å) and angles (Å) for silicate tetrahedra in three pyroxenes

	Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
T-O1	1.606 (2)	1.617 (2)	1.628 (2)
T-O2	1.580 (2)	1.585 (2)	1.589 (2)
mean, non-brg.	1.593	1.601	1.609
T-O3A1	1.660 (2)	1.647 (2)	1.637 (2)
T-O3A2	1.670 (2)	1.660 (2)	1.651 (2)
mean, brg.	1.665	1.654	1.644
mean of 4	1.629	1.627	1.626
O1-O2	2.733 (3)	2.738 (2)	2.747 (2)
O1-O3A1	2.667 (3)	2.653 (3)	2.646 (2)
O1-O3A2	2.672 (3)	2.657 (3)	2.650 (2)
O2-O3A1	2.657 (2)	2.658 (2)	2.654 (2)
O2-O3A2	2.563 (3)	2.572 (2)	2.581 (2)
O3A1-O3A2	2.639 (1)	2.638 (1)	2.636 (1)
mean of 6	2.655	2.653	2.652
T-TA2	3.627 (1)	3.622 (2)	3.620 (2)
O1-T-O2	118.09 (10)	117.55 (10)	117.23 (9)
O1-T-O3A1	109.50 (10)	108.78 (9)	108.23 (9)
O1-T-O3A2	109.24 (10)	108.40 (9)	107.87 (9)
O2-T-O3A1	110.15 (10)	110.69 (10)	110.70 (9)
O2-T-O3A2	104.09 (10)	104.86 (9)	105.64 (9)
O3A1-T-O3A2	104.65 (7)	105.06 (7)	106.63 (7)
mean of 6	109.32	109.36	109.38
T-O3-TA2	136.92 (12)	138.19 (11)	139.07 (11)
O3A2-O3A1-O3A2	167.98 (16)	169.51 (14)	170.83 (14)

Table 4-C. M(2)-O Interatomic Distances (Å) in Three Pyroxenes

	Ko ₂₅ Di ₇₅	Ko ₅₀ Di ₅₀	Ko ₇₅ Di ₂₅
M(2)-O1A1, O1B1	2.374 (2)	2.381 (2)	2.384 (2)
-O2C2, O2D2	2.357 (2)	2.376 (2)	2.384 (2)
-O3C1, O3D1	2.527 (2)	2.490 (2)	2.451 (2)
-O3C2, O3D2	2.729 (2)	2.737 (2)	2.749 (2)
mean of 6	2.419	2.416	2.406
mean of 8	2.497	2.496	2.492

the ionic radii of cations occupying M1 sites in Si-saturated type pyroxenes including high pressure phase, NaAlSi₂O₆-jadeite (Ohashi, 1978). The variation of the mean M1-O distances with the averaged ionic radii of cations occupying M1 sites in Ko-Di solid solutions is shown in Fig. 4. The mean M1-O distances of Ko₇₅Di₂₅ and Ko₅₀Di₅₀ being stable only at high pressure are shorter than the mean M1-O distances expected from the averaged ionic radii of cations occupying the M1 sites. The variation of the each M1-O distance with the composition in Ko-Di solid solutions is shown in Fig. 5.

M1-M1 distance: Sodic pyroxenes have an unique relationship in the variation of the nearest M1-M1 distances with the ionic radii of ions occupying M1 sites (Howthorne and Grundy, 1973). However, Ko deviates significantly from the trend. If the crystal chemical character of Cr³⁺ is same as those of Al and Fe, the M1-M1 distance in Ko is expected to about 3.16 Å from the ionic radius of Cr³⁺. NaCrSi₂O₆ having such imaginary Cr³⁺ is hereafter called hypo-Ko. The M1-M1 distance of the hypo-Ko-Di solid solution can be plotted on a line (Fig. 6.). The variation of the M1-M1 distances with the compositions for the refined Ko-Di solid solutions is also shown. The M1-M1 distances of the Ko-Di solid solutions are always shorter than those of the hypo-Ko-Di

solid solutions and longest in the crystals with the compositions which correspond to the both sides of the miscibility gap at high pressure.

