Clinopyroxene on the join $\text{CaMgSi}_2\text{O}_6\text{--CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6$ at low oxygen fugacity

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Abstract. Subsolidus phase relations on the join $\text{CaMgSi}_2\text{O}_6\text{--CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6$ were studied by the ordinary quenching method at $f_{\text{O}_2} = 10^{-11}$ atm and 1,100°C. Crystalline phases encountered are clinopyroxene_{ss} (ss:solid solution) (Cpx_{ss}), melilite (Mel), perovskite (Pv), spinel_{ss} (Sp_{ss}), magnetite_{ss} (Mt_{ss}) and anorthite (An). There is no Cpx_{ss} single phase field, and the following assemblages were found; $\text{Cpx}_{ss} + \text{Mel}$, $\text{Cpx}_{ss} + \text{Mel} + \text{Sp}_{ss}$, $\text{Cpx}_{ss} + \text{Mel} + \text{Pv}$, $\text{Cpx}_{ss} + \text{Mel} + \text{Sp}_{ss} + \text{Pv}$, $\text{Cpx}_{ss} + \text{Pv} + \text{Sp}_{ss} + \text{An}$, $\text{Sp}_{ss} + \text{Pv} + \text{Mel} + \text{An} + \text{Cpx}_{ss}$, $\text{Mel} + \text{Mt}_{ss} + \text{An} + \text{Sp}_{ss} + \text{Cpx}_{ss}$ + liquid and $\text{Mel} + \text{Mt}_{ss} + \text{An} + \text{Sp}_{ss} + \text{Cpx}_{ss} + \text{Pv}$. Mössbauer spectral study revealed that Cpx_{ss} contains both Fe^{2+} and Fe^{3+} in the octahedral site, and it was confirmed that the $\text{CaFe}^{3+}\text{AlSiO}_6$ content in the Cpx_{ss} at low f_{O_2} is considerably less than that in the Cpx_{ss} crystallized in air, whereas the $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$ component increases. The maximum solubility of $\text{CaTiAl}_2\text{O}_6$ component in the Cpx_{ss} at low f_{O_2} is higher than that in air. The decrease of $\text{CaFe}^{3+}\text{AlSiO}_6$ in the Cpx_{ss} at low f_{O_2} may cause increase of $\text{CaTiAl}_2\text{O}_6$ in the Cpx_{ss} .

Keywords. Clinopyroxene; perovskite; spinel; magnetite; melilite; anorthite; phase assemblages; crystalline phases.

1. Introduction

Ti-rich fassaites contain moderate to considerable amount of Tschermak's components such as $\text{CaAl}_2\text{SiO}_6$, $\text{CaFe}^{3+}\text{AlSiO}_6$ and $\text{CaTiAl}_2\text{O}_6$. Among these Tschermak's components, $\text{CaFe}^{3+}\text{AlSiO}_6$ -pyroxene is stable at 1 atm (Hijikata 1968). The stability of the clinopyroxene containing $\text{CaFe}^{3+}\text{AlSiO}_6$ component at 1 atm has been investigated by several workers; join $\text{CaMgSi}_2\text{O}_6$ (Di)- $\text{CaFe}^{3+}\text{AlSiO}_6$ (Hijikata and Onuma 1969), join $\text{CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6$ (Onuma and Akasaka 1979, 1980), join $\text{Di--CaFe}^{3+}_2\text{SiO}_6\text{--CaAl}_2\text{SiO}_6$ (Huckenholz *et al* 1974), join $\text{Di--CaAl}_2\text{SiO}_6\text{--CaFe}^{3+}\text{AlSiO}_6$ (Onuma and Yagi 1975; Onuma *et al* 1981) and join $\text{Di--CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6$ (Akasaka and Onuma 1978, 1980). At high f_{O_2} conditions, $\text{CaFe}^{3+}\text{AlSiO}_6$ -pyroxene is stable up to 43 kb (Ohashi and Hariya 1975a, b). However, at low f_{O_2} conditions, clinopyroxene stability field in the join $\text{Di--CaFe}^{3+}\text{AlSiO}_6$ reduces considerably, indicating that $\text{CaFe}^{3+}\text{AlSiO}_6$ content in clinopyroxene strongly depends on f_{O_2} (Oba and Onuma 1978). Thus various crystallization trends can be postulated in the join $\text{Di--CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6$, depending on f_{O_2} conditions (Akasaka and Onuma 1978, 1980; Onuma *et al* 1981).

