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Clinopyroxene with $Si < Al_{IV}$ in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$

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SUMMARY. Unusual clinopyroxenes were synthesized in the study of the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ in air at 1 atm. Clinopyroxene solid solution, hibonite solid solution, *X*-phase, perovskite, and corundum are present, and at subsolidus temperatures the clinopyroxene single-phase field extends up to about 19 wt% $CaTiAl_2O_6$. The $CaTiAl_2O_6$ component in the clinopyroxene however increases beyond the clinopyroxene single-phase field and attains 23 wt%. These clinopyroxene solid solutions are extremely poor in SiO_2 and extremely rich in Al_2O_3, Fe_2O_3, and TiO_2, and more than half of tetrahedral sites are occupied by Al_{IV}, contravening the aluminium avoidance principle.

THE system $CaMgSi_2O_6$(Di)-$CaAl_2SiO_6$(CaTs)-$CaFeAlSiO_6$(FATs)-$CaTiAl_2O_6$(Tp) is important in evaluating the role of pyroxene in the differentiation of undersaturated alkalic rocks (Onuma and Yagi, 1975). In the course of the study of this system an unusual aluminous clinopyroxene with $Si < Al_{IV}$ was synthesized near the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ in the subsystem $CaMgSi_2O_6$-$CaFeAlSiO_6$-$CaTiAl_2O_6$ (Akasaka and Onuma, 1980). The study of the join $CaFeAlSiO_6$-$CaTiAl_2O_6$, therefore, is needed to understand the phase relation and the nature of this anomalous clinopyroxene. Onuma and Yagi (1971) made a preliminary study of this join and demonstrated that the clinopyroxene single-phase field extends from $CaFeAlSiO_6$ to $FATs_{80}Tp_{20}$ at 1 atm, indicating that the $CaTiAl_2O_6$ component can enter into the $CaFeAlSiO_6$-pyroxene structure (the compound $CaFeAlSiO_6$ is stable at 1 atm and has the clinopyroxene structure *C2/c* (Hijikata, 1968)): in other words, a clinopyroxene with $Si < Al_{IV}$ possibly exists.

In this paper we describe the results of a re-investigation of the phase relation in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ in air at 1 atm and the nature of anomalous clinopyroxene, and discuss the possibility of contravention to the aluminium avoidance principle.

Phase relation. Starting materials were prepared by sintering mixtures of TiO_2, Fe_2O_3, Al_2O_3, SiO_2, and $CaCO_3$ at 1200 °C for 14 days with intermediate crushing. The experiments were performed by the quenching method. The data given in Table I and the phase relations obtained from these data are shown in fig. 1. The duration of runs was 2-3 hours above 1350 °C, 5-6 hours around 1300 °C, and 7-14 days, sometimes 30-90 days, below 1250 °C.

In the $CaFeAlSiO_6$-rich portion clinopyroxene, perovskite, hibonite, and an *X*-phase were encountered and a liquidus for hibonite was confirmed. The *X*-phase occurs as prismatic crystals and shows distinct pleochroism (*X′* pale yellow, *Z′* reddish brown), weak birefringence, high relief, and straight extinction. A similar phase was first found by Hijikata and Onuma (1969) in the join $CaMgSi_2O_6$-$CaFeAlSiO_6$, and later Akasaka and Onuma (1978) in the join $CaMgSi_2O_6$-$CaFeAlSiO_6$-$CaTiAl_2O_6$, who gave an average composition $Ca_{1.9}\,Mg_{1.3}\,Fe^{3+}_{3.6}\,Al_{3.0}\,Ti_{0.2}\,Si_{1.4}\,O_6$. The *X*-phase obtained in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$, however, may be similar to that reported in the join $CaSiO_3$-Fe_2O_3-Al_2O_3 by Huckenholz *et al.* (1974) ($2CaO\cdot 4(Fe^{3+},Al)_2O_3\cdot SiO_2$), because both joins do not contain magnesium.

The hibonite has also a prismatic form and shows high relief, pleochroism (*X′* pale brown, *Z′* reddish brown), and straight extinction. Its *d*-spacings shift regularly with changing bulk composition, indicating this phase to be a solid solution. The hibonite obtained from the composition $FATs_{75}Tp_{25}$ at 1200 °C contains a considerable amount of iron (SiO_2 0.6, TiO_2 4.6, Al_2O_3 52.0, Fe_2O_3 34.1, CaO 7.5, and total 98.8 wt%). The ideal formula for the hibonite solid solution is therefore $CaAl_{12-x}Fe_xO_{19}$ with subordinate amount of Ti.

