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PRELIMINARY REPORT ON THE JOIN $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ AT LOW OXYGEN FUGACITY

by

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(with 2 tables and 6 text-figures)

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Abstract

The join $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ was studied by the ordinary quenching method at 10^{-9}, 10^{-10}, and 10^{-11} atm f_{O_2}. The solubility limit of $CaFe^{3+}AlSiO_6$ in diopside is 20 mol.% at 1100°C and 10^{-9} atm f_{O_2}, 10 mol.% at 1100°C and 10^{-10} atm f_{O_2}, and 5 mol.% at 1000°C and 10^{-11} atm f_{O_2}. The temperature of upper limit for clinopyroxene(ss) single phase field decrease with decreasing f_{O_2}. The phase assemblages below the solidus temperatures in this join change as follows with increasing $CaFe^{3+}AlSiO_6$: clinopyroxene(ss), clinopyroxene(ss) + melilite, clinopyroxene(ss) + melilite + spinel(ss), clinopyroxene(ss) + melilite + spinel(ss) + anorthite. The composition of clinopyroxene(ss) crystallized from the composition Di(50)FATs(50) at 1100°C, 10^{-10} atm f_{O_2} is $Ca_{0.96}$ $(Mg_{0.48}Fe^{2+}_{0.12}Fe^{3+}_{0.26}Al_{0.14})(Al_{0.44}Si_{1.56})O_6$.

Introduction

$CaFe^{3+}AlSiO_6$ (FATs), as well as $CaAl_2SiO_6$ (CaTs) and $CaTiAl_2O_6$ (Tp), is an important constituent molecule of fassaitic pyroxene. Significance of the experimental work on the system containing this molecule has been pointed out by Onuma and Yagi (1971) and Huchenholz (1973). The join $CaMgSi_2O_6$ (Di)-FATs(Hijikata and Onuma, 1969) and the join Di-CaTs-FATs(Onuma and Yagi, 1975) were studied in air. The former join forms continuous solid solution of clinopyroxene between end-members. In the latter, CaTs content in diopside increases with increasing FATs. Oxygen fugacity, however, may give an effect on FATs content in clinopyroxene. The present paper is a brief report on the change of FATs content in clinopyroxene as a function of oxygen fugacity. Detailed discussion and petrological implication will be given elsewhere.

Experimental Results And Discussions

The gas mixture of H_2 and CO_2 was used to control oxygen fugacity. Samples were charged in $Pt_{60}Rh_{40}$ envelope and quenched into mercury. Both

glasses and clinopyroxenes(ss) were used as starting materials. These starting materials were made in air by Hijikata and Onuma (1969). The experimental results obtained by using these different starting materials are consistent to each other.

The results of quenching experiments are given in Table 1. The phase equilibrium diagrams at 10^{-9}, 10^{-10}, and 10^{-11} atm f_{O_2} are shown in Figs. 1,

Table 1 Results of quenching experiments for the system
$CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ at 10^{-9}, 10^{-10} and 10^{-11} atm f_{O_2}

Composition (mole %)		Starting material	Temp. (°C)	Time (hrs.)	Results
Di	FATs		$f_{O_2}=10^{-9}$ atm		
90	10	Gl	1155	2	Cpx only
		Xl	1155	2	Cpx only
		Xl	1165	3	Cpx+Mel
		Gl	1250	6	Cpx+Mel
80	20	Gl	1110	6	Cpx only
		Xl	1110	6	Cpx only
		Xl	1125	4	Cpx+Mel
		Gl	1200	9½	Cpx+Mel
		Xl	1220	3	Cpx+trace Gl
		Gl	1250	6	Cpx+Gl
70	30	Xl	1165	3	Cpx+Mel
		Xl	1180	4	Cpx+Mel+Gl
		Xl	1220	3	Cpx+Gl
60	40	Xl	1125	4	Cpx+Mel
		Gl	1150	6½	Cpx+Sp+trace Mel+trace Gl
		Gl	1200	9½	Cpx+Gl
		Xl	1280	1	trace Cpx+Gl
50	50	Xl	1125	4	Cpx+Mel
		Xl	1180	3	Cpx+Sp+Mel+Gl
		Gl	1200	9½	trace Cpx+Gl
		Gl	1250	3	Gl
40	60	Xl	1125	4	Cpx+Mel
		Gl	1200	9½	Sp+trace Cpx+Gl
		Xl	1220	3	trace Sp+trace Cpx+Gl
		Gl	1250	3	Gl
30	70	Gl	1150	8	Cpx+Sp+An+Mel+Gl
		Gl	1200	8½	Sp+An+Mel+Gl
		Xl	1220	3	Sp+An+Mel+Gl
		Xl	1235	1	Sp+Gl
		Xl	1280	1	Sp+Gl
20	80	Xl	1125	4	Cpx+Sp+Mel
		Xl	1180	3	Cpx+Mel+An+Sp+Gl
		Xl	1235	1	Sp+trace Mel+trace An+Gl
		Gl	1250	1	Sp+trace Mel+Gl
		Xl	1280	1	Sp+Gl
10	90	Xl	1125	6	Cpx+Sp+Mel+An
		Xl	1155	2	Sp+An+trace Cpx+trace Mel+Gl
		Xl	1260	2	Mel+Sp

