HOKKAIDO UNIVERSITY

Title	Unit-cell Dimensions of Synthetic Titanbearing Clinopyroxenes
Author(s)	Onuma, Kosuke; Hijikata, Ken-ichi; Yagi, Kenzo
Citation	Journal of the Faculty of Science, Hokkaido University. Series 4, Geology and mineralogy, 14(2), 111-121
Issue Date	1968-12
Doc URL	https://hdl.handle.net/2115/35983
Type	departmental bulletin paper
File Information	14(2)_111-122.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

UNIT-CELL DIMENSIONS OF SYNTHETIC TITAN-BEARING CLINOPYROXENES

by

Kosuke ONUMA, Ken-ichi HIJIKATA and Kenzo YAGI

(with 5 Tables and 5 Text-figures)

(Contribution from the Department of Geology and Mineralogy,
Faculty of Science, Hokkaido University. No. 1084)

Abstract

Unit-cell dimensions of Ti-bearing clinopyroxenes in the systems $CaMgSi_2O_6$–$CaTiAl_2O_6$ ($MgSi \rightleftarrows TiAl$ substitution) and $CaMgSi_2O_6$–$CaMgTi_2O_6$ ($Si \rightleftarrows Ti$ substitution) have been determined. In the clinopyroxenes in these systems the unit-cell dimensions change lineally with increasing contents of $CaTiAl_2O_6$ or $CaMgTi_2O_6$. $Si \rightleftarrows Ti$ substitution is generally more effective on the change of unit-cell dimensions than $MgSi \rightleftarrows TiAl$ substitution.

Unit-cell dimensions of clinopyroxenes in the 10 per cent Fe_2O_3 section of the system $CaMgSi_2O_6$–$CaTiAl_2O_6$–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 $MgTi \rightleftarrows 2Fe^{3+}$ and $CaTi \rightleftarrows 2Fe^{3+}$.

Contents

Introduction 111
Synthesis of clinopyroxenes 112
Measurement of unit-cell dimensions 114
Discussions 118
Acknowledgements 120
References cited 121

Introduction

BARTH (1931), KUSHIRO (1960), and YAGI and ONUMA (1967) considered that Ti^{4+} is included in natural titanaugites in the form of $CaTiAl_2O_6$. The study for the system $CaMgSi_2O_6$–$CaTiAl_2O_6$ proved that $CaTiAl_2O_6$ is incorporated into

Table 1. Unit-cell dimensions of clinopyroxenes of $CaMgSi_2O_6$-$CaTiAl_2O_6$ series

$CaMgSi_2O_6$ (wt %)	97.5	95.0	92.5	90.0	89.0
$CaTiAl_2O_6$ (wt %)	2.5	5.0	7.5	10.0	11.0
a (Å)	9.748	9.749	9.751	9.754	9.754
b (Å)	8.921	8.918	8.911	8.903	8.900
c (Å)	5.254	5.261	5.268	5.275	5.278
β (deg)	105.96	106.01	106.05	106.11	106.11
V (Å^3)	439.3	439.7	439.9	440.1	440.2

N.B.: a ±0.003; b ±0.003; c ±0.003; β ±0.03; V ±0.1

$CaMgSi_2O_6$ (diopside) at least up to 11 weight per cent (YAGI and ONUMA, 1967). While BARTH (1931) made homogeneous pyroxene crystals of the $CaMgSi_2O_6$–$CaMgTi_2O_6$ system at compositions of $(CaMgSi_2O_6)_{94}$ $(CaMgTi_2O_6)_6$ and $(CaMgSi_2O_6)_{90}$ $(CaMgTi_2O_6)_{10}$. From his experiment BARTH suggested that Ti^{4+} is also incorporated into diopside in the form of $CaMgTi_2O_6$.

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; HIJIKATA, 1969). In the present study the writers measured unit-cell dimensions of clinopyroxenes in the systems $CaMgSi_2O_6$–$CaTiAl_2O_6$ and $CaMgSi_2O_6$–$CaMgTi_2O_6$ and observed the variation of these unit-cell dimensions by the substitution of Ti^{4+} in octahedral and tetrahedral positions in clinopyroxenes.