At subsolidus temperatures in the $CaFeAlSiO_6$-rich portion, fields of clinopyroxene single-phase and clinopyroxene + perovskite + hibonite are present. At 1275°C the clinopyroxene single-phase field attains $FATs_{81}Tp_{19}$ and this field diminishes

TABLE I. *Results of quenching experiments*

Composition (wt %)		Primary phase	Liquidus temp. (°C)	Data at low temperatures (°C)
FATs	Tp			
95	5	X	not. detd.	X+gl > 1300 > Cpx+X+gl > 1287 > Cpx only
90	10	Hib	1370	Hib+gl > 1327 > Hib+X+gl > 1323 > X+gl > 1303 > X+Cpx+gl > 1287 > Cpx only
87	13	Hib	not detd.	Hib+gl > 1315 > X+gl > 1299 > X+Cpx+gl > 1293 Cpx only
85	15	Hib	1380	Hib+gl > 1304 > Hib+Cpx+gl > 1288 > Cpx only
82	18	Hib	not detd.	Cpx only at 1250 & 1200
80	20	Hib	1388	Hib+gl > 1325 > Hib+X+gl > 1304 > Hib+Cpx+gl > 1275 > Hib+Cpx+Pv+gl > 1268 > Cpx+Pv+(Hib)
75	25	Hib	1395	Hib+gl > 1304 > Hib+X+gl > 1300 > Hib+Cpx+gl > 1278 > Hib+Cpx+Pv+gl > 1258 > Cpx+Pv+Hib (no gl)
72	28	Hib	not detd.	Cpx+Hib+gl > 1283 > Cpx+Hib+Pv+gl,Cpx+Hib+Pv+(An) (no gl) at 1200
70	30	Hib	1403	Hib+gl > 1294 > Hib+Cpx+gl > 1287 > Cpx+Hib+Pv+An?+gl,Cpx+Hib+Pv+An? (no gl) at 1200
68	32	Hib	not detd.	Hib+gl 1288 Hib+Cpx+Pv+gl
60	40	Hib	„	Hib+gl > 1394 > Hib+Pv+gl > 1287 > Hib+Pv+Cpx+gl, Hib+Cpx+Pv+(An) (no gl) at 1250
50	50	Hib	„	Hib+gl > 1369 > Hib+Pv+gl > 1287 > Hib+Pv+Cpx+gl, Cpx+Hib+Pv+An (no gl) at 1200 °C
40	60	not detd.	„	Hib+Pv+gl > 1285 > Hib+Pv+Cpx+(An)+gl > 1250 > Cpx+Hib+Pv+An (no gl)
30	70	„	„	Hib+Pv+Gl > 1264 > Hib+Pv+Cpx+(An)+gl > 1250 > Hib+Pv+Cpx+An (no gl)
20	80	„	„	Hib+Pv+(An)+gl > 1275 > Hib+Pv+An (no gl)
10	90	„	„	Hib+Pv+(An)+gl 1315 Hib+Pv+Cd+An+gl > 1290 > Hib+Pv+Cd+An (no gl)

above this temperature. This fact indicates that the $CaFeAlSiO_6$-pyroxene incorporates the $CaTiAl_2O_6$ component at least up to 19 wt %. This clinopyroxene solid solution melts incongruently to *X*-phase + liquid or hibonite + liquid (fig. 1). In the central portion of the phase diagram, large fields of hibonite + liquid at high temperature and clinopyroxene + hibonite + perovskite at subsolidus temperatures are present, and between these fields the assemblage clinopyroxene + hibonite + perovskite + liquid was confirmed.

In the $CaFeAlSiO_6$-poor portion, the assemblages clinopyroxene + perovskite + hibonite + anorthite (in the composition $FATs_{50}Tp_{50}$, $FATs_{40}Tp_{60}$, and $FATs_{30}Tp_{70}$), perovskite + hibonite + anorthite (in the composition of $FATs_{20}Tp_{80}$), and perovskite + hibonite + corundum + anorthite (in the composition of $FATs_{10}Tp_{90}$) were encountered at subsolidus temperatures. The anorthite is formed by the reaction:

$$2CaFeAlSiO_6 + 5CaTiAl_2O_6 = \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{perovskite}}{5CaTiO_3} + \underset{\text{hibonite}}{CaAl_{10}Fe_2O_{19}}.$$

The assemblages including anorthite above the solidus (except perovskite + hibonite + corundum + liquid) were estimated from those of neighbouring fields, because the anorthite is sometimes difficult to identify with the microscope or by X-ray diffraction. In such a case the anorthite is shown in parenthesis in the phase diagram (fig. 1).