The present paper is a preliminary report on the stability of clinopyroxene in the join $\text{Di--CaFe}^{3+}\text{AlSiO}_6\text{--CaTiAl}_2\text{O}_6$ at low f_{O_2} condition ($f_{\text{O}_2} = 10^{-11}$ atm and 1,100°C). The nature of the clinopyroxene is also shown.

Hereafter, each Tschermak's component is abbreviated as follows; calcium Tschermak's component (CaTs) for $\text{CaAl}_2\text{SiO}_6$, titan pyroxene component (Tp) for

$\text{CaTiAl}_2\text{O}_6$ and esseneite component (Ess) for $\text{CaFe}^{3+}\text{AlSiO}_6$ which was called previously ferri-aluminum Tschermak's component (FATs) (Onuma and Yagi 1975), and has been named esseneite by Cosca and Peacor (1987).

2. Experimental method

Starting materials used were crystallized from the homogeneous glasses at 900–1,000°C. Glasses were made by melting the mixtures consisting of CaCO_3 , MgO , Fe_2O_3 , TiO_2 , Al_2O_3 and SiO_2 at 1,350–1,500°C. Pt-Pt₈₇Rh₁₃ thermocouples were calibrated at the standard melting points of NaCl (800.4°C), Au (1,062°C) and diopside (1,391.5°C). The gas mixture of H_2 and CO_2 was used to control f_{O_2} (Nafziger *et al* 1971).

The crystalline starting materials were charged in Pt₆₀Rh₄₀ envelope and heated at desired temperature and f_{O_2} . To check whether or not the assemblages are stable, the run products heated for 8 hours were reheated for more than 15 hours, and both results were compared with each other. Although Pt₆₀Rh₄₀ envelopes were used, it was observed that a part of Fe was absorbed into the envelope from the sample.

The run products were identified by optical microscope, X-ray powder diffractometer and EPMA (a JEOL JXA – 50A). Mössbauer spectrum of the clinopyroxene was analysed using 5 mCi ^{57}Co in stainless steel as a source at room temperature to determine the amount of Fe^{2+} and Fe^{3+} . The Doppler velocity was calibrated using a metal iron foil. The absorber was prepared by finely ground sample, which was pressed on Al-foils (area: 4 cm²). The Mössbauer data were obtained with a constant acceleration spectrometer using a 512-channel analyser. The spectrum was fitted to Lorentzians by the least square method with line widths and intensities constrained to be equal at each site. The LSF program of Shinno and Maeda (1981) was used for computer analysis. The quality of the fit was judged by the χ^2 value.

3. Results

3.1 Phase assemblages

In this study, the experiment was made at 1,100°C and $f_{\text{O}_2} = 10^{-11}$ atm, corresponding to magnetite-wüstite buffer. The results of the quenching experiments are given in figure 1. Clinopyroxene solid solution (Cpx_{ss}), melilite (Mel), perovskite (Pv), spinel solid solution (Sp_{ss}), magnetite solid solution (Mt_{ss}) and anorthite (An) are encountered.

There is no single phase field of clinopyroxene. The assemblages of Cpx_{ss} + Mel, Cpx_{ss} + Mel + Sp_{ss} and Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + liquid(L) were confirmed in the 10 wt% Tp section. In the 20 wt% and 30 wt% Tp sections, the assemblages of Cpx_{ss} + Mel + Pv, Cpx_{ss} + Mel + Sp_{ss} + Pv and Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + Pv are observed. In the 40 wt% Tp section, the assemblages of Cpx_{ss} + Pv + Sp_{ss} + An and Sp_{ss} + Pv + Mel + An + Cpx_{ss} are found. In the assemblages of Cpx_{ss} + Mel, Cpx_{ss} + Mel + Sp_{ss} , Cpx_{ss} + Mel + Pv, Cpx_{ss} + Mel + Sp_{ss} + Pv and Cpx_{ss} + Pv + Sp_{ss} + An, clinopyroxene_{ss} is the most dominant phase. On the other hand, in the assemblages of Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + L and Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + Pv, melilite and magnetite_{ss} are the most dominant phases, associated with very small amounts

Figure 1. Phase relations in the join Di-Ess-Tp at $f_{O_2} = 10^{-11}$ atm and 1,100°C
A: anorthite, C: clinopyroxene_{ss}, L: liquid, M: melilite, Mt: magnetite_{ss}, P: perovskite,
S: spinel_{ss}.

of clinopyroxene_{ss}. In the assemblage of $Sp_{ss} + Pv + Mel + An + Cpx_{ss}$, spinel_{ss} and perovskite are the most dominant phases, with very small amounts of clinopyroxene_{ss}.