Since natural titanaugites usually contain considerable amounts of Fe^{3+} (Deer, Howie and Zussman, 1963), the clinopyroxenes in the system $CaMgSi_2O_6$–$CaTiAl_2O_6$–Fe_2O_3 were also studied to understand the role of Fe^{3+} 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), Al_2O_3, $CaCO_3$, TiO_2, and MgO certified reagents were

Table 2. Unit-cell dimensions of clinopyroxenes of $CaMgSi_2O_6$-$CaMgTi_2O_6$ series

$CaMgSi_2O_6$ (wt %)	95	90
$CaMgTi_2O_6$ (wt %)	5	10
a (Å)	9.765	9.787
b (Å)	8.930	8.933
c (Å)	5.267	5.289
β (deg)	106.00	106.17
V (Å^3)	441.5	444.1

N.B.
a ±0.003
b ±0.003
c ±0.003
β ±0.03
V ±0.1

Table 3. Results of quenching experiments for the system $CaMgSi_2O_6$-$CaTiAl_2O_6$-Fe_2O_3

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 : $CaMgSi_2O_6$; Tp : $CaTiAl_2O_6$; Hm : Fe_2O_3; px : clinopyroxene; fo ; forsterite, pv : perovskite ; mt : magnetite

Table 4. Unit-cell dimensions of clinopyroxenes in the system $CaMgSi_2O_6$-$CaTiAl_2O_6$-Fe_2O_3

Comp. of Mix. (wt %)				
$CaMgSi_2O_6$	90	85	80	70
$CaTiAl_2O_6$	0	5	10	20
Fe_2O_3	10	10	10	10
a (Å)	9.766	9.777	9.782	9.796
b (Å)	8.921	8.906	8.890	8.867
c (Å)	5.274	5.290	5.304	5.334
β (deg)	106.08	106.06	106.05	106.08
V (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 (Å^3) ±0.1

used as the source. Al_2O_3 was ignited at 1500°C for 5 hrs, MgO at 1440°C for 3 hrs, and $CaCO_3$ 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 HIJIKATA (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.

$CaMgSi_2O_6$–$CaTiAl_2O_6$ System: In the clinopyroxenes in this system it is

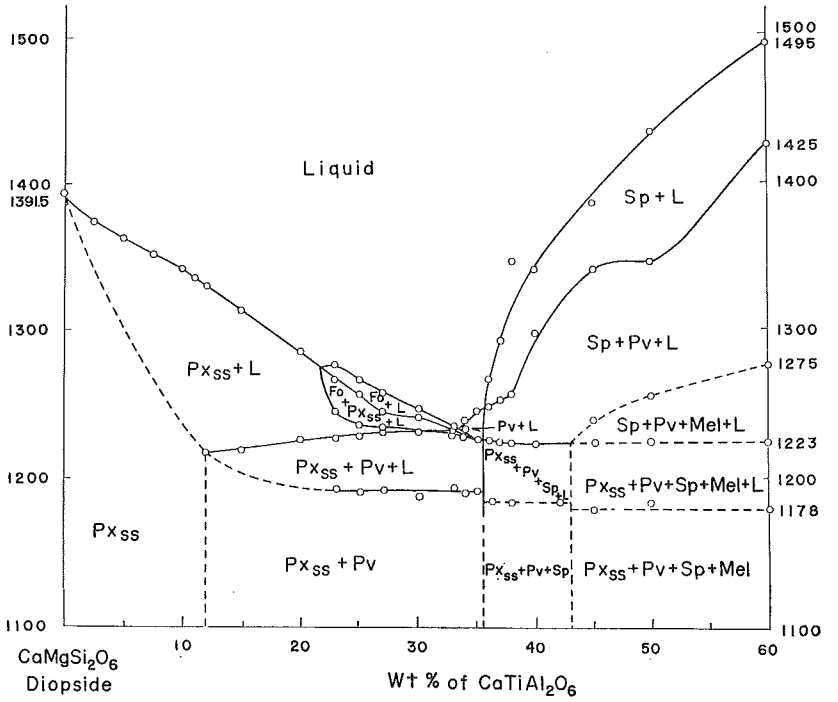

Fig. 1
Phase equilibrium diagram for the system $CaMgSi_2O_6$-$CaTiAl_2O_6$ (YAGI and ONUMA, 1967).

