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PHASE RELATIONS AND THE NATURE OF CLINOPYROXENE SOLID SOLUTIONS IN THE SYSTEM $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$

by

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(with 6 tables and 25 text-figures)

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Abstract

The phase relations in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 1 atm were studied and the phase diagram of the join was constructed. The solubility limit of $CaAl_2SiO_6$ in acmite is about 6 wt %. When the $CaAl_2SiO_6$ content increases, the phase assemblages below the solidus temperature in this join change as follows: clinopyroxene$_{ss}$ (ss: solid solution), clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$, (clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$ + hematite), clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$ + melilite$_{ss}$, nepheline$_{ss}$ + plagioclase$_{ss}$ + melilite$_{ss}$ + $(CaO.6Al_2O_3)_{ss}$, and plagioclase$_{ss}$ + melilite$_{ss}$ + $(CaO.6Al_2O_3)_{ss}$. At high temperatures pyroxene$_{ss}$ melts incongruently to hematite and liquid.

The phase relations in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at high pressures from 10 to 30 kb at 950°C were studied. The solubility of $CaAl_2SiO_6$ in $NaFe^{3+}Si_2O_6$ attains 70 wt % at 18 kb, at 950°C. At 1250°C there is a complete series of solid solutions between these two end-members. The phase assemblages change as follows with the increase of pressure: clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$, clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$.

The pressure-composition sections for the join $Ac_{60}Di_{40}$–CaTs**, the join $Ac_{20}Di_{80}$–CaTs, the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$, and the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$ were constructed at high pressures from 8 to 25 kb, at 1050°C. The pressure-temperature diagrams of the composition $Ac_{30}Di_{20}CaTs_{50}$, $Ac_{10}Di_{40}CaTs_{50}$, $Ac_{21}Di_{14}CaTs_{65}$, and $Ac_{15}Di_{10}CaTs_{75}$ were constructed. The solubility of $CaAl_2SiO_6$ in the pyroxene in the system $Na^{3+}FeSi_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ is controlled not only by pressure, but also by temperature, and is facilitated at high pressures and high temperatures. At higher pressure and higher temperature, it is expected that there is a complete series of solid solutions among $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$ and $CaAl_2SiO_6$. The unit-cell parameters of clinopyroxene solid solutions change continuously with the change of the composition. The phase assemblages change as follows with the increase of pressure: in the acmite-rich region, clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$ + clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$, and in the diopside-rich region, clinopyroxene$_{ss}$ + plagioclase$_{ss}$ +

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** (henceforth abbreviation are used: acmite = Ac, diopside = Di, $CaAl_2SiO_6$ = CaTs, clinopyroxene = Px, nepheline$_{ss}$ = Ne, plagioclase$_{ss}$ = Pl, melilite$_{ss}$ = Mel, spinel = Sp, $(CaO.6Al_2O_3)_{ss}$ = CA_6, garnet$_{ss}$ = Gar, and corundum$_{ss}$ = Cor).

melilite$_{ss}$ + spinel, clinopyroxene$_{ss}$, clinopyroxene$_{ss}$ + garnet$_{ss}$ + plagioclase$_{ss}$ + spinel, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$.

Based on the phase relations mentioned above and the changes of unit-cell parameters of clinopyroxene$_{ss}$ in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$, it is estimated that the aluminous pyroxene molecules contained in the clinopyroxene$_{ss}$ changes as follows with the increase of pressure: ($CaFe^{3+}AlSiO_6$ + $CaAl_2SiO_6$), ($CaAl_2SiO_6$), and ($CaAl_2SiO_6$ + $NaAlSi_2O_6$).

Calculation scheme for pyroxene end-members is also discussed, based on the present experimental results.