3.2 Crystalline phases

Clinopyroxene_{ss} forms rounded grains, dark green in colour, suggesting the presence of Fe^{2+} . The compositions of the clinopyroxenes crystallized at $f_{O_2} = 10^{-11}$ atm and 1,100°C are listed in table 1. Although total Fe is indicated as Fe_2O_3 , the Mössbauer spectral study suggests that these clinopyroxenes contain moderate amount of FeO. The Mössbauer spectrum of the clinopyroxene coexisting with small amount of melilite at the bulk composition of $Di_{60}Ess_{30}Tp_{10}$ (No. 3 in table 1) is indicated in figure 2. Least squares fitting was tried assuming that a small amount of melilite coexisting with this clinopyroxene does not significantly disturb the Mössbauer spectral analysis of the clinopyroxene, because the iron-åkermanite component in the melilite is less than 50 wt% as shown below. However, the Mössbauer spectrum (figure 2) is relatively poor, which may be due not only to the existence of melilite but also to the compositional heterogeneity caused by the absorption of Fe^{2+} into Pt-Rh envelope from the sample. The spectrum was successfully fitted to two doublets. ^{57}Fe hyperfine data of the doublets (table 2) are characteristic ones of Fe^{2+} and Fe^{3+} at the octahedral site of clinopyroxene (Akasaka 1983). The estimated site occupancies of Fe at the octahedral site are 0.08 for Fe^{2+} and 0.22 for Fe^{3+} , based on the area ratio of the Mössbauer doublets by the equation $Fe^{2+}/Fe^{3+} = A(Fe^{2+})/A(Fe^{3+})$, where A is area ratio of doublets. Though the charge of Ti could not be determined directly in the present study, it is presumed to be tetravalent in the f_{O_2} condition, where Fe^{3+} is

Table 1. Compositions* of the clinopyroxenes crystallized at $f_{O_2} = 10^{-11}$ atm and 1,100°C in the join Di-Ess-Tp.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Bulk	Di 80	Di 70	Di 60	Di 50	Di 30	Di 70	Di 60	Di 50	Di 40	Di 30	Di 20	Di 10	Di 60	Di 20
Comp.	Ess 10	Ess 20	Ess 30	Ess 40	Ess 60	Ess 10	Ess 20	Ess 30	Ess 40	Ess 50	Ess 60	Ess 70	Ess 10	Ess 50
(wt%)	Tp 10	Tp 10	Tp 10	Tp 10	Tp 10	Tp 20	Tp 20	Tp 20	Tp 20	Tp 20	Tp 20	Tp 20	Tp 30	Tp 30
Phase**	CM	CM	CM	CM	CMS	CMF	CMF	CMF	CMSP	CMSP	CMSP	MMtASCP	CPSA	CPSA
SiO ₂	46.9(6)	43.8(13)	41.0(8)	37.6(8)	32.2(4)	41.8(4)	38.7(7)	35.0(2)	32.7(2)	29.6(5)	25.2(4)	23.5(2)	35.4(4)	24.9(6)
TiO ₂	3.4(2)	3.4(1)	3.3(1)	3.4(2)	3.4(2)	6.7(2)	6.9(1)	6.6(1)	6.6(2)	6.4(2)	6.8(1)	6.5(1)	10.1(2)	9.0(5)
Al ₂ O ₃	6.0(3)	8.1(2)	10.0(1)	12.3(2)	16.9(2)	10.9(2)	12.9(2)	14.7(5)	16.7(3)	18.4(4)	20.2(1)	23.0(3)	14.9(4)	23.8(6)
Fe ₂ O ₃ ***	3.3(2)	7.6(4)	10.6(2)	12.8(4)	19.6(5)	3.2(5)	6.3(4)	9.2(4)	13.0(3)	16.0(5)	20.4(4)	22.9(7)	3.4(4)	14.4(7)
MgO	15.7(6)	13.6(3)	11.3(1)	9.5(2)	6.1(4)	13.6(6)	11.2(4)	9.3(4)	7.4(4)	5.7(5)	3.7(3)	1.8(1)	11.0(3)	4.0(3)
CaO	24.5(2)	24.1(6)	24.2(3)	24.6(4)	23.5(5)	23.9(4)	23.9(3)	24.5(4)	24.0(5)	24.1(4)	23.6(3)	24.1(5)	24.2(2)	23.7(9)
Total	99.8	100.6	100.4	100.2	101.7	100.10	99.9	99.3	100.4	100.2	99.9	101.8	99.0	99.8
Cations per 6 oxygens														
Si	1.73	1.63	1.54	1.44	1.24	1.54	1.45	1.34	1.26	1.16	1.01	0.93	1.34	0.98
Al ^{IV}	0.26	0.36	0.45	0.56	0.76	0.46	0.55	0.66	0.74	0.84	0.95	1.07	0.66	1.02
Al ^{VI}	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.02	0.00	0.00	0.00	0.01	0.08
Ti	0.09	0.09	0.09	0.10	0.10	0.19	0.19	0.19	0.19	0.19	0.20	0.19	0.29	0.27
Fe	0.09	0.21	0.30	0.37	0.57	0.09	0.18	0.27	0.37	0.47	0.61	0.68	0.10	0.42
Mg	0.86	0.75	0.63	0.54	0.35	0.75	0.63	0.53	0.43	0.33	0.22	0.11	0.62	0.23
Ca	0.97	0.96	0.98	1.01	0.97	0.94	0.96	1.01	0.99	1.01	1.01	1.02	0.98	0.99
	4.00	4.00	3.99	4.02	3.99	3.98	3.98	4.00	4.00	4.00	4.00	4.00	4.00	3.99