M2-O₈ polyhedron: The M2 sites are coordinated by 8 oxygen atoms. Four are shared with the M1 octahedra and four with the silicate tetrahedral chains. The each M2-O distance is listed in Table 4-C. The M2-O1 distances and the M2-O2 distances of Ko₇₅Di₂₅ and Ko₅₀Di₅₀ are longer than those expected from the values of Ko, Ko₃₅Di₇₅ and Di(KD-group). On the other hand, the M2-O3 distances of Ko₇₅Di₂₅ and Ko₅₀Di₅₀ are shorter than those expected from the values of KD-group. The variation of the mean 6(M2-O) and 8(M2-O) distances with 6(M1-O) distances is shown in Fig. 7. It is recognized that there are two groups in the variation. One of them is KD-group and the other Ko₇₅Di₂₅ and Ko₅₀Di₅₀-group. Ko₇₅Di₂₅ and Ko₅₀Di₅₀ have M2 sites coordinated by 8 oxygen atoms more evenly bonded to Na⁺ and Ca²⁺ than those expected from the values of KD-group.

Table 5-A. Thermal ellipsoids of Ko₂₅Di₇₅

Atom	Axis	rms ampli- tude, Å	Angle (°) with a	Angle (°) with b	Angle (°) with c
M1	1	0.068	53 (10)	90	53 (10)
	2	0.077	90	180	90
	3	0.081	143 (10)	90	37 (10)
M2	1	0.077	66 (2)	90	40 (2)
	2	0.083	90	180	90
	3	0.124	156 (2)	90	50 (2)
T	1	0.063	51 (31)	76 (13)	58 (33)
	2	0.065	45 (31)	79 (17)	148 (33)
	3	0.072	73 (13)	162 (13)	92 (15)
O1	1	0.067	40 (13)	97 (8)	67 (14)
	2	0.084	52 (14)	96 (20)	157 (14)
	3	0.095	80 (14)	10 (14)	93 (18)
O2	1	0.077	118 (8)	150 (14)	75 (26)
	2	0.086	80 (15)	103 (24)	146 (26)
	3	0.109	30 (7)	116 (7)	90 (9)
O3	1	0.072	33 (67)	92 (33)	73 (69)
	2	0.075	61 (72)	113 (9)	151 (45)
	3	0.099	104 (8)	155 (9)	67 (9)

Table 5-B. Thermal ellipsoids of Ko₅₀Di₅₀

Atom	Axis	rms ampli- tude, Å	Angle (°) with a	Angle (°) with b	Angle (°) with c
M1	1	0.062	20 (17)	90	86 (17)
	2	0.068	70 (17)	90	176 (17)
	3	0.082	90	0	90
M2	1	0.095	66 (2)	90	41 (2)
	2	0.100	90	180	90
	3	0.133	156 (2)	90	49 (2)
T	1	0.062	1 (10)	90 (4)	107 (11)
	2	0.071	91 (11)	97 (5)	162 (10)
	3	0.088	90 (4)	173 (5)	83 (5)
O1	1	0.061	38 (10)	89 (5)	68 (9)
	2	0.084	53 (10)	104 (8)	134 (9)
	3	0.108	98 (6)	166 (8)	76 (7)
O2	1	0.078	52 (10)	54 (7)	70 (16)
	2	0.092	63 (12)	73 (11)	159 (15)
	3	0.117	49 (6)	139 (5)	96 (7)
O3	1	0.068	27 (48)	87 (13)	80 (47)
	2	0.073	64 (48)	103 (7)	163 (30)
	3	0.105	93 (6)	167 (6)	77 (6)