Introduction

Acmite and diopside are the important pyroxene components which are contained in aegirine, aegirine-augite, and omphacite. These clinopyroxenes occur widely in the sedimentary rocks, alkalic rocks, crystalline schists and eclogite. These clinopyroxenes generally contain variable amounts of Al_2O_3: aegirines and aegirine-augites contain about 1 to 6 wt %, and the amount of Al_2O_3 in omphacite attains to over 12 wt %. Judging from the chemical formula of these clinopyroxenes, Al atom is able to occupy in the tetrahedral site and the octahedral site in pyroxene structure. The occurrence of clinopyroxene changes the degree of the aluminum partition between both sites in the clinopyroxene (Kushiro, 1962; White, 1964; Aoki and Kushiro, 1968). Moreover, it is observed that the amount of 4-coordinated aluminum in natural clinopyroxenes decreases with increasing sodium content in it; in other words, the amount of total Tschermak's molecules decreases with increasing sodium content. On the other hand, it is well known that Al atoms in silicate minerals are generally found in 4-coordination site at high temperature and relatively low pressure and tend to take 6-coordination at high pressure and relatively low temperature (Thompson, 1947; Buerger, 1948). Therefore, it is expected that the coordination number of Al atoms in clinopyroxene is controlled by the physico-chemical condition at which the clinopyroxene crystallized. Aluminum in most of aegirine, aegirine-augite, and omphacite occupies both octahedral site and tetrahedral site in clinopyroxene structure, but the degree of the partition between both sites is different in each clinopyroxene. $CaAl_2SiO_6$ is one of the important pyroxene molecule containing Al_2O_3. Okamura et al. (1974) reported that a half of Al atoms in this compound occupies the octahedral site and the other half occupies the tetrahedral site. The studies of clinopyroxene$_{ss}$ in the system $NaFe^{3+}Si_2O_6$ – $CaMgSi_2O_6$–$CaAl_2SiO_6$ offer the important information for the behavior of aluminum in aegirines, aegirine-augites and omphacites against physico-chemical condition. Three end-members and two joins in this system have been studied experimentally. Both acmite and diopside have a very wide stability

field under the various physical conditions (Bowen et al., 1930; Gilbert, 1969; Bailey, 1969; Boyd and England, 1963). Ca-Tschermak's molecule is a stable compound with clinopyroxene structure at high pressure and high temperature (Clark et al., 1962; Hays, 1966; Hijikata and Yagi, 1967). Yagi (1966) constructed the phase diagram for the join acmite-diopside at 1 atm and confirmed the presence of a complete solid solution series between acmite and diopside. A study of the join acmite–diopside at 10 kb was reported by Cassie (1971). Schairer and Yoder (1970) reported the phase relation in the join $CaMgSi_2O_6$–$CaAl_2SiO_6$ at 1 atm Clark et al. (1962) and Hijikata (1969) reported the investigation of the join $CaMgSi_2O_6$–$CaAl_2SiO_6$ at high pressure.

The present experimental studies have been made to determine the phase relations in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ and to clarify the effect of pressure and temperature on the solubility of $CaAl_2SiO_6$ in clinopyroxenes along the join $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$, and to determine the variation of aluminous pyroxene components in the clinopyroxene solid solutions against pressure in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$.

The petrological implication of the present system will be given elswhere (Onuma and Yoshikawa, in preparation).

Experimental method

$CaCO_3$, Al_2O_3, Fe_2O_3, SiO_2, and $Na_2Si_2O_5$ were used as the sources of CaO, Al_2O_3, Fe_2O_3, SiO_2, and Na_2O. $Na_2Si_2O_5$ was prepared by the same method as described by Schairer (1959). These mixtures were ground with ethyle alcohol (guaranteed reagent) in an agate mortar. All of these mixtures were heated below the solidus temperatures (800°C to 1250°C) for 3 to 7 weeks in air at 1 atm with intermediate crushing. All of the starting materials, except that in the composition $Ac_{60}Di_{15}CaTs_{25}$, were prepared by this method. Since in acmite-rich composition a small amount of Fe_2O_3 might remain without reaction by this method, the glass was prepared from a part of each sintered material mentioned above and was crystallized below the solidus temperatures. The starting material of the composition $Ac_{60}Di_{15}CaTs_{25}$ was prepared by the latter method. Only the clinopyroxene was synthesized from the glass of the composition $Ac_{20}CaTs_{80}$ at 20 kb and 950°C, whereas at the same temperature and pressure the assemblage of clinopyroxene + garnet + corundum was obtained, when the stable crystalline mixture at 1 atm for the same composition as $Ac_{20}CaTs_{80}$ was used as starting material. The clinopyroxene synthesized from the glass has much lower birefringence and has

somewhat larger unit-cell volume than that of the clinopyroxene synthesized from the crystalline mixture, and the unit-cell volume of this clinopyroxene lies above the variation curve of the unit-cell volumes between acmite and Ca-Tschermak's molecule (Fig. 17). These facts suggest that the clinopyroxene synthesized from glass is a metastable phase, and that the glass is not suitable as starting material in this system.