2, and 3, respectively. Clinopyroxene(ss) (ss: solid solution), melilite, spinel(ss) and anorthite are encountered throughout the experimental conditions. A maximum phase assemblage obtained in the present study is clinopyroxene(ss) + melilite + spinel(ss) + anorthite + liquid + gas showing univariant assemblage

Table 1 (continued)

Composition (mole %)		Starting material	Temp. ($^\circ$C) $f_{O_2}=10^{-10}$ atm	Time (hrs.)	Results
Di	FATs				
90	10	Gl	1110	10	Cpx only
		Xl	1110	10	Cpx only
		Gl	1120	5	Cpx+Mel
		Xl	1120	5	Cpx+Mel
		Xl	1260	2	fritted cake, Cpx+Mel
		Xl	1275	2	Cpx+Gl
80	20	Gl	1065	8	Cpx only
		Xl	1065	8	Cpx only
		Xl	1070	8	Cpx+Mel
		Xl	1210	3	fritted cake, Cpx+Mel
		Xl	1215	2	Cpx+Mel+trace Gl
		Gl	1250	5	Cpx+trace Mel+Gl
		Xl	1260	2	Cpx+Gl
75	25	Gl	1240	2	Cpx+trace Gl
70	30	Xl	1170	3½	Cpx+Mel
		Xl	1180	6	Cpx+Mel+trace Gl
		Xl	1240	2	Cpx+Gl
		Xl	1320	1½	trace Cpx+Gl
60	40	Xl	1140	3	Cpx+Mel
		Gl	1150	5	Cpx+Mel+Gl
		Xl	1225	3	Cpx+Gl
		Gl	1225	5	Cpx+Gl
		Xl	1275	2	trace Cpx+Gl
		Xl	1290	2	Gl
50	50	Xl	1115	5	well fritted, Cpx+Mel
		Gl	1120	5	Cpx+trace Mel+Gl
		Xl	1180	6	Cpx+Mel+Sp+Gl
		Gl	1200	8½	Cpx+Gl
		Xl	1240	2	trace Cpx+Gl
		Xl	1245	3	Gl
40	60	Xl	1115	5	well fritted, Cpx+Mel+Sp
		Xl	1120	5	Cpx+Mel+Sp+trace Gl
		Xl	1170	3½	Sp+trace Cpx+trace Mel+Gl
		Gl	1200	8	Sp+Gl
		Xl	1270	2	trace Sp+trace An+Gl
		Xl	1275	2	Gl
30	70	Gl	1100	6	Cpx+Mel+Sp
		Xl	1190	3½	Cpx+Sp+trace An+Gl
		Xl	1245	3	Sp+trace An+Gl
		Xl	1275	2	Sp+An+Gl
		Xl	1280	1	trace Sp+Gl
		Xl	1300	1	trace Sp+Gl
		Xl	1310	2	Gl

in the six-component system $Fe-O-CaO-MgO-Al_2O_3-SiO_2$. It is surrounded by four five-phase assemblages; clinopyroxene(ss) + melilite + spinel(ss) + an-

Table 1 (continued)

