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UNIT-CELL DIMENSIONS OF SYNTHETIC TITAN-BEARING CLINOPYROXENES

by

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(with 5 Tables and 5 Text-figures)

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Abstract

Unit-cell dimensions of Ti-bearing clinopyroxenes in the systems $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ ($\text{MgSi} \rightleftharpoons \text{TiAl}$ substitution) and $\text{CaMgSi}_2\text{O}_6$ - $\text{CaMgTi}_2\text{O}_6$ ($\text{Si} \rightleftharpoons \text{Ti}$ substitution) have been determined. In the clinopyroxenes in these systems the unit-cell dimensions change linearly with increasing contents of $\text{CaTiAl}_2\text{O}_6$ or $\text{CaMgTi}_2\text{O}_6$. $\text{Si} \rightleftharpoons \text{Ti}$ substitution is generally more effective on the change of unit-cell dimensions than $\text{MgSi} \rightleftharpoons \text{TiAl}$ substitution.

Unit-cell dimensions of clinopyroxenes in the 10 per cent Fe_2O_3 section of the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ - Fe_2O_3 were also determined. Rate of increase or decrease of unit-cell dimensions of these clinopyroxenes is rather similar to that in the first two series. This might be caused by the substitution of $\text{MgTi} \rightleftharpoons 2\text{Fe}^{3+}$ and $\text{CaTi} \rightleftharpoons 2\text{Fe}^{3+}$.

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Introduction

BARTH (1931), KUSHIRO (1960), and YAGI and ONUMA (1967) considered that Ti^{4+} is included in natural titanaugites in the form of $\text{CaTiAl}_2\text{O}_6$. The study for the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ proved that $\text{CaTiAl}_2\text{O}_6$ is incorporated into

Table 1. Unit-cell dimensions of clinopyroxenes of CaMgSi₂O₆-CaTiAl₂O₆ series

CaMgSi ₂ O ₆ (wt %)	97.5	95.0	92.5	90.0	89.0
CaTiAl ₂ O ₆ (wt %)	2.5	5.0	7.5	10.0	11.0
<i>a</i> (Å)	9.748	9.749	9.751	9.754	9.754
<i>b</i> (Å)	8.921	8.918	8.911	8.903	8.900
<i>c</i> (Å)	5.254	5.261	5.268	5.275	5.278
β (deg)	105.96	106.01	106.05	106.11	106.11
<i>V</i> (Å ³)	439.3	439.7	439.9	440.1	440.2

N.B.: *a* \pm 0.003; *b* \pm 0.003; *c* \pm 0.003; β \pm 0.03; *V* \pm 0.1

CaMgSi₂O₆ (diopside) at least up to 11 weight per cent (YAGI and ONUMA, 1967). While BARTH (1931) made homogeneous pyroxene crystals of the CaMgSi₂O₆-CaMgTi₂O₆ system at compositions of (CaMgSi₂O₆)₉₄(CaMgTi₂O₆)₆ and (CaMgSi₂O₆)₉₀(CaMgTi₂O₆)₁₀. From his experiment BARTH suggested that Ti⁴⁺ is also incorporated into diopside in the form of CaMgTi₂O₆.

The study on the change of unit-cell dimensions of clinopyroxenes by ion substitution, especially clinopyroxene solid solutions between diopside and some other molecules, has been made by several workers (SAKATA, 1957; COLEMAN, 1962; HIZIKATA, 1969). In the present study the writers measured unit-cell dimensions of clinopyroxenes in the systems CaMgSi₂O₆-CaTiAl₂O₆ and CaMgSi₂O₆-CaMgTi₂O₆ and observed the variation of these unit-cell dimensions by the substitution of Ti⁴⁺ in octahedral and tetrahedral positions in clinopyroxenes.

Since natural titanaugites usually contain considerable amounts of Fe³⁺ (Deer, Howie and Zussman, 1963), the clinopyroxenes in the system CaMgSi₂O₆-CaTiAl₂O₆-Fe₂O₃ were also studied to understand the role of Fe³⁺ in unit-cell dimensions of Ti-bearing clinopyroxenes.