All runs at high pressure were carried out with the piston-cylinder type high pressure apparatus under dry condition. Most of the samples were charged in gold capsules, while platinum capsules were used for runs at high temperatures than 1050°C. The glass cell described by Hariya and Kennedy (1968) was used as pressure transmitting medium. Temperatures were measured with chromel-alumel thermocouples for runs at lower temperatures, and Pt-$Pt_{87}Rh_{13}$ thermocouples for runs at higher temperatures than 1250°C. No correction was made for the effect of pressure on the e.m.f. of the thermocouple. All pressures reported in this paper have been corrected for friction. The friction corrections for all runs attained to 13% of the observed pressure. Pressure variation of ±0.5 kb and temperature variations of ±15°C were noted during the run. All experimental products were quenched under the conditions as nearly isobaric as possible in the piston-cylinder apparatus. Since graphite was used as a heater in this experiment, all runs seem to have been carried out in rather reducing environment. However, Fe^{2+} could not be detected in the Mössbauer spectra of acmite, the clinopyroxene$_{ss}$ of $Ac_{50}CaTs_{50}$ composition synthesized at 20 kb and 950°C, and the clinopyroxene$_{ss}$ of $Ac_{60}Di_{15}CaTs_{25}$ composition synthesized at 25 kb and 1050°C.

Run products were examined with a petrographic microscope and X-ray powder diffraction. Most of the run products synthesized under these high pressure conditions consisted of aggregates of very fine grained crystals, less than about 10 μ. Therefore, X-ray method was chiefly used for phase identification, and it was not possible to determine the composition of each phase in run products by an electron microprobe.

All X-ray powder diffraction scans were carried out with a Rigaku Denki powder diffractometer equipped with a crystal monochrometer, using CuKα radiation at 35 Kv and 20 mA at room temperature. Reflections used in determining the unit-cell parameters of the clinopyroxenes were obtained at scanning speed of 1/4° per minute, with silicon as an external standard. Reflection was indexed by comparing the powder patterns with those of acmite (Clark, Appleman and Papike, 1969), Ca-Tschermak's molecule (Hays, 1966), diopside (Clark, Appleman and Papike, 1968a), and omphacite (Clark and Papike, 1969). Calculation of the cell parameters was accomplished with the aid of the program written by Sakurai (1967) at the FACOM 230-60 and

230-75 computer system of the Hokkaido University Computing Center. The unit-cell parameters of garnets were determined with silicon as an external standard.

Previous Works

(1) Phase relation in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 1 atm in air.

Fig. 1 shows the phase diagram of the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 1 atm by Yoshikawa and Onuma (1975). The data of $NaFe^{3+}Si_2O_6$ in Fig. 1 are quoted from Bowen et al. (1930), and those of $CaAl_2SiO_6$ from Schairer and Yoder (1970). The maximum solubility of $CaAl_2SiO_6$ in acmite is between 5 and 7 wt%, corresponding to about 2.8 wt% Al_2O_3. When the $CaAl_2SiO_6$