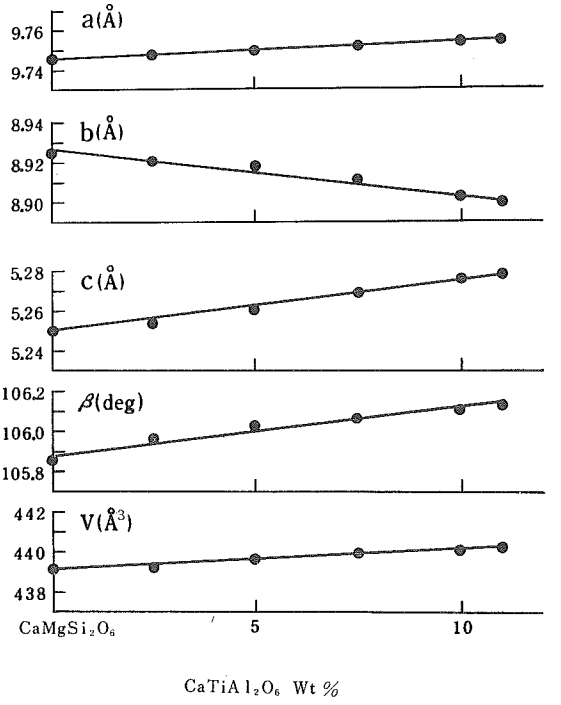

Fig. 2
Variation of unit-cell dimensions of $CaMgSi_2O_6$-$CaTiAl_2O_6$ series clinopyroxenes.

assumed that Ti^{4+} occupied octahedral position and Al^{3+} tetrahedral position; that is, Mg in $CaMgSi_2O_6$ is replaced by Ti^{4+}, accompanied by the substitution of Si by Al^{3+} (henceforth abbreviated MgSi⇄TiAl substitution). YAGI and ONUMA (1967) showed that $CaTiAl_2O_6$ can be soluble in $CaMgSi_2O_6$ 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 lineally with increasing content of $CaTiAl_2O_6$, i.e., a, c, β and V increase, whereas b decreases. Rate of increase or decrease of unit-cell dimensions is: $a=0.0009$Å, $b=-0.0022$Å, $c=0.0025$Å, $\beta=0.024°$, and $V=0.09$Å^3 for each weight per cent of $CaTiAl_2O_6$. 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:

$a=0.0009\times(CaTiAl_2O_6)$ wt %$+9.745$ Å
$b=-0.0022\times(CaTiAl_2O_6)$ wt %$+8.925$ Å
$c=0.0025\times(CaTiAl_2O_6)$ wt %$+5.250$ Å
$\beta=0.024\times(CaTiAl_2O_6)$ wt %$+105.87°$
$V=0.09\times(CaTiAl_2O_6)$ wt %$+439.2$ Å^3

$CaMgSi_2O_6$–$CaMgTi_2O_6$ system: BARTH (1931) made synthetic clinopyroxenes of this system and suggested that Ti^{4+} can replace Si without accompanying replacement of other ions. Later SEGNIT (1953) also suggested that TiO_2 can replace SiO_2 in diopside to a small extent.

Clinopyroxenes of the composition $(CaMgSi_2O_6)_{95}(CaMgTi_2O_6)_5$ and $(CaMgSi_2O_6)_{90}(CaMgTi_2O_6)_{10}$ in weight per cent were synthesized and their unit-cell