* Parentheses are standard deviations; ** Abbreviations are the same as in figure 1; *** Total iron as Fe₂O₃.

Figure 2. ^{57}Fe Mössbauer spectrum at 298°K for the clinopyroxene crystallized at $f_{\text{O}_2} = 10^{-11}$ atm and 1,100°C from the bulk composition of $\text{Di}_{60}\text{Ess}_{30}\text{Tp}_{10}$.

Table 2. ^{57}Fe hyperfine data^a of Fe^{2+} and Fe^{3+} of the octahedrals site in the clinopyroxene

FWHH(mm/s) ^b		Area Ratio(%)		I.S. (mm/s) ^c		Q.S.(mm/s)		χ^2 ^d
Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	
0.76(2)	0.72(2)	72(7)	28(7)	0.32(1)	1.14(1)	0.90(2)	2.05(2)	1.4

^a Spectrum taken with the ^{57}Co in stainless steel source. Standard deviations in parentheses; ^b Full width at the half height; ^c Isomer shift referred to a metallic iron absorber; ^d Per degree of freedom.

present (Dowty and Clark 1973). Thus the structural formula can be represented as follows; $\text{Ca}_{0.98}\text{Mg}_{0.63}\text{Fe}^{2+}_{0.08}\text{Fe}^{3+}_{0.22}\text{Ti}_{0.09}\text{Al}_{0.45}\text{Si}_{1.54}\text{O}_{6.00}$ and the end member contents are Di: 53.9, Hd: 9.2, Ess: 23.6, CaTs: 2.6, Tp: 9.5, En: 3.0 and Qz: -1.8 wt%. Thus, the Ess content of this clinopyroxene_{ss} is considerably less than that of the clinopyroxene crystallized in air, whereas the $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$ (Hd) increases characteristically. This would hold for other clinopyroxene_{ss} in the present study. As indicated in table 1, Tp content in the clinopyroxenes increases depending on the bulk composition of the starting materials, and the TiO_2 content of the clinopyroxene at $\text{Di}_{60}\text{Ess}_{10}\text{Tp}_{30}$ attains up to 10 wt%. The clinopyroxenes of Nos. 12 and 14 in table 1 are Si-deficient clinopyroxenes, with the content of Si being less than that of Al in the tetrahedral site (Onuma and Akasaka 1979, 1980).

Table 3. Compositions of melilite, spinel and anorthite crystallized from the starting material of $\text{Di}_{10}\text{Ess}_{80}\text{Tp}_{10}$ at $f_{\text{O}_2} = 10^{-11}$ atm and $1,100^\circ\text{C}$.