Composition (mole %)		Starting material	Temp. (°C)	Time (hrs.)	Results
Di	FATs		$f_{O_2}=10^{-10}$ atm		
20	80	Gl	1100	6	Cpx+Mel+Sp+An
		Xl	1110	5	Sp+An+Mel+trace Cpx+Gl
		Xl	1170	3½	Sp+An+Mel+Gl
		Xl	1290	2	Sp+trace An+trace Mel+Gl
		Xl	1300	1	Sp+trace Mel+Gl
		Xl	1320	1½	Sp+trace Mel+Gl
10	90	Xl	1120	5	Sp+An+Mel+trace Cpx+Gl
		Xl	1130	5	Sp+An+Mel+trace Cpx+Gl
		Xl	1140	5	Sp+Mel+trace An+Gl
		Xl	1290	2	Mel+An+trace Sp+Gl
		Xl	1300	1	trace Sp+trace Mel+Gl
			$f_{O_2}=10^{-11}$ atm		
90	10	Gl	1040	6	Cpx only
		Xl	1040	6	Cpx only
		Gl	1045	5	Cpx+Mel
		Xl	1045	5	Cpx+Mel
		Xl	1260	2	Cpx+Mel
		Xl	1270	2	Cpx+Mel+trace Gl
80	20	Gl	1000	8	Cpx+Mel
		Gl	1200	7	fritted, Cpx+Mel
		Xl	1210	3	Cpx+Mel+trace Gl
80	20	Xl	1260	2	Cpx+Mel+trace Gl
		Xl	1270	2	Cpx+trace Gl
70	30	Gl	1150	7½	fritted, Cpx+Mel
		Gl	1160	3	Cpx+Mel+trace Gl
		Xl	1160	3	Cpx+Mel+trace Gl
		Xl	1240	1	Cpx+Mel+Gl
		Gl	1250	9	Cpx+Gl
60	40	Gl	1100	17½	Cpx+Mel
		Xl	1225	5	Cpx+Mel+Gl
		Xl	1270	2	Cpx+Gl
50	50	Xl	1060	5	Cpx+Mel
		Gl	1075	12	Cpx+Sp+Mel+Gl
		Xl	1160	3	Cpx+Mel+trace Sp+Gl
		Gl	1170	8	Cpx+Mel+Gl
		Xl	1170	8	Cpx+Mel+Gl
		Xl	1210	3	Cpx+Mel+Gl
		Xl	1220	3	Cpx+Gl
		Xl	1240	1	trace Cpx+Gl
		Gl	1250	4	Gl
40	60	Xl	1060	5	Cpx+Mel
		Gl	1200	9½	Cpx+trace Mel+trace Sp+Gl
		Xl	1210	3	Sp+An+Mel+Gl
		Xl	1220	3	Sp+An+Gl
		Gl	1250	4	trace Sp+trace An+Gl
		Xl	1260	2	trace Sp+Gl
		Xl	1270	2	Gl

Table 1 (continued)

Composition (mole %)		Starting material	Temp. (°C)	Time (hrs.)	Results
Di	FATs				
30	70	Gl	1075	12	Cpx+Mel+Sp
		Xl	1190	3	Sp+Mel+trace An+Gl
		Xl	1220	3	Sp+An+trace Mel+Gl
		Gl	1225	5	Sp+An+Gl
30	70	Xl	1270	2	trace Sp+Gl
20	80	Xl	1060	5	Cpx+Mel+Sp
		Xl	1160	3	Sp+Mel+trace An+trace Cpx+Gl
		Xl	1170	3	Sp+Mel+An+Gl
		Gl	1260	2	Mel+trace Sp+trace An+Gl
		Xl	1260	2	Mel+trace Sp+trace An+Gl
		Xl	1270	2	Sp+trace An+Gl
10	90	Xl	1050	5	Cpx+Sp+Mel+An
		Xl	1120	3	Cpx+Sp+Mel+An+Gl
reversal runs in air					
80	20	Cpx+Gl	1200	336	Cpx only
70	30	Cpx+Mel	1200	168	Cpx only
		Cpx+Mel+Gl	1200	336	Cpx only
60	40	Cpx+Mel	1200	168	Cpx only
50	50	Cpx+Mel+Gl	1200	336	Cpx only
40	60	Cpx+Mel+Sp+Gl	1200	336	Cpx only
20	80	Cpx+Mel+Sp+An	1200	672	Cpx only