Since at low temperature the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ is regarded as a part of the five-component system CaO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2, the assemblages clinopyroxene + hibonite + perovskite + anorthite + liquid and hibonite + perovskite + corundum + anorthite + liquid are univariant, and as indicated by the subsolidus assemblages, crystallization ceases on the univariant line or on the divariant surface, because clinopyroxene and hibonite form solid solutions.

Clinopyroxene solid solutions. The X-ray diffraction patterns of the clinopyroxene solid solutions synthesized in this study at 1200 °C for 30 days, were compared with those of $CaFeAlSiO_6$-pyroxene indexed in the space group *C2/c* (the powder pattern data were published elsewhere

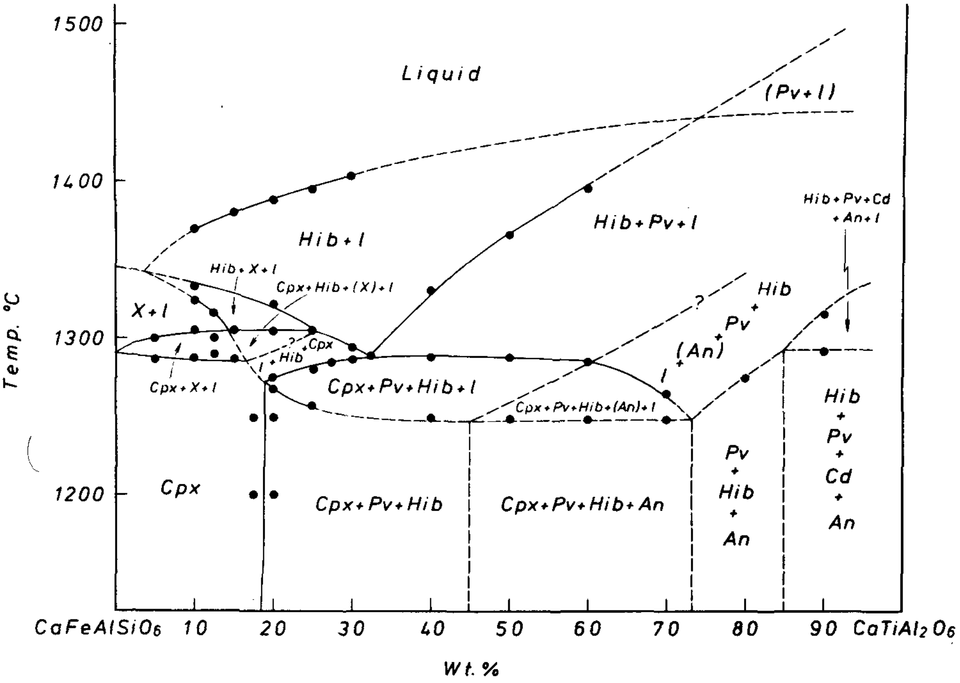

FIG. 1. Phase diagram of the join $CaFeAlSiO_6$-$CaTiAl_2O_6$. Cpx, clinopyroxene solid solution; Hib, hibonite solid solution; X, X-phase; Pv, perovskite; Cd, corundum; An, anorthite.

(Onuma and Akasaka, 1979)). The unit-cell parameters of $CaFeAlSiO_6$-pyroxene were recalculated on the basis of the X-ray powder diffraction data obtained by Hijikata (1968) with the following results: a 9.785, b 8.783, c 5.364 Å, β 105.84°, V 443.5 Å^3.

The cell parameters change linearly with an increase of the $CaTiAl_2O_6$ component up to 25 wt%; a(0.018 Å/10%Tp), c(0.009 Å/10%Tp), and V(1.6 Å^3/10%Tp) increase and b(−0.001 Å/10%Tp) decreases slightly (Table II, fig. 2). There are, however, discontinuities in the curves between $FATs_{75}Tp_{25}$ and $FATs_{72}Tp_{28}$, and all the cell-parameters decrease with the bulk composition of the join, indicating that the nature of solid solution changes.

The compositions of these clinopyroxene solid solutions were analysed with the microprobe (Table III). The clinopyroxenes crystallized from the starting materials of $FATs_{85}Tp_{15}$ and $FATs_{82}Tp_{18}$ have the same compositions as those of the starting materials (Table III) within experimental error, supporting the result of quenching experiment which show only clinopyroxene solid solution as the stable phase in this field. The $CaTiAl_2O_6$ component in the clinopyroxene increases beyond the single-phase field and attains 23 wt% (Table III).