Synthesis of Clinopyroxenes

Five grams of each mixture of a desired pyroxene composition were prepared by weighing raw materials. Pure quartz (purified by the method described by SCHAIRER and BOWEN, 1956), Al₂O₃, CaCO₃, TiO₂, and MgO certified reagents were

Table 2. Unit-cell dimensions of clinopyroxenes of CaMgSi₂O₆-CaMgTi₂O₆ series

CaMgSi ₂ O ₆ (wt %)	95	90	N.B.
CaMgTi ₂ O ₆ (wt %)	5	10	
<i>a</i> (Å)	9.765	9.787	<i>a</i> \pm 0.003
<i>b</i> (Å)	8.930	8.933	<i>b</i> \pm 0.003
<i>c</i> (Å)	5.267	5.289	<i>c</i> \pm 0.003
β (deg)	106.00	106.17	β \pm 0.03
<i>V</i> (Å ³)	441.5	444.1	<i>V</i> \pm 0.1

Table 3. Results of quenching experiments for the system
CaMgSi₂O₆-CaTiAl₂O₆-Fe₂O₃

Composition (wt %)			Temp. °C.	Time	Phases
Di	Tp	Hm			
85	5	10	1320	1 1/2 hr	glass
			1315	1 1/2 hr	px+fo+glass
			1260	15 hr	px+trace fo+trace mt?+glass
			1250	10 days	px+rare mt?+glass
			1220	10 days	px+pv+glass
80	10	10	1315	1 hr	glass
			1310	1 hr	fo+glass
			1300	1 hr	fo+glass
			1295	2 hr	fo+rare px+glass
			1250	15 hr	rare fo+px+glass
			1240	48 hr	trace fo+px+pv+glass
			1230	48 hr	px+pv+glass
70	20	10	1285	1 hr	glass
			1280	1 hr	rare fo+glass
			1260	2 hr	fo+glass
			1255	4 hr	fo+px+glass
			1240	48 hr	trace+fo+glass
			1230	48 hr	trace fo+px+pv+glass
			1220	10 days	px+pv+glass

Di: CaMgSi₂O₆; Tp: CaTiAl₂O₆; Hm: Fe₂O₃; px: clinopyroxene; fo: forsterite, pv: perovskite; mt: magnetite

Table 4. Unit-cell dimensions of clinopyroxenes in the system
CaMgSi₂O₆-CaTiAl₂O₆-Fe₂O₃

Comp. of Mix. (wt %)				
CaMgSi ₂ O ₆	90	85	80	70
CaTiAl ₂ O ₆	0	5	10	20
Fe ₂ O ₃	10	10	10	10
<i>a</i> (Å)	9.766	9.777	9.782	9.796
<i>b</i> (Å)	8.921	8.906	8.890	8.867
<i>c</i> (Å)	5.274	5.290	5.304	5.334
β (deg)	106.08	106.06	106.05	106.08
<i>V</i> (Å ³)	441.5	442.7	443.30	445.2

N.B.: *a* (Å) ± 0.003 ; *b* (Å) ± 0.003 ; *c* (Å) ± 0.003 ; β (deg) ± 0.03 ; *V* (Å³) ± 0.1

used as the source. Al₂O₃ was ignited at 1500°C for 5 hrs, MgO at 1440°C for 3 hrs, and CaCO₃ was dried at 110°C for 24 hrs, respectively, to eliminate completely the hygroscopic water. After grinding in an agate mortar with pure ethyl alcohol, these materials were transferred to a 20 cc platinum crucible. Then the mixture

was melted at 1400°C for about 2 hrs and quenched in water. The glass obtained by this method was crushed and melted again. Usually two or three fusions with intermediate quenching and crushing were required to obtain homogeneous glass. The homogeneity of the glass was tested under the microscope by its uniformity of refractive indices. The crushed glass was heated at 800° to 1000°C with intermediate crushing, until the powder no longer fritted and crystallization was complete. This crystalline material was further heated at 1200°C for 2 days to promote crystallization and to get better crystals.

Measurement of Unit-cell Dimensions

X-ray method: The details of X-ray method is described by HIZIKATA (1969). The diffraction patterns of the clinopyroxenes in question were compared with the indexed pattern of a pure synthetic diopside. The peaks of the clinopyroxenes in question, which correspond completely to those of pure diopside, are shifted regularly with change in composition.