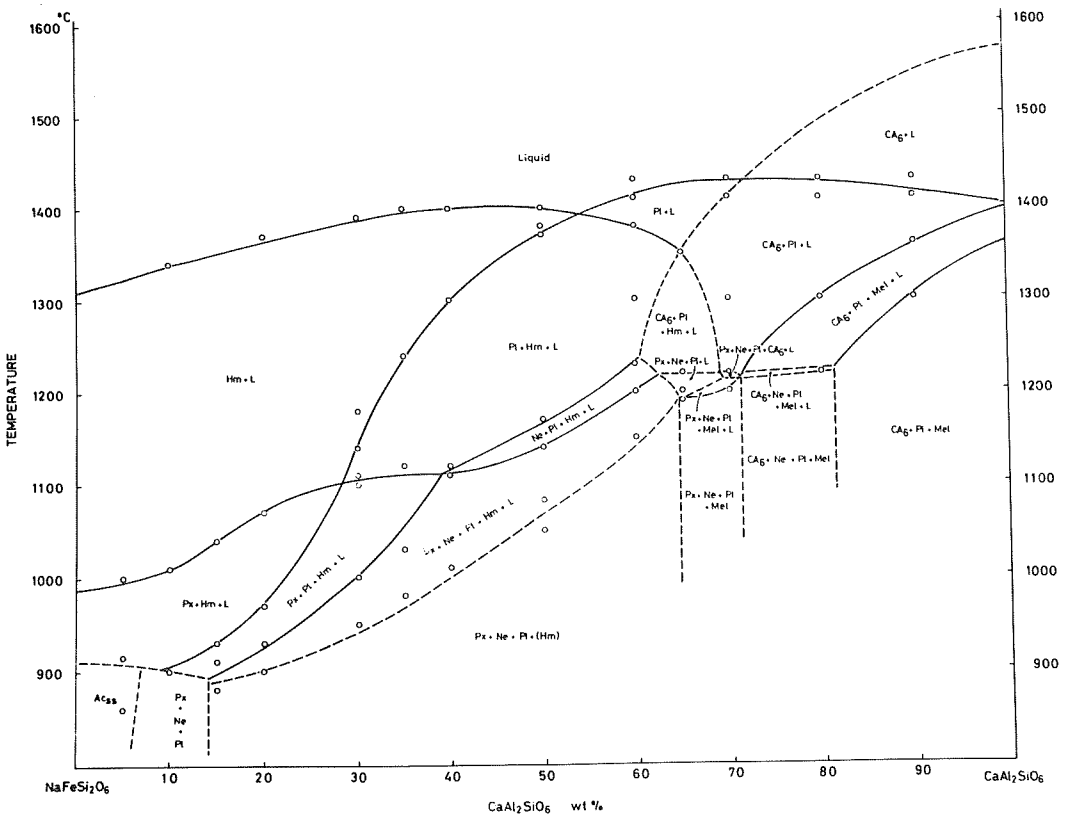


Fig. 1 Phase diagram of the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 1 atm. Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Hem = hematite, Mel = melilite solid solution, CA_6 = $CaO.6Al_2O_3$ solid solution, L = liquid. The data of $NaFe^{3+}Si_2O_6$ are quoted from Bowen et al. (1930), and those of $CaAl_2SiO_6$ from Schairer and Yoder (1970).

content in the join increases, the phase assemblages below the solidus temperature change as follows: clinopyroxene$_{SS}$, clinopyroxene$_{SS}$ + nepheline$_{SS}$ + plagioclase$_{SS}$, clinopyroxene$_{SS}$ + nepheline$_{SS}$ + plagioclase$_{SS}$ + hematite, clinopyroxene$_{SS}$ + nepheline$_{SS}$ + plagioclase$_{SS}$ + melilite$_{SS}$, nepheline$_{SS}$ + plagioclase$_{SS}$ + melilite$_{SS}$ + $(CaO.6Al_2O_3)_{SS}$, and plagioclase$_{SS}$ + melilite$_{SS}$ + $(CaO.6Al_2O_3)_{SS}$. At high temperature the clinopyroxene$_{SS}$ melts incongruently to hematite and liquid. Since magnetite, in addition to the above crystals, appears at higher temperature in the acmite-rich region, this join is a section of six-component system (six crystalline phases and liquid at invariant point) in the strict sense. At lower temperature, however, only six phases (five crystalline phases and liquid) are encountered, so that this join can be treated as a section of five-component system. Although the fields of clinopyroxene$_{SS}$ + nepheline$_{SS}$ + plagioclase$_{SS}$ + melilite$_{SS}$ + liquid and $(CaO.6Al_2O_3)_{SS}$ + nepheline$_{SS}$ + plagioclase$_{SS}$ + melilite$_{SS}$ + liquid, both univariant assemblage, were not confirmed, these fields are expected theoretically to exist.

(2) Phase relations in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at high pressures.