	Melilite	Magnetite _{ss}	Anorthite
SiO_2	31.27	0.90	42.62
TiO_2	0.47	14.54	0.09
Al_2O_3	18.13	16.46	35.83
FeO^*	9.55	65.82	0.72
MgO	2.55	2.02	0.01
CaO	37.44	0.80	20.08
Total	99.41	100.54	99.35
Structural formula			
O	7.00	4.00	8.00
Si	1.49	0.03	1.99
Ti	0.02	0.39	0.00
Al	1.02	0.69	1.97
Fe	0.38	1.97	0.03
Mg	0.18	0.11	0.00
Ca	1.91	0.03	1.01
	5.00	3.22	5.00
End member components (mol %)			
$\text{Ca}_2\text{Fe}^{2+}\text{Si}_2\text{O}_7$	37	Fe_2TiO_4	36
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	50	FeFe_2O_4	29
$(\text{Ca}, \text{Mg})_2\text{MgSi}_2\text{O}_7$	13	MgAl_2O_4	10
		FeAl_2O_4	22
		CaSiO_3	3

* Total Fe as FeO

Melilite forms rounded grains, pale greenish in colour with low birefringence. The composition of melilite at the bulk composition of $\text{Di}_{10}\text{Ess}_{80}\text{Tp}_{10}$ is listed in table 3. The structural formula was calculated assuming that Fe is divalent. The ideal value (5:7) of the (total cation):oxygen ratio supports this assumption. The melilite contains 37 mol% of iron-åkermanite component ($\text{Ca}_2\text{Fe}^{2+}\text{Si}_2\text{O}_7$), 50 mol% of gehlenite component ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and 13 mol% of åkermanite component ($\text{Ca}_2\text{MgSi}_2\text{O}_7$). Thus, melilite in this join is a solid solution of these end members with various ratios depending on the phase assemblages.

Perovskite can be identified by its high relief under microscope and the X-ray powder diffraction pattern.

The relation between spinel_{ss} and magnetite_{ss} is an unsolved problem in the present study. Although EPMA analyses of spinels have not been carried out, X-ray powder diffraction patterns suggest that the spinel_{ss} in the assemblages of $\text{Cpx}_{ss} + \text{Mel} + \text{Sp}_{ss}$, $\text{Cpx}_{ss} + \text{Mel} + \text{Sp}_{ss} + \text{Pv}$ and $\text{Cpx}_{ss} + \text{Pv} + \text{Sp}_{ss} + \text{An}$ is a solid solution of MgAl_2O_4 and FeAl_2O_4 and that the spinel_{ss} in the assemblage of $\text{Sp}_{ss} + \text{Pv} + \text{Mel} + \text{An} + \text{Cpx}_{ss}$ is ferrian-spinel ($\text{Mg}(\text{Al}, \text{Fe})_2\text{O}_4$). On the other hand, magnetite_{ss} crystallized from the starting material of $\text{Di}_{10}\text{Ess}_{80}\text{Tp}_{10}$, which occurs in the region of

Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + L, is a complex solid solution (table 3). The estimated $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ value given by the charge balance calculation is 0.69. The end member contents based on this value are 36 mol% of ulvöspinel component (Fe_2TiO_4), 29 mol% of magnetite component (Fe_3O_4), 10 mol% of spinel component (MgAl_2O_4), 22 mol% of hercynite component (FeAl_2O_4) and 3 mol% of wollastonite component (CaSiO_3).

Anorthite is confirmed by the X-ray powder diffraction and EPMA. This phase is nearly pure with trace amount of Fe (table 3).

4. Discussions

The phase assemblages in the 10 wt% Tp section, Cpx_{ss} + Mel and Cpx_{ss} + Mel + Sp_{ss}, are consistent with the results in the join Di-Ess by Oba and Onuma (1978). The assemblage of Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} + L in the present study is shown as "Cpx_{ss} + Mel + Sp_{ss} + An + L" by Oba and Onuma. They suggested that melilite contains iron-åkermanite component at low f_{O_2} conditions, and that spinel is a solid solution between MgAl_2O_4 - FeAl_2O_4 - Fe_3O_4 . This suggestion is consistent with the present results. However, the present study also shows that melilite is more complex solid solution consisting of åkermanite, iron-åkermanite and gehlenite components, and magnetite_{ss} is composed of ulvöspinel, magnetite, hercynite and spinel components. Based on the present results, the phase assemblage of Mel + Mt_{ss} + An + Sp_{ss} + Cpx_{ss} in the join Di-Ess may be represented by the following equation:

As the compositions of melilite and spinel_{ss} in the assemblages of Cpx_{ss} + Mel + Sp_{ss} and Cpx_{ss} + Mel are not known, it is difficult to construct equations representing these assemblages. The following equations may be one possible representation of these assemblages:

and

In the join Di-Ess-Tp, these reactions become more complicated, because of the addition of Tp component.