CaMgSi₂O₆-CaTiAl₂O₆ System: In the clinopyroxenes in this system it is

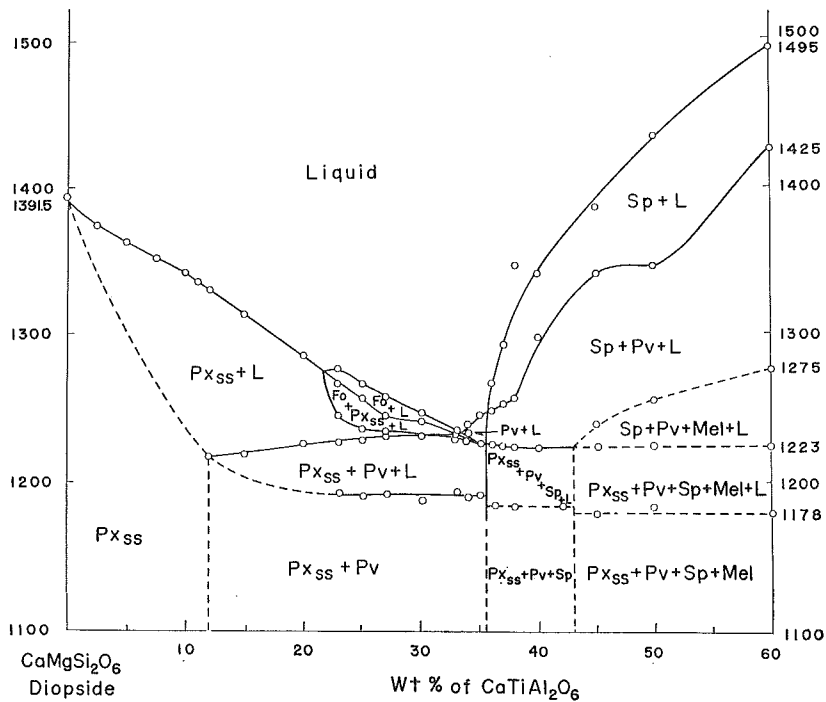


Fig. 1
Phase equilibrium diagram for the system CaMgSi₂O₆-CaTiAl₂O₆ (YAGI and ONUMA, 1967).

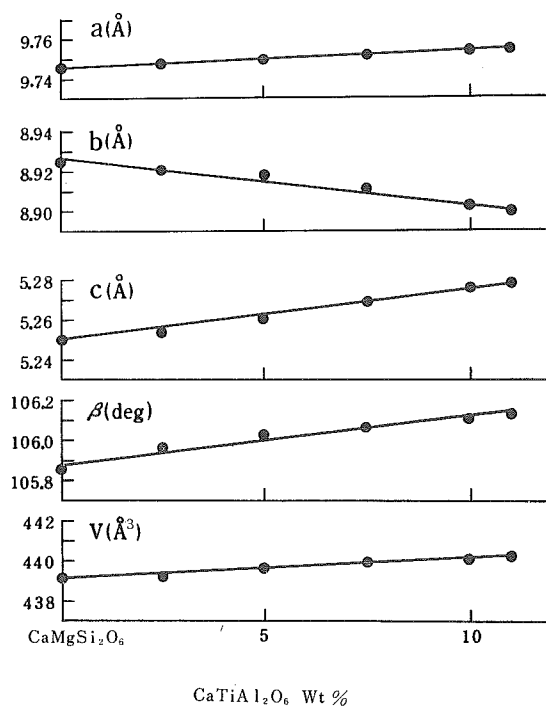


Fig. 2

Variation of unit-cell dimensions of $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ series clinopyroxenes.

assumed that Ti^{4+} occupied octahedral position and Al^{3+} tetrahedral position; that is, Mg in $\text{CaMgSi}_2\text{O}_6$ is replaced by Ti^{4+} , accompanied by the substitution of Si by Al^{3+} (henceforth abbreviated $\text{MgSi} \rightleftharpoons \text{TiAl}$ substitution). YAGI and ONUMA (1967) showed that $\text{CaTiAl}_2\text{O}_6$ can be soluble in $\text{CaMgSi}_2\text{O}_6$ at least up to 11 weight per cent and that this part of the phase diagram is truly binary in nature (Fig. 1).