It is noted that the clinopyroxene solid solutions are extremely poor in SiO_2 and extremely rich in Al_2O_3, Fe_2O_3, and TiO_2, and when the atomic ratios are calculated on the basis of $O = 6$, Si in the tetrahedral sites is < 1 per formula unit (Table III).

In the experimental study of the $3MnO \cdot Al_2O_3 \cdot 3SiO_2$-$3Y_2O_3 \cdot 5Al_2O_3$ system, Yoder and Keith (1951) showed that the complete substitution of aluminium for silicon in an orthosilicate. Forman (1951) reported a xanthophyllite which has more aluminium than silicon in the tetrahedral sites (Al/Si = 2.8/1.2). However, clinopyroxene with Si < Al has never been found in natural rocks or in synthetic systems.

Discussion. As described above, the clinopyroxene in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ are extremely poor in SiO_2 and rich in Al_2O_3, and Si in tetrahedral sites is < 1 per formula unit. If the deficiency of Si is compensated by Al, more than half of the tetrahedral sites are occupied by Al. This assumption contravenes the aluminium avoidance principle. To avoid this contravention, the distribution of Ti in tetrahedral sites must be assumed to make $Si + Ti = 1$ per formula unit. Hartman (1969), however, claimed that the relative preference of Al, Fe^{3+}, and Ti for the tetrahedral sites in silicate is demonstrated to be in the order

TABLE II. *Unit-cell parameters of the clinopyroxenes crystallized at 1210 °C for 30 days in the system* $CaFeAlSiO_6$-$CaTiAl_2O_6$

Composition (wt %)						
FATs	Tp	*a*(Å)	*b*(Å)	*c*(Å)	*β*(°)	*V*(A³)
100	0	9.785(2)	8.783(1)	5.364(2)	105.84(3)	443.5(2)
85	15	9.812(4)	8.776(1)	5.377(2)	105.78(4)	445.6(3)
82	18	9.819(5)	8.777(1)	5.381(2)	105.74(4)	446.3(3)
80	20	9.821(2)	8.781(1)	5.383(1)	105.69(3)	446.9(2)
75	25	9.828(1)	8.780(1)	5.386(1)	105.71(2)	447.4(1)
72	28	9.816(2)	8.767(1)	5.320(1)	105.73(2)	445.6(2)
70	30	9.805(3)	8.766(1)	5.376(1)	105.78(4)	444.7(2)
60	40	9.803(5)	8.769(1)	5.377(2)	105.88(4)	444.6(2)
50	50	9.803(4)	8.767(1)	5.374(2)	105.92(4)	444.1(2)

FATs = $CaFeAlSiO_6$. Tp = $CaTiAl_2O_6$.

TABLE III. *Compositions of the clinopyroxenes crystallized at 1200 °C for 30 days in the join* $CaFeAlSiO_6$-$CaTiAl_2O_6$

Bulk comp. (wt %)	FATs 85 Tp 15 Cpx		FATs 82 Tp 18 Cpx		FATs 80 Tp 20 Cpx + Pv + (Hib?)		FATs 75 Tp 25 Cpx + Pv + Hib		FATs 70 Tp 30 Cpx + Pv + Hib	
phase assemb.	S.M.	Cpx	S.M.	Cpx	S.M.	Cpx	S.M.	Cpx	S.M.	Cpx
SiO_2	20.68	20.50	19.95	20.00	19.46	19.84	18.25	19.17	17.03	19.18
TiO_2	5.04	5.23	6.04	5.94	6.72	6.60	8.39	7.58	10.07	7.68
Al_2O_2	23.97	23.44	24.64	24.50	25.08	24.87	26.19	25.72	27.30	26.79
Fe_2O_3	27.49	26.44	26.51	26.35	25.86	25.58	24.25	23.98	22.62	22.96
CaO	22.83	22.46	22.86	22.91	22.88	22.45	22.92	22.77	22.77	22.88
Total		98.07		99.70		99.34		99.22		99.49
Cations per 6 oxygens										
Si		0.85		0.82		0.81		0.78		0.78
Al^{IV}		1.15		1.18		1.19		1.22		1.22
		2.00		2.00		2.00		2.00		2.00
Al^{VI}		0.00		0.00		0.01		0.02		0.06
Ti		0.16		0.18		0.20		0.23		0.23
Fe^{3+}		0.83		0.81		0.79		0.74		0.70
Ca		1.00		1.01		0.99		1.00		1.00
		1.99		2.00		1.99		1.99		1.99
End-member components										
FATs		83.7		81.8		79.7		74.8		71.4
Tp		15.7		17.7		19.8		22.8		23.0
CaTs		−0.3		0.2		0.3		1.6		5.0
Total		99.3		99.7		99.8		99.2		99.4