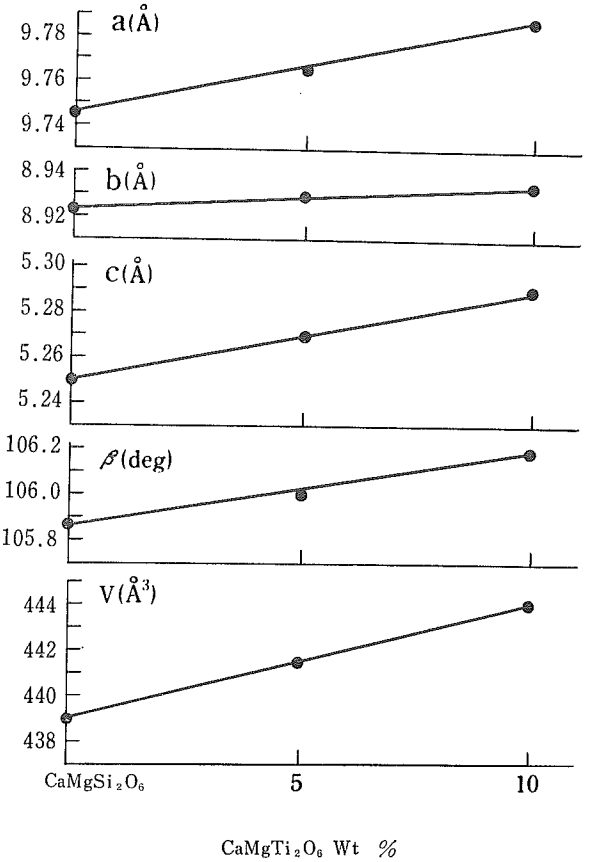

Fig. 3
Variation of unit-cell dimensions of $CaMgSi_2O_6$-$CaMgTi_2O_6$ series clinopyroxenes.

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

Here the unit-cell dimensions also change lineally with increase of $CaMgTi_2O_6$. Rate of increase of unit-cell dimensions for each weight per cent of $CaMgTi_2O_6$ is: a=0.0042Å, b=0.0008Å, c=0.0039Å, β=0.03°, and V=0.49Å^3. The relation betwen unit-cell dimensions and composition of clinopyroxenes of this system is given as follows:

$$a=0.0042\times(CaMgTi_2O_6)\text{ wt }\%+9.745\text{ Å}$$
$$b=0.0008\times(CaMgTi_2O_6)\text{ wt }\%+8.925\text{ Å}$$
$$c=0.0039\times(CaMgTi_2O_6)\text{ wt }\%+5.250\text{ Å}$$
$$\beta=0.03\times(CaMgTi_2O_6)\text{ wt }\%+105.87°$$
$$V=0.49\times(CaMgTi_2O_6)\text{ wt }\%+439.2\text{ Å}^3$$

$CaMgSi_2O_6$–$CaTiAl_2O_6$–Fe_2O_3 system: Ten weight per cent Fe_2O_3 was added to the system $CaMgSi_2O_6$–$CaTiAl_2O_6$ 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 (Ca, Mg) TiO_3 in composition, owing to liberation of Mg from clinopyroxene structure by $Mg\rightleftarrows Fe^{3+}$ 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 $(CaMgSi_2O_6)_{85}$ $(CaTiAl_2O_6)_5$ $(Fe_2O_3)_{10}$ (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
CaO	20.32	23.25
Na_2O	2.55	
K_2O	0.05	
Total	100.48	100.00

1 Ferriaugite from Katzenbuckel
2 Mixture of $(CaMgSi_2O_6)_{85}$ $(CaTiAl_2O_6)_5$ $(Fe_2O_3)_{10}$

$CaTiAl_2O_6$ content at 10 weight per cent Fe_2O_3 in the mixtures. It is noticed that unit-cell dimensions also change lineally with increasing contents of $CaTiAl_2O_6$ 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 $CaTiAl_2O_6$ in the host mixture is as follows: $a=0.0015$Å, $b=-0.0027$Å, and $c=0.0031$Å. These values are more or less similar to those of clinopyroxenes in the system $CaMgSi_2O_6$–$CaTiAl_2O_6$.