The composition of clinopyroxenes and data on the variation of unit-cell dimensions are given in Table 1 and Fig. 2. The data of synthetic diopside were measured by HIJIKATA (1969).

Unit-cell dimensions change linearly with increasing content of $\text{CaTiAl}_2\text{O}_6$, i.e., a , c , β and V increase, whereas b decreases. Rate of increase or decrease of unit-cell dimensions is: $a=0.0009\text{\AA}$, $b=-0.0022\text{\AA}$, $c=0.0025\text{\AA}$, $\beta=0.024^\circ$, and $V=0.09\text{\AA}^3$ for each weight per cent of $\text{CaTiAl}_2\text{O}_6$. Rate of increase of a is rather small compared with that of c or rate of decrease of b .

The relation between unit-cell dimensions and composition of clinopyroxenes of this system is as follows:

$$\begin{aligned}
 a &= 0.0009 \times (\text{CaTiAl}_2\text{O}_6) \text{ wt } \% + 9.745 \text{ \AA} \\
 b &= -0.0022 \times (\text{CaTiAl}_2\text{O}_6) \text{ wt } \% + 8.925 \text{ \AA} \\
 c &= 0.0025 \times (\text{CaTiAl}_2\text{O}_6) \text{ wt } \% + 5.250 \text{ \AA} \\
 \beta &= 0.024 \times (\text{CaTiAl}_2\text{O}_6) \text{ wt } \% + 105.87^\circ \\
 V &= 0.09 \times (\text{CaTiAl}_2\text{O}_6) \text{ wt } \% + 439.2 \text{ \AA}^3
 \end{aligned}$$

CaMgSi₂O₆-CaMgTi₂O₆ system: BARTH (1931) made synthetic clinopyroxenes of this system and suggested that Ti⁴⁺ can replace Si without accompanying replacement of other ions. Later SEGNI^T (1953) also suggested that TiO₂ can replace SiO₂ in diopside to a small extent.

Clinopyroxenes of the composition (CaMgSi₂O₆)₉₅(CaMgTi₂O₆)₅ and (CaMgSi₂O₆)₉₀(CaMgTi₂O₆)₁₀ in weight per cent were synthesized and their unit-cell

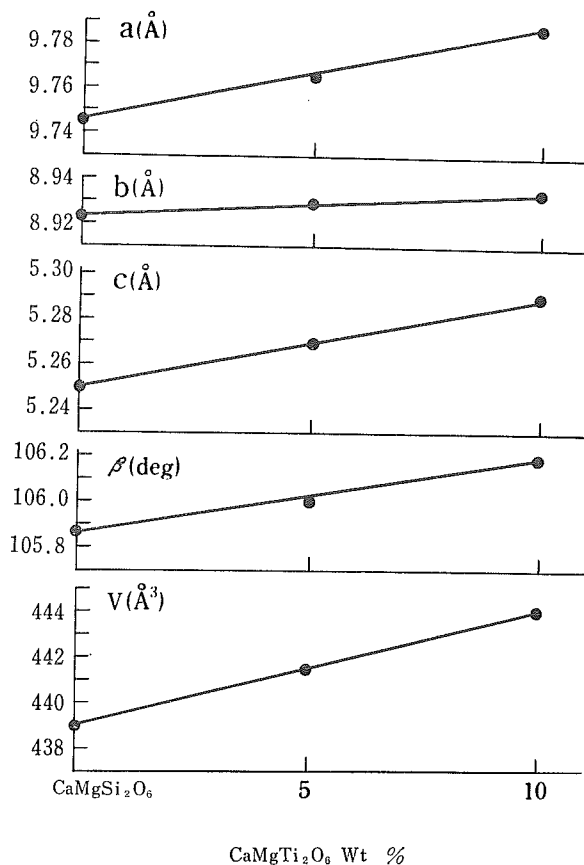


Fig. 3

Variation of unit-cell dimensions of CaMgSi₂O₆-CaMgTi₂O₆ series clinopyroxenes.

dimensions were measured in the present study as shown in Table 2 and Fig. 3.