$Al \geqslant Fe^{3+} > Ti$. Later this suggestion was supported by Huggins *et al.* (1977) in their study of synthetic titanium garnet, and if this holds for clinopyroxene the Si-deficiency should be compensated by Al and Fe^{3+} rather than by Ti.

The clinopyroxene crystals obtained in this study, however, are too small in size to carry out a structural analysis. Therefore, cell parameters were used to estimate the type of substitution. The *c* parameter is affected by both cation distribution in tetrahedral sites and $M1/M2$ sites (Peacor, 1967), but the former is more sensitive to change (Sakata, 1957; Clark *et al.*, 1962). Sakata gave the change in *c* parameter for each 0.1 Al per formula unit + 0.008 Å. Onuma *et al.* (1968) demonstrated that the change in *c* parameter by $Si \rightleftharpoons Ti$ substitution in the $CaMgSi_2O_6$–$CaMgTi_2O_6$ is 0.0039 Å/1 wt % $CaMgTi_2O_6$, which corresponds to 0.033 Å for each 0.1 Ti per formula unit. The change in *c* parameter of the clinopyroxene obtained in this study is 0.009 for each 0.1 Al and Ti per formula unit.

Comparing the data in this study with those of Sakata (1957) and Onuma *et al.* (1968), the value 0.009 is too small to assume the $Si \rightleftharpoons Ti$ substitution in tetrahedral sites and is very similar to the value 0.008 given by Sakata (1957) for $MgSi \rightleftharpoons AlAl$ substitution. If the cation distribution in tetrahedral sites is more effective to the change of *c* parameter than that in $M1$ sites, the coupled substitution $Fe^{3+}Si \rightleftharpoons TiAl$ is the more probable cause of the Si deficiency in tetrahedral sites than the $Si \rightleftharpoons Ti$ substitution.

In our previous study on the join $CaMgSi_2O_6$–$CaFeAlSiO_6$–$CaTiAl_2O_6$ (Akasaka and Onuma, 1980), we also showed that the Si deficiency in the tetrahedral sites is compensated by Al, resulting in formation of clinopyroxene with Si < 1 per formula unit.

In the clinopyroxene obtained in this study, since sufficient Al is present to compensate for Si deficiency in the tetrahedral sites, Ti^{4+} and Fe^{3+} are indicated as being placed in octahedral sites. Some workers pointed out that the $CaFeAlSiO_6$-pyroxene, because ferric iron occupies tetrahedral sites, should be expressed as $Ca(Fe^{3+}_{1-x}Al_x)^{IV}(Al_{1-x}Fe^{3+})^{IV}SiO_6$ (Ohashi and Hariya, 1973; Huckenholz *et al.*, 1974). The results of the structural analysis of the $CaFeAlSiO_6$-pyroxene (Ghose *et al.*, 1975) or Al-pyroxene from Oka (Peacor, 1967), however, indicate that essentially all the tetrahedral sites are occupied by Si and Al with negligible amount of Fe^{3+} and Ti^{4+}.

The clinopyroxenes obtained in this study could be completely indexed in the space group $C2/c$ as shown before. Indexing the aluminous pyroxene as $C2/c$ requires complete Al–Si disorder on tetrahedral site (Peacor, 1967; Okamura *et al.*, 1974; Wood and Henderson, 1978) and hence contravenes the aluminium avoidance principle.

Okamura *et al.* (1974) stated: there are domains with short-range Al–Si order in $CaAl_2SiO_6$ clinopyroxene, and random distribution of Al and Si among tetrahedral sites does not necessarily mean that the aluminium avoidance rule is violated. Wood (1976) on the basis of thermodynamical analysis suggested that Al–Si order is implied in the tetrahedral sites of $CaMgSi_2O_6$–$CaAl_2SiO_6$ clinopyroxene series. Newton *et al.* (1977) also suggested that there is some Al–Si order at the $CaAl_2SiO_6$ end of the $CaMgSi_2O_6$–$CaAl_2SiO_6$ series.