Table 5-C. Thermal ellipsoids of Ko₇₅Di₂₅

Atom	Axis	rms ampli- tude, Å	Angle (°) with a	Angle (°) with b	Angle (°) with c
M1	1	0.055	40 (6)	90	66 (6)
	2	0.068	50 (6)	90	156 (6)
	3	0.069	90	0	90
M2	1	0.086	66 (2)	90	41 (2)
	2	0.095	90	180	90
	3	0.140	156 (2)	90	49 (2)
T	1	0.058	15 (6)	76 (5)	100 (9)
	2	0.068	85 (9)	86 (10)	168 (10)
	3	0.076	76 (5)	165 (6)	97 (10)
O1	1	0.060	32 (10)	99 (7)	76 (10)
	2	0.081	58 (10)	72 (17)	156 (15)
	3	0.092	91 (11)	20 (15)	70 (16)
O2	1	0.076	52 (7)	40 (6)	90 (16)
	2	0.089	77 (12)	86 (14)	174 (11)
	3	0.106	40 (7)	130 (6)	96 (10)
O3	1	0.057	93 (17)	72 (5)	22 (9)
	2	0.071	168 (7)	80 (7)	80 (16)
	3	0.105	102 (6)	159 (5)	70 (4)

DISCUSSION

Cr-O-Cr coupling: Sodic pyroxenes have an unique relationship in the variation of the M1-M1 distances with the ionic radii of ions occupying M1 sites (Hawthorne and Grundy, 1973). However, Ko deviates significantly from the trend and has a shorter M1-M1 distance (Clark, Appleman and Papike, 1969). The M1-M1 distance in NaVS₂O₈-pyroxene is anomalously short as in Ko (Fujita and Ohashi, unpublished data).

Fig. 3. Non-bridging and bridging Si-O distances plotted against the compositions in Ko-Di solid solutions. Solid circles represent the mean distances, and the associated vertical line connects the individual values. Open circles are the mean of the four Si-O distances.

Fig. 4. Variation of the averaged ionic radii of cations occupying M1 sites and mean (M1-O) distances in Ko-Di solid solutions.

In Cr_2O_3 , V_2O_5 and Ti_2O_3 , the M-M distances are anomalously short (Prewitt, Shannon, Rogers and Sleight, 1969). Metal-metal bonds are expected in them (Goodenough, 1965). Hawthorne and Grundy (1973) predicted that the short M1-M1 distance in $\text{NaCrSi}_2\text{O}_6$ and the suspected ano-

malous M1-M1 distances in NaVSi_2O_6 and $\text{NaTiSi}_2\text{O}_6$ should also be due to M-M bonds.

However, Ko has a M1 site coordinated by 6 oxygen atoms more evenly bonded in length to Cr^{+3} than in other sodic pyroxenes at room temperature and high temperature (Cameron, Sueno, Prewitt and Papike, 1973). So, it is more reasonable to consider that the shortness of M1-M1 distance at room temperature and high temperature is due to the geometrical feature of the M1- O_6 bonds. The cause of the short M1-M1 distance may not due to metal-metal bonds, but metal-oxygen bonds.

As shown in Fig. 6, the M1-M1 distances of the Ko-Di solid solutions are shorter than those of the hypo-Ko-Di solid solutions.

Fig. 5. M1-O distances plotted against the compositions in Ko-Di solid solutions. Open circles represent the individual values. Solid circles represent the mean distances.

The difference in Ko solid solutions is larger than that in Di solid solution. The shortness of M1-M1 distance of Ko solid solutions may depend on the shortness of the averaged M1-O distance and the geometrical feature of the M1-O₆ bonds. From the variation of M1-M1 distances, it is expected that Cr-O-Cr couplings exist in Ko solid solutions. On the other hand, random distributions of Mg and Cr ions are expected in Di solid solutions.