Cpx = clinopyroxene, Mel = melilite, An = anorthite, Sp = spinel, Gl = glass.
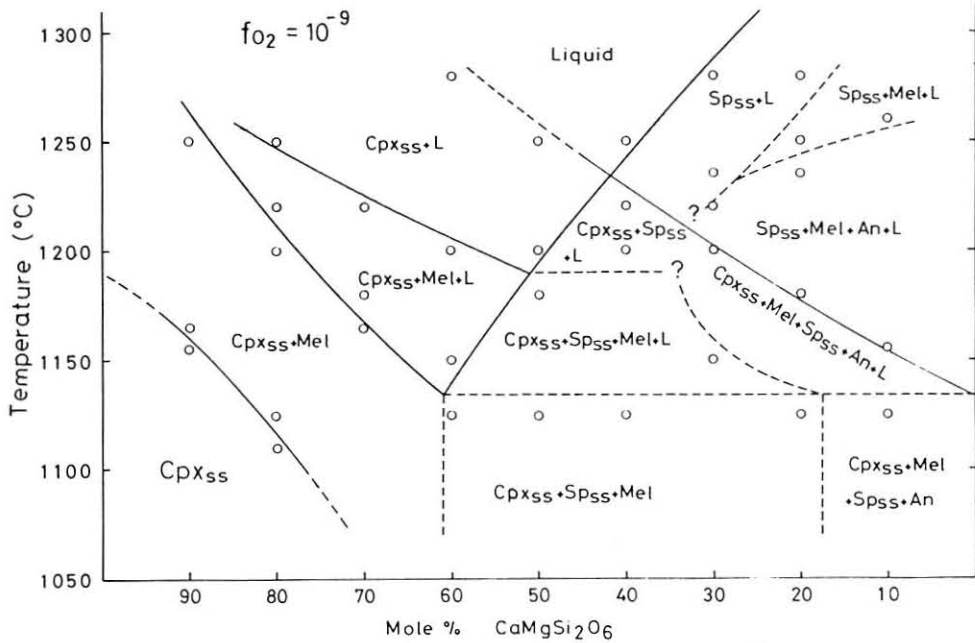
Fig. 1 Phase diagram of the join CaMgSi$_2$O$_6$-CaFe^{3+}AlSiO$_6$ at 10^{-9} atm f$_{O_2}$. Abbreviations are the same as in Table 1.

orthite + gas, clinopyroxene(ss) + melilite + spinel(ss) + liquid + gas, melilite + spinel(ss) + anorthite + liquid + gas, and clinopyroxene(ss) + spinel(ss) + anorthite + liquid + gas. When FATs content in this join increases, the phase assemblage at subsolidus temperatures changes as follows: clinopyroxene(ss), clinopyroxene(ss) + melilite, clinopyroxene(ss) + melilite + spinel(ss), clinpyroxene(ss) + melilite + spinel(ss) + anorthite. Di and FATs form a complete solid solution in air at 1 atm (Hijikata and Onuma, 1969), but the solubility of FATs in diopside has limit at low oxygen fugacity. The solubility of FATs in diopside decreases with increasing temperature as shown in Figs. 1, 2, and 3. At higher temperature clinopyroxene(ss) breaks down by the following reaction:

$$CaMgSi_2O_6 + CaFe^{3+}AlSiO_6 = CaFe^{2+}Si_2O_7 + MgSiO_3 + \tfrac{1}{2}Al_2O_3 + \tfrac{1}{4}O_2$$
<div align="center">iron-akermanite</div>
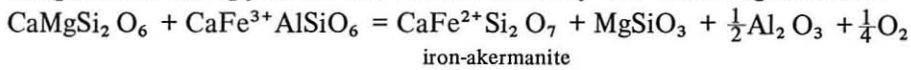
Melilite including iron-akermanite molecule appears and $MgSiO_3$ and Al_2O_3 enter into clinopyroxene(ss) as probably Mg-Tschermak's molecule.
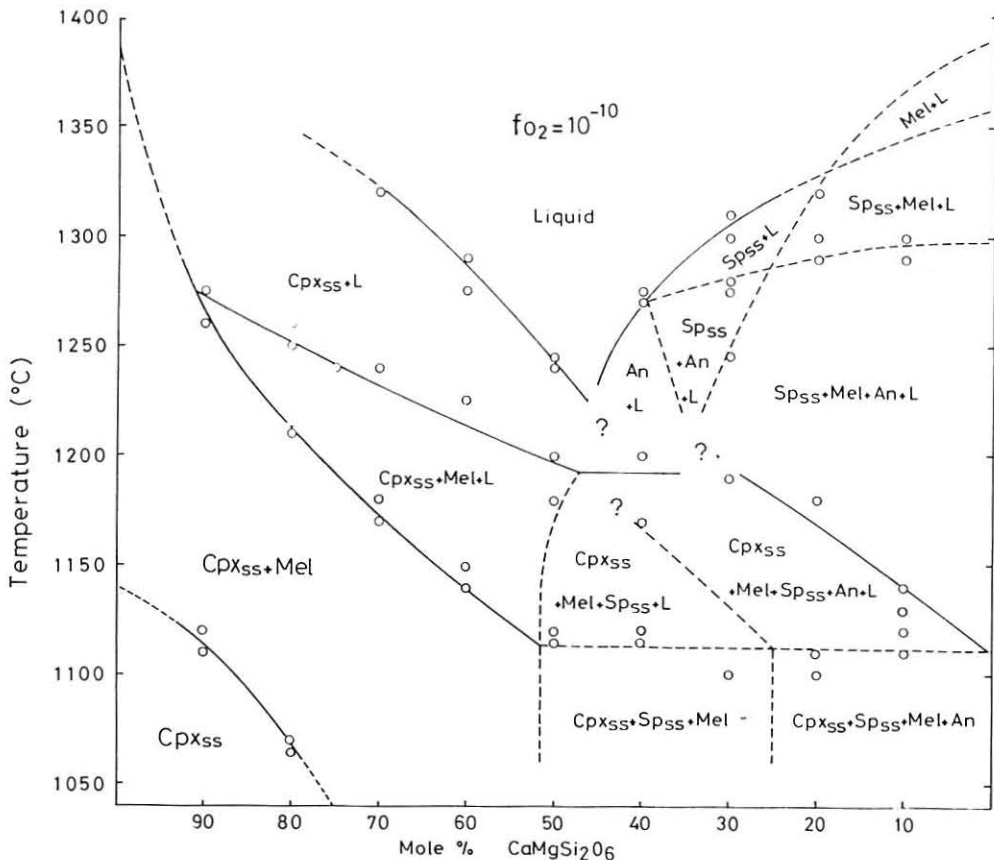
Fig. 2 Phase diagram of the system $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ at 10^{-10} atm f_{O_2}. Abbrevations are the same as in Table 1.
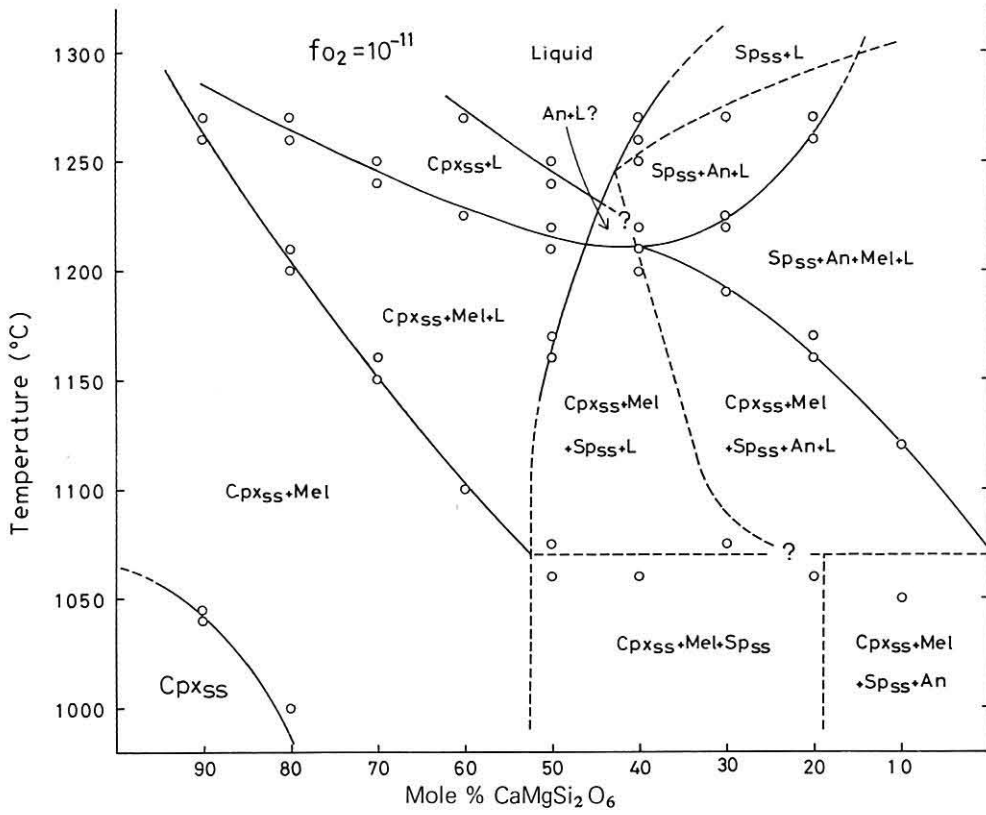
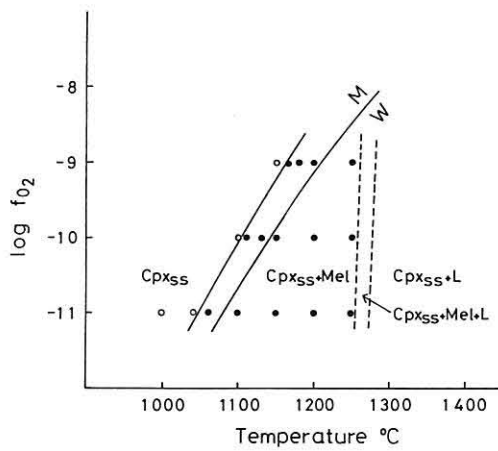**Fig. 3** Phase diagram of the join $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ at 10^{-11}. Abbrevations are the same as in Table 1.