The solubility of Ess component in clinopyroxene at low f_{O_2} condition provides an interesting problem. Oba and Onuma (1978) revealed that the single phase field of clinopyroxene containing Ess component depends strongly on the f_{O_2} condition and determined the solubility limit of Ess component in diopside to be 5 mol% at 1,000 °C and 10^{-11} atm f_{O_2} . However, as mentioned before, the clinopyroxene_{ss} in the present study contains 24 wt% (22 mol%) of Ess component at least, indicating that the Ess component persists at the low f_{O_2} condition near magnetite-wüstite buffer. Oba and Onuma (1978) also determined the solubility limit of Ess component in diopside to be 10 mol% at 1,100°C and 10^{-10} atm f_{O_2} . On the other hand, they also indicated that the clinopyroxene crystallized from the starting material (Di₅₀Ess₅₀ (mol%) in composition) at the same experimental conditions contains Ess component of 26 mol%. Thus, the "solubility limit of Ess component in diopside" determined by Oba and Onuma does not imply the maximum solubility of Ess component in clinopyroxene at their experimental conditions. According to the results of the present study and the variation of unit cell parameters of the clinopyroxenes crystallized at 1,100°C and $f_{O_2} = 10^{-11}$ atm by Oba and Onuma (1978), the maximum solubility of Ess in clinopyroxene at these experimental conditions can be estimated about 24 wt% (22 mol%). The present result also indicates that the solubility of Ess component decreases with decreasing f_{O_2} . This is consistent with the result by Oba and Onuma (1978).

Tp content in the clinopyroxene at low f_{O_2} condition poses another interesting problem. The TiO₂ contents of the clinopyroxenes crystallized from starting materials of Di₆₀Ess₁₀Tp₃₀ and Di₂₀Ess₅₀Tp₃₀ at 1,100°C and $f_{O_2} = 10^{-11}$ atm attain up to 10.1 and 9.0 wt%, respectively (table 1 nos. 13 and 14), whereas the clinopyroxenes crystallized from the same starting materials in air contain 8.8 and 8.4 wt% TiO₂, respectively (Akasaka and Onuma 1980). This fact suggests that the maximum solubility of Tp in the clinopyroxenes crystallized at low f_{O_2} condition is higher than that in the clinopyroxenes crystallized in air. Based on the fact that maximum solubility of Tp in the clinopyroxene decreases with increasing Ess contents (Akasaka and Onuma 1980), the reason for the increase of Tp content in the clinopyroxene at low f_{O_2} may be attributed to the decrease of Ess content in the clinopyroxene.

It has been emphasized that the Ess content in the clinopyroxene strongly depends on f_{O_2} condition (Oba and Onuma 1978 and others). In fact, the esseneite and Ess-rich clinopyroxene in a coal-fire buchite from Buffalo, Wyoming, coexists with Fe³⁺-rich melilite, hematite and magnesioferrites, suggesting that it was formed at high f_{O_2} condition (Foit *et al* 1987). Cosca and Peacor (1987) also mentioned that Ess-rich pyroxenes are generally favoured at high temperature and high f_{O_2} . On the other hand, Ti-augite in alkali olivine basalt from Tahiti, which is estimated to have formed at $f_{O_2} = 10^{-11}$ atm and 1,020°C, is rich in Fe²⁺ and coexists with olivine, plagioclase, alkali feldspar, leucite, titanomagnetite (magnetite₃₀ulvöspinel₇₀) and ilmenite (Tracy and Robinson 1977). Since the bulk composition of the alkali olivine basalt is different from that of the present study, the assemblages and the compositions of clinopyroxenes are different from each other. Nevertheless, the facts that both clinopyroxenes include considerable amounts of Fe²⁺ and that they coexist with titanomagnetite support the estimated crystallization conditions of the Tahiti alkali olivine basalt. Thus, generally speaking, it is confirmed that the Ess content in clinopyroxenes is controlled by f_{O_2} . It has been also noticed that the behaviour of Fe is more complicated in the ferrian salite in alkali gabbro from Kauai, Hawaii

(Johnston and Stout 1984). If clinopyroxene crystallizes with other phases containing Fe, complex zoning may be formed.

Some problems still remain unsolved in the present investigation on the join Di-Ess-Tp at low f_{O_2} conditions: (i) clinopyroxenes in this join deviate from the stoichiometry at low f_{O_2} condition, (ii) Fe is absorbed into the metal envelope from the samples, resulting in the heterogeneous run products and (iii) difficulty in attaining equilibrium because of relatively short run duration.

In spite of all these problems the results of this study present useful information which cannot be obtained by experiments in air.

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