The clinopyroxenes in this study, however, have excess Al in tetrahedral sites, and therefore despite the above suggestion, the result in this study indicates that the aluminium avoidance principle is violated in the clinopyroxene with $Si < Al_{IV}$.

Recently a notable study in this line was carried out by Ohashi *et al.* (1979), which strongly supports our conclusion. They made a structural analysis of a clinopyroxene having the composition of $Ca_{1.00}Sc_{0.84}Ti_{0.27}Al_{1.16}Si_{0.73}O_6$, and demonstrated that this clinopyroxene belongs to the space group $C2/c$ and the tetrahedral sites are occupied by 36.5 atomic % Si, 58 % Al, and only 5.5 % Ti which are distributed in a completely disordered state. They concluded on the basis of this fact that the Al-O-Al bond exists in this pyroxene and the aluminium avoidance principle is violated.

Thus in the single-phase field of clinopyroxene solid solution, all the $CaTiAl_2O_6$ component enters into the $CaFeAlSiO_6$-pyroxene structure with the $Fe^{3+}Si \rightleftharpoons TiAl$ substitution and the cell parameters change linearly. In the clinopyroxene + perovskite + hibonite field, perovskite, hibonite, and $CaAl_2SiO_6$ component are formed by the following reaction and the $CaAl_2SiO_6$ component enters into the clinopyroxene structure in addition to the $CaTiAl_2O_6$ component:

$$2CaFeAlSiO_6 + 4CaTiAl_2O_6 = 2CaAl_2SiO_6 + \underset{\text{perovskite}}{3CaTiO_3} + \underset{\text{hibonite}}{(CaO + 3Al_2O_3 + 2Fe_2O_3 + TiO_2)}$$

The amounts, however, are too small to produce an effect on the variation trends of the cell parameters.

The clinopyroxene in the composition $FATs_{70}Tp_{30}$, which crystallized as clinopyroxene + hibonite + perovskite at 1200 °C, has the $CaAl_2SiO_6$ component (Table III), and the Al_{IV}/Si ratios in the tetrahedral sites of the clinopyroxenes crystallized from the compositions of $FATs_{75}Tp_{25}$ and $FATs_{70}Tp_{30}$ are the same, suggesting that the $Fe^{3+}Si \rightleftharpoons TiAl$ substitution reaches a maximum at

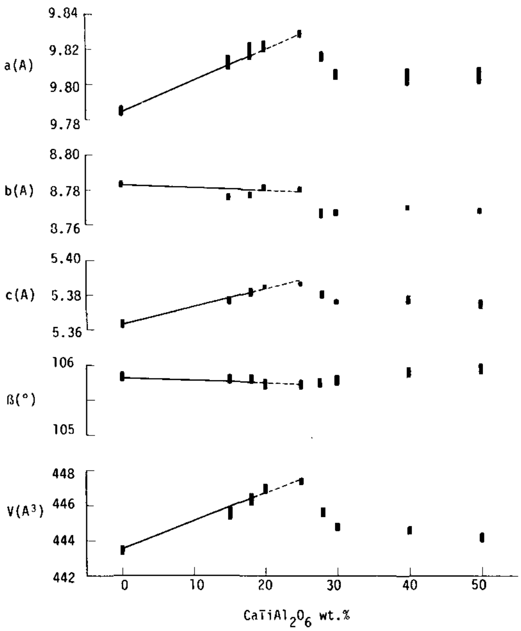

FIG. 2. Unit-cell parameters of the clinopyroxene solid-solution in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$ crystallized at 1210 °C for 30 days.

the composition of $FATs_{75}Tp_{25}$, and in the region richer in the $CaTiAl_2O_6$ component than this composition only the $Fe^{3+} \rightleftharpoons Al$ substitution in *M*1 sites occurs and this may be a cause of the decrease of cell parameters (fig. 2). Huckenholz *et al.* (1974) showed that the entrance of the $CaAl_2SiO_6$ component into the $CaFeAlSiO_6$-pyroxene decreases the cell parameters considerably. In the clinopyroxene + hibonite + perovskite + anorthite assemblage, the $CaAl_2SiO_6$ component is also expected from the following reaction:

$$4CaFeAlSiO_6 + 4CaTiAl_2O_6 = CaAl_2SiO_6 + \underset{\text{perovskite}}{4CaTiO_3} + \underset{\text{hibonite}}{CaAl_8Fe_4O_{19}} + \underset{\text{anorthite}}{CaAl_2Si_2O_8}$$

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