It is interesting that the composition of mixture $(CaMgSi_2O_6)_{85}(CaTiAl_2O_6)_5(Fe_2O_3)_{10}$ 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 $CaMgSi_2O_6$–$CaTiAl_2O_6$ coupled substitution $MgSi\rightleftarrows TiAl$ is assumed, and in those of the system $CaMgSi_2O_6$–$CaMgTi_2O_6$ $Si\rightleftarrows Ti$ substitution occurs and Ti^{4+} occupies tetrahedral position. In the clinopyroxenes of the system $CaMgSi_2O_6$–$CaTiAl_2O_6$–Fe_2O_3 both $MgSi\rightleftarrows 2Fe^{3+}$ and $CaSi\rightleftarrows 2Fe^{3+}$ substitutions are assumed in addition to the $MgSi\rightleftarrows TiAl$ 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 $MgSi\rightleftarrows TiAl$ and $Si\rightleftarrows Ti$, but the rate of increase in unit-cell dimensions, especially in a, is always higher in $Si\rightleftarrows Ti$ substitution than in $MgSi\rightleftarrows TiAl$ 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 $MgSi\rightleftarrows TiAl$ substitution, while it increases by $Si\rightleftarrows Ti$ substitution. Rate of decrease of b in $MgSi\rightleftarrows TiAl$ substitution is higher than rate of increase of b in $Si\rightleftarrows Ti$ substitution.

3. The $MgSi\rightleftarrows TiAl$ 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 $Si\rightleftarrows Al$ substitution in synthetic aluminian diopside. In $MgSi\rightleftarrows TiAl$ substitution, however, a increases though the rate is lower. This may be due to the $Mg\rightleftarrows Ti$ substitution in octahedral position.

4. In their study on $CaMgSi_2O_6$–$CaFe_2^{3+}SiO_6$ clinopyroxenes, HUCKENHOLZ, SCHAIRER and YODER (1968) showd that a, c, and V increase and b decreases, while

β remains essentially constant with increasing $CaFe_2^{3+}SiO_6$. They also investigated system $CaMgSi_2O_6$–Fe_2O_3 and suggested the substitution of $MgSi \rightleftarrows 2Fe^{3+}$ and $CaSi \rightleftarrows 2Fe^{3+}$ in the clinopyroxenes of this system.

The change of unit-cell dimensions of clinopyroxenes in the system $CaMgSi_2O_6$ –$CaTiAl_2O_6$–Fe_2O_3 with increasing $CaTiAl_2O_6$ shows a similar tendency to that of $CaMgSi_2O_6$–$CaFe_2^{3+}SiO_6$ mentioned above. In the present case, therefore, substitutions $MgTi \rightleftarrows 2Fe^{3+}$ and $CaTi \rightleftarrows 2Fe^{3+}$ are assumed in addition to $MgSi \rightleftarrows TiAl$ substitution, though excess Ca, Mg and Ti^{4+} may probably crystallize as perovskite (Ca, Mg) 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 $MgSi \rightleftarrows TiAl$ substitution is not so effective on the change of unit-cell dimensions of clinopyroxenes.

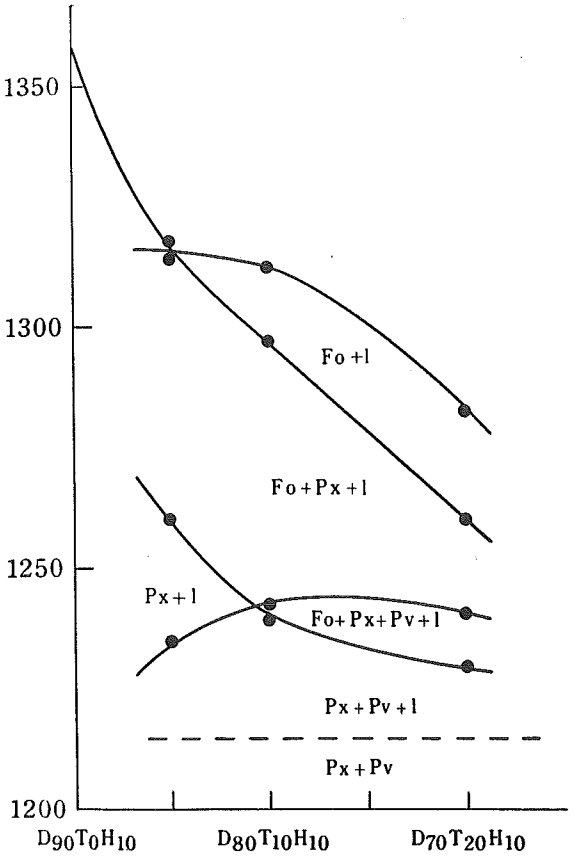

Fig. 4

Phase equilibrium diagram for 10 per cent Fe_2O_3 section of the system $CaMgSi_2O_6$-$CaTiAl_2O_6$-Fe_2O_3.