Fig. 2 shows an isothermal section of the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at high pressures from 10 to 30 kb at 950°C (Yoshikawa, 1976). All starting

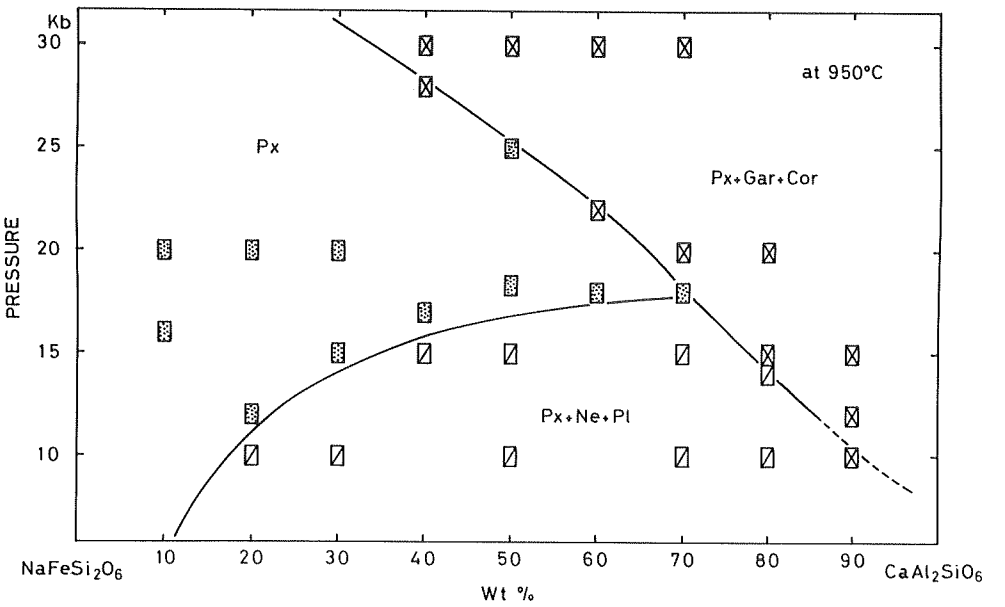


Fig. 2 Pressure-composition section for the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 950°C. Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Gar = garnet solid solution, Cor = cornundum solid solution.

materials consist of the stable assemblages at 1 atm. In some cases, however, reversed experiments were made: in the composition $Ac_{60}CaTs_{40}$, for example, clinopyroxene formed at 950°C and 17 kb was used as starting material for the run at 950°C and 15 kb, getting the same result as that obtained from the starting material composed of clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$. It shows that $CaAl_2SiO_6$ solubility in $NaFe^{3+}Si_2O_6$ increases with increasing pressure and this degree of solubility attains at least to 70 wt% at 950°C and 18 kb. Acmite incorporates $CaAl_2SiO_6$ up to 80 wt% at 1150°C, and up to 90 wt% at 1250°C under the high pressure condition. On the other hand, $CaAl_2SiO_6$ is stable as clinopyroxene at 1250°C above 11 kb (Hijikata and Yagi, 1967), or above 12.5 kb (Hays, 1966). Therefore, these two end-members may form a complete solid solution at 1250°C. The stability range of clinopyroxene solid solutions against pressure rapidly decreases with increasing content of $CaAl_2SiO_6$ in acmite. The phase assemblages under high pressure conditions change from lower to higher pressure as follows: clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$, clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$.

Experimental Results

In the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ clinopyroxene$_{ss}$, nepheline$_{ss}$, plagioclase$_{ss}$, melilite$_{ss}$, spinel, $(CaO.6Al_2O_3)_{ss}$, hematite, magnetite, garnet$_{ss}$, and corundum$_{ss}$ were encountered.

Table 1 Experimental results for the system $NaFe^{3+}Si_2O_6$-$CaMgSi_2O_6$-$CaAl_2SiO_6$ at high temperatures and high pressures

Composition (wt %) Ac Di CaTs	Starting material	Temp. (°C)	Press. (kb)	Time (hrs.)	Results
60 15 25	Px+Ne+Pl	1050	12	36	Px+(Ne+Pl)?
			13.5	42	Px
			15	60	Px
			20	60	Px
			25	30	Px
		1150	20	50	Px
45 30 25	Px+Ne+Pl	1050	10	48	Px+Ne+Pl
			13	20	Px
			20	36	Px
			24	25	Px
			25	30	Px+small amt. of Gar