The isotropic and anisotropic temperature factors of M1 include some important informations. The isotropic temperature factors of T, O1, O2 and O3 are largest in Ko₅₀Di₅₀ and M2 largest in Ko₇₅Di₂₅. The former may depend on the effect of mixing and the latter may depend on the weakness of the sodium-oxygen bonding and the effect of mixing. The isotropic temperature factor of M1 is largest in Ko₂₅Di₇₅. This may depend on the random distribution of Mg²⁺ and Cr³⁺ in M1 sites. In the M1 ellipsoid, the axis being parallel to the b axis is longest in Ko₅₀Di₅₀. This trend can be explained by the positional disorder caused by the coexistence of coupled Cr-O-Cr ions and disordered Mg and Cr ions.

The characteristic nature recognized in the M1-M1 distance of Ko becomes more clearer at high temperature (Cameron,

Fig. 6. M1-M1 distances plotted against the compositions in Ko-Di solid solutions.

Fig. 7. (a) Mean 8 (M2-O) and (b) mean 6 (M2-O) distances plotted against mean 6 (M1-O) distances in Ko-Di solid solutions.

Sueno, Prewitt and Papike, 1973). That is, the increase in the M1-M1 distance with increasing temperature is smallest in Ko. Ko solid solutions may have the same nature. At room temperature, the M1-M1 distance of Ko₅₀Di₅₀ is nearly equal to that of Ko₂₅Di₇₅. However, at high temperature, the M1-M1 distance of Ko₅₀Di₅₀ may be shorter than that of Ko₂₅Di₇₅ under the influence of Cr-O-Cr couplings. The increase in the M1-M1 distance of Ko₂₅Di₇₅ with increasing temperature may be nearly equal to the increase in that of Di. In the M1 ellipsoid of Ko₅₀Di₅₀, the axis being parallel to the b axis may be unusually longer at high temperature. The observed and expected M1-M1 distances at 400°C are shown in Fig. 8. Hypo-Ko means NaCrSi₂O₆ including imaginary Cr³⁺ having a crystal chemical character being same with those of Al³⁺ and Fe³⁺.

High pressure structure: NaAlSi₂O₆ (jadeite) is high pressure phase and has no stability field at 1 atm (Bell, 1964). However, the

geometrical feature of $M2-O_8$ polyhedron in Jd is isomorphous to that of sodic pyroxenes being stable at 1 atm. Although the mean $6(M1-O)$ distance in Jd is short in absolute terms, the distance is not anomalously short (Prewitt and Burnham, 1966). On the other hand, $Ko_{75}Di_{25}$ and $Ko_{50}Di_{50}$ being stable only at high pressure have shorter $M1-O$ distances than those expected from the averaged ionic radii of cations occupying the M1 sites (Fig. 4). Their mean $8(M2-O)$ and $6(M2-O)$ distances are longer than those expected from the values of Ko, $Ko_{25}Di_{75}$ and Di (KD-group) (Fig. 7). The synthetic condition of $Ko_{25}Di_{75}$ is same with those of $Ko_{75}Di_{25}$ and $Ko_{50}Di_{50}$ (Ohashi, 1977). However, $Ko_{25}Di_{75}$ is stable at 1 atm and the geometrical feature of $M2-O_8$ polyhedron is isomorphous to those of KD-group. In $Ko_{50}Di_{50}$ and $Ko_{75}Di_{25}$, the $M2-O1$ and $M2-O2$ distances are longer than those expected from the values of KD-group and the $M2-O3$ distances shorter than those.

Fig. 8. $M1-M1$ distances at room temperature and $400^\circ C$ plotted against the compositions in Ko-Di solid solutions. Small circles represent the observed and calculated distances, and large circles represent the expected distances.

It is possible to consider that the characteristic structures of $Ko_{75}Di_{25}$ and $Ko_{50}Di_{50}$ depend on the coexistence of coupled Cr^{+3} -O-Cr and disordered Mg^{+2} and

Cr^{+3} . The cell volumes of $Ko_{75}Di_{25}$ and $Ko_{50}Di_{50}$ are smaller than those expected from the values of KD-group. Therefore, the characteristic structures may suggest at least partly those at high pressure. It is expected that the geometrical feature of $M2-O_8$ polyhedron in the Si saturated type pyroxene becomes similar to that of the Tschermak's molecule type pyroxene at high pressure (Ohashi and Ii, 1978). Structure parameters of five pyroxenes belonging to Ko-Di system support this expectation.