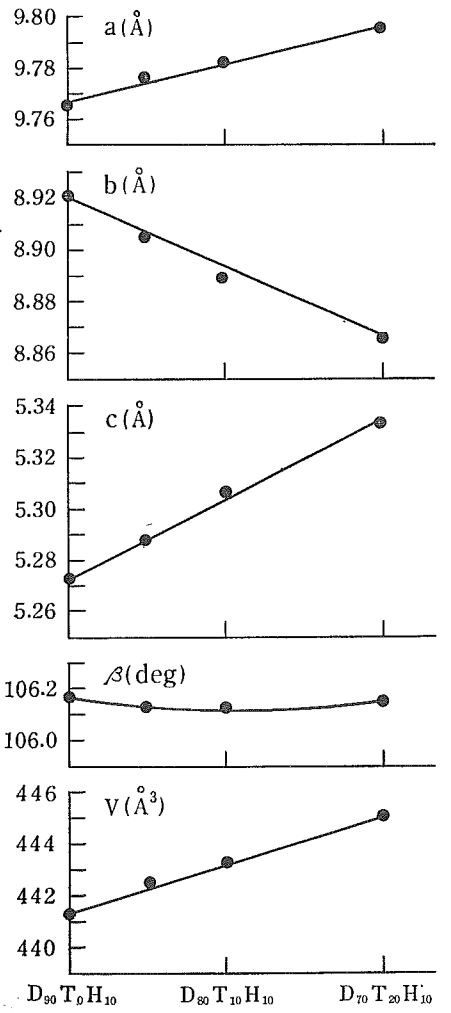

Fig. 5
Variation of unit-cell dimensions of clinopyroxenes in the system $CaMgSi_2O_6$-$CaMgTi_2O_6$-Fe_2O_3.
D: $CaMgSi_2O_6$, T: $CaTiAl_2O_6$, H: Fe_2O_3.

Acknowledgements

Part of the cost for the present study was defrayed by the Grant for Scientific Researches by the Ministry of Education of Japan. Mr. S. TERADA of Hokkaido University helped the writers in preparation of the figures.

References cited

BARTH, T. F. W. (1931): Pyroxen von Hiva Oa, Marquesas-Inseln und die Formel titanhältiger Augite. N. Jb. Min. Beil. Bd. 64 A, 217–224.

COLEMAN, L. C. (1962): Effect of ionic substitution on the unit-cell dimensions of synthetic diopside. Geol. Soc. Am. Buddington Volume, 429–446.

DEER, W. A., HOWIE, R. A. and ZUSSMAN, J. (1963): Rock-forming minerals, Vol. 2, Longmans, Green and Co. pp. 379.

HIJIKATA, K. (1969): Unit-cell dimensions of clinopyroxenes in the system $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$. J. Fac. Sci Hokkaido Univ. Ser. IV, 14, 149–157.

HUCKENHOLZ, H. G., SCHAIRER, J. F. and YODER, H. S., Jr. (1968): Synthesis and stability of ferri-diopside. Carn. Inst. Wash. Year Book, 66, 335–346.

KUSHIRO, I. (1960): Si-Al relation in clinopyroxenes from igneous rocks. Am. J. Sci. 258, 548–554.

ONUMA, K. and YAGI, K. (1967): The system diopside-akermanite-nepheline. Am. Min. 52, 227–243.

SAKATA, Y. (1957): Unit-cell dimensions of synthetic aluminian diopside. Jap. J. Geol. Geogr. 28, 161–168.

SEGNIT, E. R. (1953): Some data on synthetic aluminous and other pyroxenes. Min. Mag. 30, 218–226.

YAGI, K. and ONUMA, K. (1967): The join $CaMgSi_2O_6$-$CaTiAl_2O_6$ and its bearing on the titanaugites. J. Fac. Sci. Hokkaido Univ. Ser. IV, 13, 463–148.

YODER, H. S., Jr., and TILLEY, C. E. (1962): Origin of basalt magma: an experimental study of natural and synthetic rock system. J. Petr. 3, 342–532.

(Manuscript received August 2, 1968)