Here the unit-cell dimensions also change linearly with increase of $\text{CaMgTi}_2\text{O}_6$. Rate of increase of unit-cell dimensions for each weight per cent of $\text{CaMgTi}_2\text{O}_6$ is: $a=0.0042\text{\AA}$, $b=0.0008\text{\AA}$, $c=0.0039\text{\AA}$, $\beta=0.03^\circ$, and $V=0.49\text{\AA}^3$. The relation between unit-cell dimensions and composition of clinopyroxenes of this system is given as follows:

$$\begin{aligned} a &= 0.0042 \times (\text{CaMgTi}_2\text{O}_6) \text{ wt } \% + 9.745 \text{ \AA} \\ b &= 0.0008 \times (\text{CaMgTi}_2\text{O}_6) \text{ wt } \% + 8.925 \text{ \AA} \\ c &= 0.0039 \times (\text{CaMgTi}_2\text{O}_6) \text{ wt } \% + 5.250 \text{ \AA} \\ \beta &= 0.03 \times (\text{CaMgTi}_2\text{O}_6) \text{ wt } \% + 105.87^\circ \\ V &= 0.49 \times (\text{CaMgTi}_2\text{O}_6) \text{ wt } \% + 439.2 \text{ \AA}^3 \end{aligned}$$

CaMgSi₂O₆-CaTiAl₂O₆-Fe₂O₃ system: Ten weight per cent Fe_2O_3 was added to the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ in order to investigate the effect of Fe^{3+} on the unit-cell dimensions of Ti-bearing clinopyroxenes. A preliminary phase equilibrium diagram for this section is presented in Fig. 4 with the quenching data listed in Table 3. The experimental method used on this section is the same as described elsewhere (YAGI and ONUMA, 1967).

Homogeneous clinopyroxene phase was not obtained in this system and very small amount of perovskite appears always associated with clinopyroxene. The perovskite is probably $(\text{Ca}, \text{Mg}) \text{TiO}_3$ in composition, owing to liberation of Mg from clinopyroxene structure by $\text{Mg} \rightleftharpoons \text{Fe}^{3+}$ substitution. Therefore the exact composition of clinopyroxenes can not be estimated from the phase diagram. Unit-cell dimensions of the clinopyroxenes crystallized at 1200°C are given in Table 4 with the composition of mixtures from which the clinopyroxenes crystallized out. Fig. 5 shows the relation between the unit-cell dimensions of the clinopyroxenes and

Table 5. Chemical composition of ferriaugite from Katzenbuckel and the mixture of $(\text{CaMgSi}_2\text{O}_6)_{85}$ $(\text{CaTiAl}_2\text{O}_6)_5$ $(\text{Fe}_2\text{O}_3)_{10}$ (wt percent)

	1	2	
SiO_2	50.35	46.75	
TiO_2	1.91	1.70	
Al_2O_3	3.09	2.15	
Fe_2O_3	7.77	10.00	
FeO	0.32		
MnO	0.30		
MgO	13.83	16.15	Ferriaugite from
CaO	20.32	23.25	Katzenbuckel
Na_2O	2.55		2 Mixture of
K_2O	0.05		$(\text{CaMgSi}_2\text{O}_6)_{85}$
			$(\text{CaTiAl}_2\text{O}_6)_5$
			$(\text{Fe}_2\text{O}_3)_{10}$
Total	100.48	100.00	

$\text{CaTiAl}_2\text{O}_6$ content at 10 weight per cent Fe_2O_3 in the mixtures. It is noticed that unit-cell dimensions also change linearly with increasing contents of $\text{CaTiAl}_2\text{O}_6$ in the mixtures, i.e., a , c and V increase and b decreases considerably, while β remains almost constant.