IMMISIBILITY PHENOMENA The maximum solubility of Ko molecule in Di is 24 wt% at 1 atm and $1140^\circ C$ (Ikeda and Yagi, 1972). Within the M1 site of Di solid solutions, Mg^{+2} and Cr^{+3} ions may be completely disordered. It is expected that when the content of Cr^{+3} is low, Cr^{+3} can be randomly distributed. On the other hand, it is expected that when the contents of Cr^{+3} increase and the averaged $M1-O$ distances decrease, a part of Cr^{+3} can form Cr-O-Cr couplings and phase separation can occur. That is, in Ko solid solution, it is expected that Cr^{+3} ions form Cr-O-Cr couplings. The solubility of Di molecule in Ko is negligible small at 1 atm and increases very much with increasing pressure (Ikeda and Ohashi, 1974). These facts mean that the coexistence of coupled Cr^{+3} and disordered Mg^{+2} and Cr^{+3} is not stable at 1 atm and increases the stability with increasing pressure.

The reason why the immiscibility field exists in Ko-Di system at 1 atm and high pressure is not known. However, by implication we may predict that the stabilization of Cr^{+3} in a distorted octahedron site may be the cause of the immiscibility

phenomena and the characteristic structure in Ko-Di system. Although the study of the octahedral distortion based on the structure parameters is in progress, the crystal field spectra show that the octahedral distortions become to minimum in the crystals having the compositions corresponded to the both sides of the immiscibility field (Ohashi, unpublished data).

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コスモクロル輝石—透輝石固溶体の結晶化学

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1200°C, 20 Kb で合成した $\text{Ko}_{75}(\text{NaCrSi}_2\text{O}_6: 75 \text{ mol}\%) \text{Di}_{25}(\text{CaMgSi}_2\text{O}_6: 25 \text{ mol}\%)$, $\text{Ko}_{50}\text{Di}_{50}$ 及び $\text{Ko}_{25}\text{Di}_{75}$ の結晶構造をリファインした。 Ko-Di 系固溶体の M1-M1 距離は、重要な意味を含んでいるようである。すなわち、M1-M1 距離は、M1 サイトを占める陽イオンの平均イオン半径から予想される距離よりも短く、また高圧における不混和域の両側に相当する組成を有する結晶において、もっとも長い。 Ko 固溶体中の Cr^{+3} イオンは、 Cr-O-Cr カップリングを形成しており、 Di 固溶体中の Cr^{+3} イオンは完全に無秩序に分布していると思われる。高圧相である $\text{Ko}_{75}\text{Di}_{25}$ と $\text{Ko}_{50}\text{Di}_{50}$ のセル・ボリュームは、 Ko , $\text{Ko}_{25}\text{Di}_{75}$ 及び Di のセル・ボリュームから期待される値よりも小さい。 $\text{Ko}_{75}\text{Di}_{25}$ と $\text{Ko}_{50}\text{Di}_{50}$ の M1-O 距離は、M1 サイトを占めている陽イオンの半径から期待される距離よりも短い。 $\text{Ko}_{75}\text{Di}_{25}$ と $\text{Ko}_{50}\text{Di}_{50}$ の 8(M2-O) 及び 6(M2-O) の平均距離は、 Ko , $\text{Ko}_{25}\text{Di}_{75}$ 及び Di の平均距離から期待される値よりも長い。 $\text{Ko}_{75}\text{Di}_{25}$ と $\text{Ko}_{50}\text{Di}_{50}$ の個性的な構造は、高圧下における構造をすくなくとも部分的には示しているであろう。