Composition (wt %) Ac Di CaTs	Starting material	Temp. (°C)	Press. (kb)	Time (hrs.)	Results
30 45 25	Px+Pl+Mel?	1050	10	45	Px+(Ne+Pl)?
			13	24	Px
			21	29	Px
15 60 25	Px+Pl+Mel?	1050	8	26.5	Px+Pl+Mel+Sp?
			10	18	Px
			15	26	Px
			17	36	Px
			19	30	Px+small amt. of Gar
36 24 40	Px+Pl+Mel+Ne	1050	13	44	Px+(Pl+Ne)?
			16	46	Px
			18	48	Px
			20	48	Px+small amt. of Gar
24 36 40	Px+Pl+Mel+Ne	1050	11	40	Px+Pl+Ne
			12	50	Px+small amt. of Gar
			20	50	Px+Gar+Cor?
12 48 40	Px+Pl+Mel+Ne	1050	10.5	48	Px+Pl+Mel+Sp?
			12	48	Px+Gar+(Pl+Ne)?
			15	72	Px+Gar+Cor?
			20	57	Px+Gar+Cor?
		1200	13	30	Px
45 5 50	Px+Ne+Pl	1050	18	48	Px
40 10 50	Px+Ne+Pl	1050	10	64	Px+Ne+Pl
			12	46	Px+Ne+Pl
			14	50	Px+Ne+Pl
			15	45	Px
			18	36	Px+small amt. of Gar
35 15 50	Px+Pl+Mel+Ne	1050	13	47	Px+Ne+Pl
			15	45	Px+Ne+Pl
		1050	16.5	49	Px
			17	47	Px
30 20 50	Px+Pl+Mel+Ne	1000	12	60	Px+Ne+Pl+Gar?
		1050	13	48	Px+Gar+Ne+Pl
			15	38	Px+Gar+Cor?+(Pl+Ne)?
		1100	14	48	Px+small amt. of Pl
		1150	14	48	Px+small amt. of Pl
			16	49	Px+Gar+Cor?
	Px		18	49	Px
	Px+Pl+Mel+Ne	1200	15	36	Px+(Pl+Ne)?
			17	36	Px
		1250	13.5	52	Px
			17	35	Px

Composition (wt %) Ac Di CaTs	Starting material	Temp. (°C)	Press. (kb)	Time (hrs.)	Results
			18	36	Px
			20	36	Px
25 25 50	Px+Pl+Mel+Ne+Sp?	1050	10	72	Px+Pl+Ne?
			12	50.5	Px+small amt. of Pl and Ne
			15	48	Px+Gar+(Pl+Ne)?
			20	118	Px+Gar+Cor?
20 30 50	Px+Pl+Mel+Sp	1050	8	60	Px+Pl+Ne?
			10	72	Px+Pl+Ne?
		1050	12	48	Px+Gar+(Pl+Ne)?
			15	56	Px+Gar+Cor
		1250	17	23	Px
15 35 50	Px+Pl+Mel+Sp	1050	10	95	Px+Gar+(Pl+Ne)?
10 40 50	Px+Pl+Mel+Sp	1000	11	75	Px+Gar+Pl+Sp
		1050	8	57	Px+Pl+Mel+Sp
			9	46	Px+Pl+Mel+Sp
			11	47	Px+Gar+Pl+Sp
			13	58	Px+Gar+Cor?
			17	40	Px+Gar+Cor?
			20	58	Px+Gar+Cor?
		1150	8	48	Px+Pl+Mel+Sp?
			11	44	Px+small amt. of Pl, Sp and Mel
			12	44	Px
			13	40	Px+Gar+Pl+Sp
			15	46	Px+small amt. of Gar
			18	40	Px+Gar+Cor?
		1200	16	30	Px+small amt. of Gar, Pl and Sp
		1250	11	24	Px+Pl+small amt. of Mel and Sp
			12	26	Px
			16	22	Px
5 45 50	Px+Pl+Mel+Sp	1050	8	46	Px+Pl+(Mel+Sp)?
			10	50	Px
			12	48	Px+Gar+Cor
21 14 65	Mel+Pl+Ne+ Cor+CA_6	950	11	90	Px+Gar+Ne+Pl
		1050	10	45	Px+Ne+Pl
			12	60	Px+Ne+Pl
			13	34	Px+Cor+Gar?
			15	65	Px+Gar+Cor?
		1150	12	46	Px+Ne+Pl
			14	46	Px+small amt. of Gar, Pl and Ne
			18	46	Px+small amt. of Gar
		1200	18	30	Px