Fig. 4 Log f_{O_2} -T diagram for the $Di_{90}FATs_{10}$ bulk composition. M = magnetite, W = wüstite.
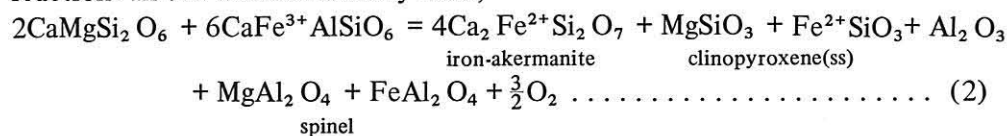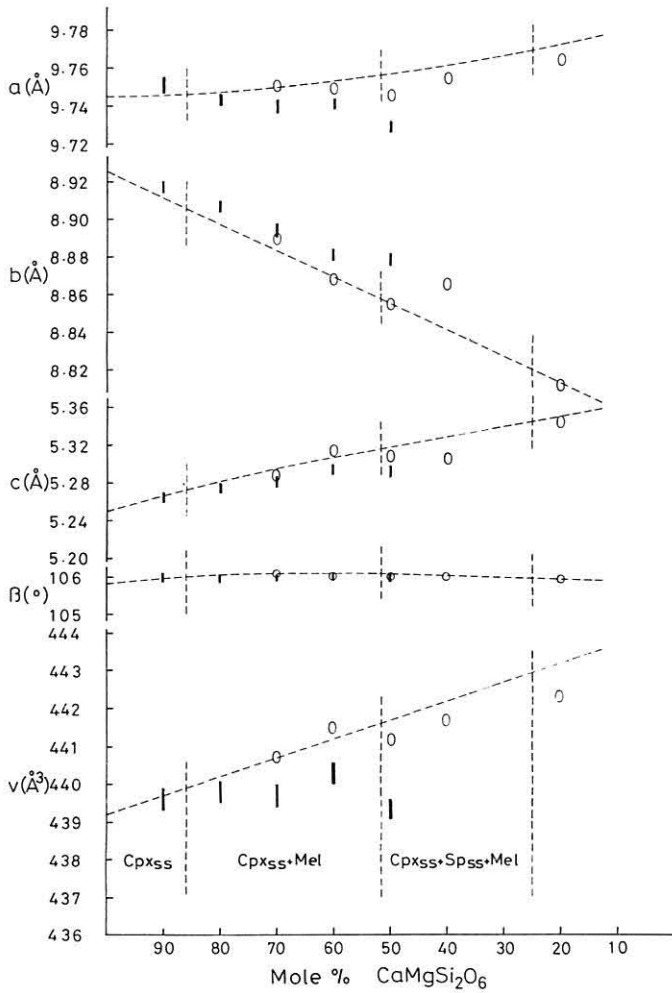
The solubility limit of FATs in diopside is as follows: 20 mol.% at 1100°C, 10^{-9} atm; 10 mol.% at 1100°C, 10^{-10} atm; and 5 mol.% at 1050°C, 10^{-11}. The temperature of upper limit for clinopyroxene(ss) single phase field decreases with decreasing oxygen fugacity and the relationship between this temperature and oxygen fugacity is shown in Fig. 4.

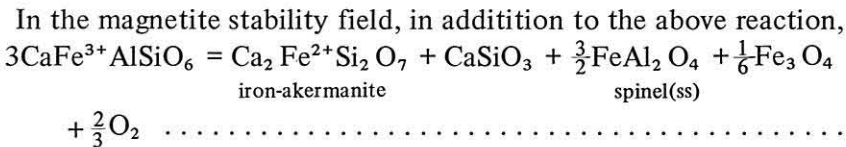**Table 2**   Unit-cell dimensions of clinopyroxene solid solutions