Since the amount of perovskite associated with clinopyroxene is very small, the composition of clinopyroxene is estimated not to be much different from that of mixture though the exact values remain unknown. Rate of increase or decrease of unit-cell dimensions of clinopyroxenes for each weight per cent $\text{CaTiAl}_2\text{O}_6$ in the host mixture is as follows: $a=0.0015\text{\AA}$, $b=-0.0027\text{\AA}$, and $c=0.0031\text{\AA}$. These values are more or less similar to those of clinopyroxenes in the system $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6$.

It is interesting that the composition of mixture $(\text{CaMgSi}_2\text{O}_6)_{85}(\text{CaTiAl}_2\text{O}_6)_5(\text{Fe}_2\text{O}_3)_{10}$ is similar to some natural clinopyroxenes. For example a ferriaugite described by YODER and TILLEY (1962) from Katzenbukel, Germany is compared with this composition in Table 5. Similarity of the two is distinct in this table.

Discussions

In clinopyroxenes of the system $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6$ coupled substitution $\text{MgSi}\rightleftharpoons\text{TiAl}$ is assumed, and in those of the system $\text{CaMgSi}_2\text{O}_6\text{-CaMgTi}_2\text{O}_6$ $\text{Si}\rightleftharpoons\text{Ti}$ substitution occurs and Ti^{4+} occupies tetrahedral position. In the clinopyroxenes of the system $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6\text{-Fe}_2\text{O}_3$ both $\text{MgSi}\rightleftharpoons 2\text{Fe}^{3+}$ and $\text{CaSi}\rightleftharpoons 2\text{Fe}^{3+}$ substitutions are assumed in addition to the $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution. Therefore the clinopyroxenes described here afford important criteria on the effect of various ionic substitutions on the unit-cell dimensions. Their characteristic features are described below.

1. The values a , c and V increase by both substitutions $\text{MgSi}\rightleftharpoons\text{TiAl}$ and $\text{Si}\rightleftharpoons\text{Ti}$, but the rate of increase in unit-cell dimensions, especially in a , is always higher in $\text{Si}\rightleftharpoons\text{Ti}$ substitution than in $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution. This may suggest that the substitution of Ti^{4+} in tetrahedral position is more effective on the change of a than substitution of Ti^{4+} in octahedral position.

2. The value b decreases by $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution, while it increases by $\text{Si}\rightleftharpoons\text{Ti}$ substitution. Rate of decrease of b in $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution is higher than rate of increase of b in $\text{Si}\rightleftharpoons\text{Ti}$ substitution.

3. The $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution is most effective on the change of c , while not so effective on that of a . SAKATA (1957) showed that a , b and β decrease and c increases with $\text{Si}\rightleftharpoons\text{Al}$ substitution in synthetic aluminian diopside. In $\text{MgSi}\rightleftharpoons\text{TiAl}$ substitution, however, a increases though the rate is lower. This may be due to the $\text{Mg}\rightleftharpoons\text{Ti}$ substitution in octahedral position.

4. In their study on $\text{CaMgSi}_2\text{O}_6\text{-CaFe}_2^{3+}\text{SiO}_6$ clinopyroxenes, HUCKENHOLZ, SCHAIRER and YODER (1968) showed that a , c , and V increase and b decreases, while

β remains essentially constant with increasing $\text{CaFe}_2^{3+}\text{SiO}_6$. They also investigated system $\text{CaMgSi}_2\text{O}_6\text{-Fe}_2\text{O}_3$ and suggested the substitution of $\text{MgSi}\rightleftharpoons 2\text{Fe}^{3+}$ and $\text{CaSi}\rightleftharpoons 2\text{Fe}^{3+}$ in the clinopyroxenes of this system.

The change of unit-cell dimensions of clinopyroxenes in the system $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6\text{-Fe}_2\text{O}_3$ with increasing $\text{CaTiAl}_2\text{O}_6$ shows a similar tendency to that of $\text{CaMgSi}_2\text{O}_6\text{-CaFe}_2^{3+}\text{SiO}_6$ mentioned above. In the present case, therefore, substitutions $\text{MgTi}\rightleftharpoons 2\text{Fe}^{3+}$ and $\text{CaTi}\rightleftharpoons 2\text{Fe}^{3+}$ are assumed in addition to $\text{MgSi}\rightleftharpoons \text{TiAl}$ substitution, though excess Ca, Mg and Ti^{4+} may probably crystallize as perovskite $(\text{Ca, Mg})\text{TiO}_3$, presence of which was confirmed by X-ray diffraction patterns.