Composition (wt %) Ac Di CaTs	Starting material	Temp. (°C)	Press. (kb)	Time (hrs.)	Results
		1250	12.5	24	Px+Ne+Pl
			14	24	Px
			16	24	Px
			18	24	Px
7 28 65	Mel+Pl+Sp	1050	8	87	Px+Pl+small amt. of Gar and Sp
			13	97.5	Px+Gar+Pl+Sp
			15	72	Px+Gar+Cor?
		1350	13	13	Px
15 10 75	Mel+Pl+Cor+Ne?	950	15	84	Px+Gar+Cor?
			20	84	Px+Gar+Cor?
		1000	10	144	Px+Ne+Pl
			12	83	Px+Pl+Ne+Gar
		1050	10	47	Px+Pl+Ne
			11	48	Px+small amt. of Gar, Ne and Pl
			13	60	Px+Gar+Cor?
			15	48	Px+Gar+Cor?
			20	48	Px+Gar+Cor
			25	85	Gar+Px+Cor
		1150	12	58	Px+small amt. of Pl and Ne
			14	52	Px+small amt. of Gar
			20	43	Px+small amt. of Gar
	Px+Gar (after 1150°C, 14kb, 49 hr.)		12	58	Px+small amt. of Pl and Ne
	Mel+Pl+Cor+Ne?	1200	14	36	Px+Gar+Cor?
			20	34	Px+Gar?
		1250	14	30	Px+Ne+Pl
			15.5	30	Px
			18	35	Px
			20	24	Px
5 20 75	Mel+Pl+Sp	1050	8	46	Px+Pl+Sp+Gar?
		1050	10	47	Px+Gar+Pl+Sp
			12	50	Px+Gar+Pl+Sp
			14	64	Px+Gar+Pl+Sp
			17	86	Px+Gar+Pl+Sp
			20	70	Px+Gar+Sp+Pl?
		1350	16	7	Px
6 4 90	Mel+Pl+Sp+ CA_6+Cor	1050	10	60	Px+Gar+Pl+Sp?
			13	64	Px+Gar+Cor
		1350	15	17	Px
2 8 90	Mel+Pl+Sp+ CA_6+Cor	1050	17	70	Gar+Px+Pl+Sp+Cor?

Ac = $NaFe^{3+}Si_2O_6$, Di = $CaMgSi_2O_6$, CaTs = $CaAl_2SiO_6$, Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Mel = melilite solid solution, Sp = spinel, CA_6 = $CaO.6Al_2O_3$ solid solution, Cor = corundum solid solution, Gar = garnet solid solution.

(1) Phase relations in the join $Ac_{60}Di_{40}$–CaTs at high pressures.

Fig. 3 shows an isothermal section of the join $Ac_{60}Di_{40}$CaTs at high pressures from 10 to 25 kb at 1050°C, and the experimental data at high pressure are given in Table 1. It shows that $CaAl_2SiO_6$ solubility in the clinopyroxene of the composition $Ac_{60}Di_{40}$ increases with increasing pressure and this degree of solubility attains to about 45 wt% at 1050°C and 14.5 kb. The phase assemblages under high pressure change at follows with the increase of pressure: in the CaTs-poor region, clinopyroxene$_{ss}$ + plagioclase$_{ss}$, clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$, and in the CaTs-rich region, clinopyroxene$_{ss}$ + garnet$_{ss}$ + plagioclase$_{ss}$ + (spinel), and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$.