Composition (mole %)		Temp. (°C)	f_{O_2} atm	a(Å)	b(Å)	c(Å)	β(°)	V(Å³)
Di	FATs							
90	10	1100	10^{-10}	9.746(3)	8.917(3)	5.262(3)	105.95(3)	439.7(3)
		1100	10^{-11}	9.751(3)	8.920(3)	5.253(3)	105.92(3)	439.3(3)
80	20	1100	10^{-10}	9.743(3)	8.906(3)	5.272(2)	105.92(3)	439.8(3)
		1100	10^{-11}	9.739(3)	8.905(3)	5.273(3)	105.93(3)	439.6(3)
70	30	1100	10^{-10}	9.470(3)	8.894(3)	5.280(3)	105.95(3)	439.7(3)
		1100	10^{-11}	9.738(3)	8.893(3)	5.284(3)	105.96(3)	440.0(3)
60	40	1100	10^{-10}	9.470(3)	8.881(3)	5.293(3)	105.95(3)	440.3(3)
		1100	10^{-11}	9.736(3)	8.883(3)	5.282(3)	105.97(3)	439.2(3)
50	50	1100	10^{-10}	9.729(3)	8.878(3)	5.290(3)	105.95(3)	439.3(3)
		1100	10^{-11}	9.724(3)	8.884(3)	5.276(3)	106.00(3)	438.2(3)
40	60	1100	10^{-11}	9.714(3)	8.881(3)	5.276(3)	105.96(3)	437.8(3)
70	30	1200	in air	9.752(3)	8.889(3)	5.288(3)	106.03(3)	440.8(3)
60	40	1200	in air	9.750(3)	8.868(3)	5.313(3)	106.00(4)	441.6(3)
50	50	1200	in air	9.745(3)	8.855(3)	5.315(3)	106.01(3)	441.2(3)
40	60	1200	in air	9.754(3)	8.867(3)	5.303(3)	106.00(3)	441.7(3)
20	80	1200	in air	9.764(3)	8.811(3)	5.344(4)	105.96(3)	442.3(3)

The unit-cell dimensions of clinopyroxene(ss) in the present join are given in Table 2 and the variation against compositions is shown in Figs. 5 and 6. The dashed lines show the variation of the unit-cell dimensions of the clinopyroxene(ss) crystallized in air (Hijikata, 1968). The variation trend of the clinopyroxene(ss) in the single phase field agrees with that obtained in air. However, when clinopyroxene(ss) coexists with other phases, variation trends of *a* and *V* leave the dashed line and become to coincide with the variation of solid solution between Di and CaTs or $MgSiO_3$ molecule. This phenomenon means that FATs is no more stable and the nature of clinopyroxene(ss) changes. $MgSiO_3$ as well as $Fe^{2+}SiO_3$ is probably formed by the following reaction: In the wüstite stability field,

$$2CaMgSi_2O_6 + 6CaFe^{3+}AlSiO_6 = 4Ca_2Fe^{2+}Si_2O_7 + MgSiO_3 + Fe^{2+}SiO_3 + Al_2O_3$$
$$\text{iron-akermanite} \qquad \text{clinopyroxene(ss)}$$

$$+ MgAl_2O_4 + FeAl_2O_4 + \tfrac{3}{2}O_2 \dots\dots\dots\dots\dots\dots\dots (2)$$
$$\text{spinel}$$

Fig. 5 Unit-cell dimensions of the clinopyroxene crystallized at $1100°C$ and 10^{-10} atm f_{O_2}. The dashed lines: the variation of unit-cell dimensions of the clinopyroxene(ss) crystallized in air (Hijikata, 1968).
Bar: the present data of clinopyroxenes. open ellipse: the data of clinopyroxene obtained in a reversal experiment at $1200°C$ in air.

In the magnetite stability field, in addittion to the above reaction,

$$3CaFe^{3+}AlSiO_6 = Ca_2 Fe^{2+}Si_2 O_7 + CaSiO_3 + \tfrac{3}{2}FeAl_2 O_4 + \tfrac{1}{6}Fe_3 O_4$$

iron-akermanite   spinel(ss)