It is evident from the inspection on Tables 1 and 4 that occupation of both octahedral and tetrahedral positions by Fe^{3+} in addition to $\text{MgSi}\rightleftharpoons \text{TiAl}$ substitution is not so effective on the change of unit-cell dimensions of clinopyroxenes.

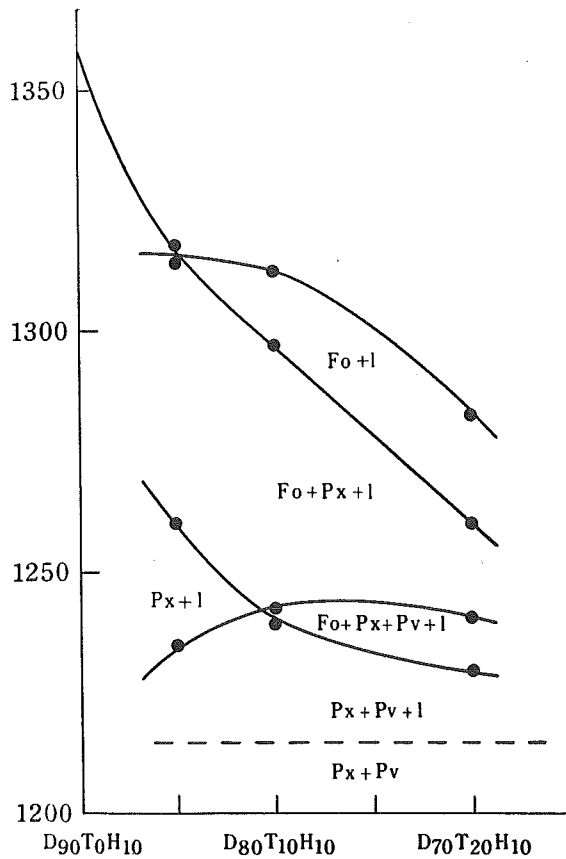
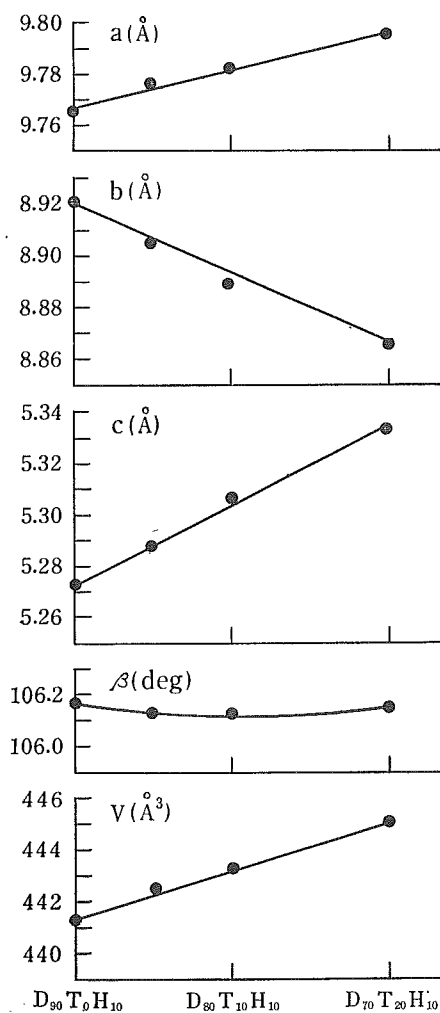


Fig. 4

Phase equilibrium diagram for 10 per cent Fe_2O_3 section of the system $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6\text{-Fe}_2\text{O}_3$.

**Fig. 5**

Variation of unit-cell dimensions of clinopyroxenes in the system
 $\text{CaMgSi}_2\text{O}_6$ - $\text{CaMgTi}_2\text{O}_6$ - Fe_2O_3 .

D: $\text{CaMgSi}_2\text{O}_6$, T: $\text{CaTiAl}_2\text{O}_6$, H: Fe_2O_3 .

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