$$+ \tfrac{2}{3}O_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

From the equations (2) and (3), $CaFe^{2+}Si_2 O_6$ malecule is expected in the clinopyroxene(ss) in magnetite stability field. Unit-cell dimensions of melilite indicate that this mineral contains a considerable amount of iron akermanite. Seifert (1973) reported that ferroakermanite component can enter into
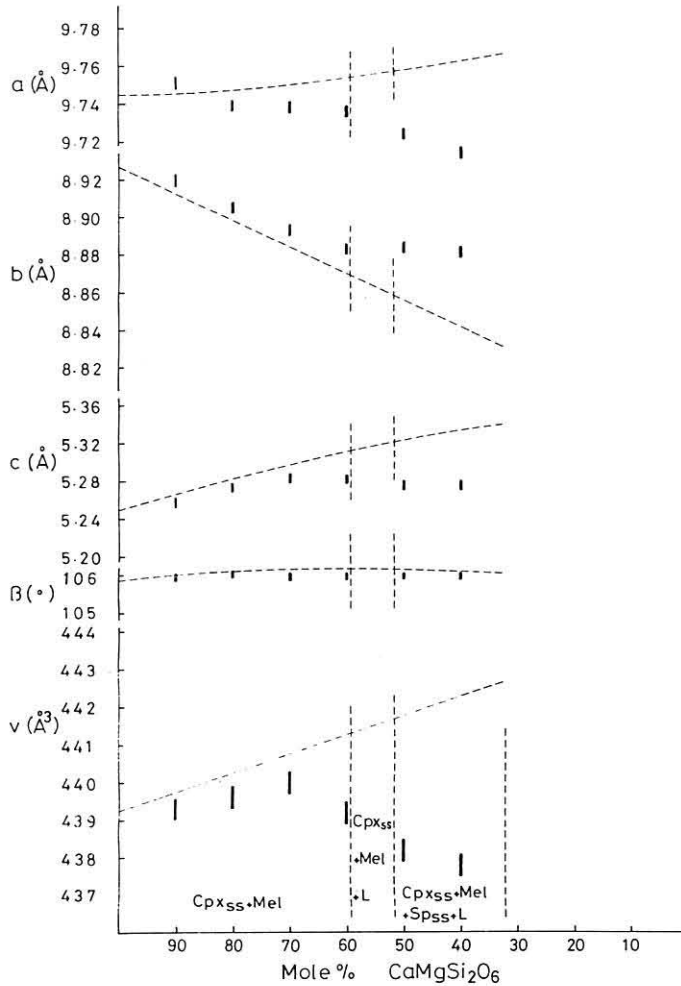
Fig. 6   Unit-cell dimensions of the clinopyroxene crystallized at $1100°C$ and 10^{-11} atm f_{O_2}. The dashed lines: the variation of the unit-cell dimensions of the clinopyroxene(ss) crystallized in air (Hijikata, 1968).

akermanite up to 73 wt.% under suitable condition of oxygen fugacity. However, the melilite obtained in the present study is assumed to be a complicate solid solution involving gehlenite ($Ca_2 Al_2 SiO_7$) and iron gehlenite ($Ca_2 Fe^{3+}AlSiO_7$), in addition to iron akermanite. In the wüstite stability field iron gehlenite can not be expected.

Color of spinel(ss) varies from green in subliquidus region to dark green in subsolidus region. Unit-cell dimension of spinel(ss) is 8.123Å in wüstite stability field and 8.312Å in magnetite stability field. These observations indicate that the spinel(ss) contains considerable amount of hercynite

$(Fe^{2+}Al_2O_4)$ and magnetite molecules as expected from the equations of (2) and (3).

Reversal experiments were carried out. For example, the composition of Di(50)FATs(50) crystallized into the assemblage of clinopyroxene(ss) + melilite + spinel(ss) at $1100°C$, 10^{-10} atm f_{O_2}. The chemical composition of the clinopyroxene(ss) in this assemblage is $Ca_{0.96}(Mg_{0.48}Fe^{2+}_{0.12}Fe^{3+}_{0.26}Al_{0.14})$ $(Al_{0.44}Si_{1.56})O_6$. Then, this crystalline mixture was heated at $1200°C$ for 336 hours in air. Only clinopyroxene(ss) was obtained without any other phases. The unit-cell dimensions of this clinopyroxene(ss) fall very close to the dashed line in Fig. 5, indicating that equilibrium is attained.

Yagi (1966) suggested that when f_{O_2} in the magma is higher pyroxene becomes more acmitic, whereas when f_{O_2} is lower pyroxene includes more hedenbergite molecule. The present study indicates that clinopyroxene crystallized in the magnetite stability field contains CaTs as well as hedenbergite molecule.

Ohashi and Hariya (1975) reported that FATs pyroxene is stable at 1100 – 1500°C, 41 – 43 kb in the hematite stability field. They (1975) also showed that FATs pyroxene becomes unstable above 6 kb under the $MnO - Mn_3O_4$ and $Fe_2O_3 - Fe_2O_4$ buffer conditions.

These observations and the results of present study imply that the entering of FATs into diopside is influenced by oxygen fugacity rather than pressure.

Acknowledgement

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