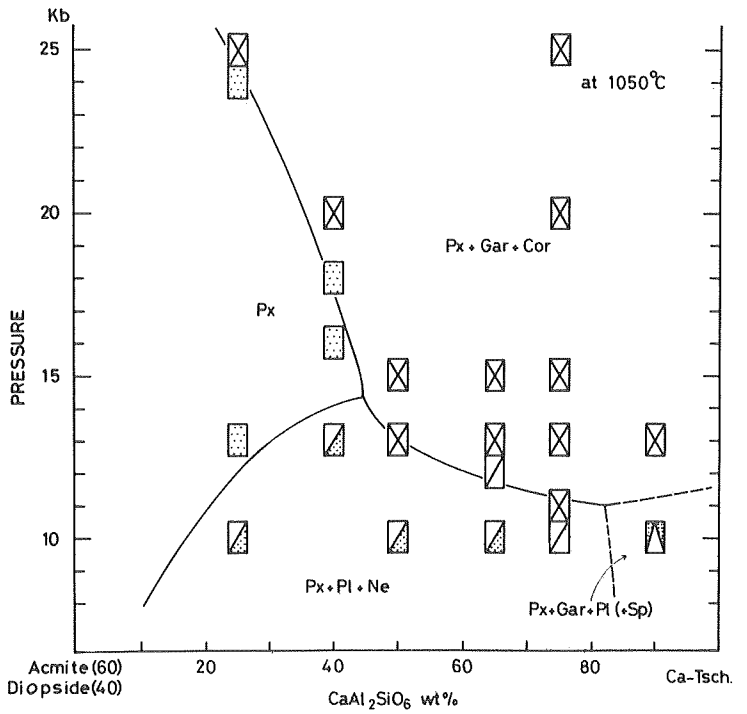


Fig. 3 Pressure-composition section for the join ($NaFe^{3+}Si_2O_6$ 60 wt% + $CaMgSi_2O_6$ 40 wt%)–$CaAl_2SiO_6$ at 1050°C. Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Sp = spinel, Gar = garnet solid solution, Cor = corundum solid solution.

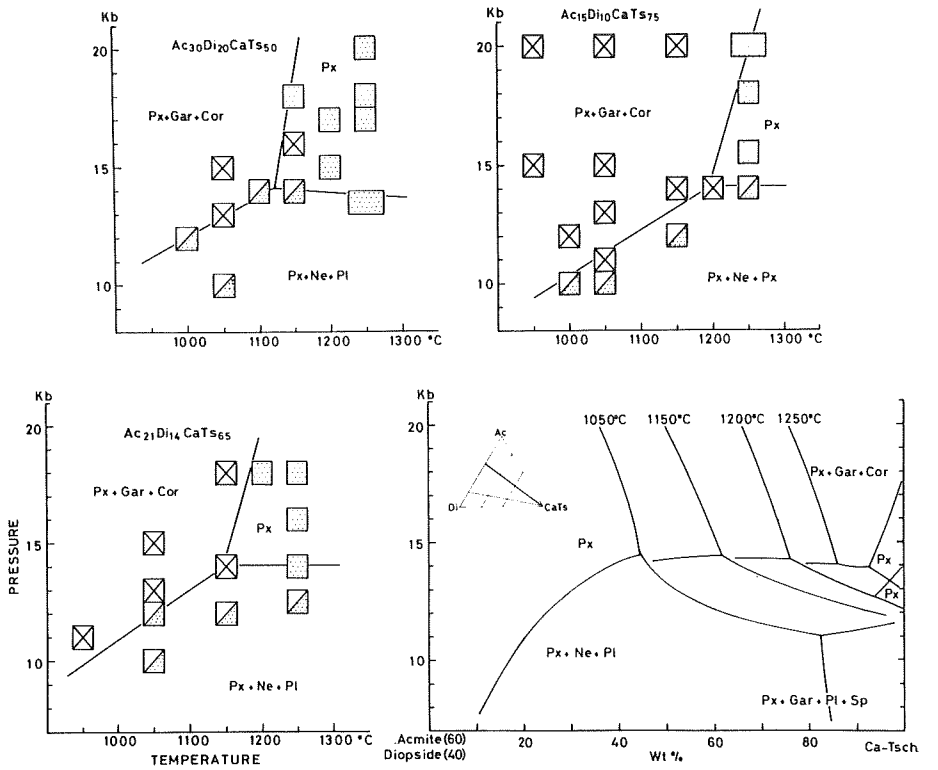


Fig. 4 (top left) Temperature-pressure plane of the composition $Ac_{30}Di_{20}CaTs_{50}$.
Fig. 5 (bottom left) Temperature-pressure plane of the composition $Ac_{21}Di_{14}CaTs_{65}$.
Fig. 6 (top right) Temperature-pressure plane of the composition $Ac_{15}Di_{10}CaTs_{75}$.
Fig. 7 (bottom right) Pressure-composition sections for the join $Ac_{60}Di_{40}$–CaTs at 1050°C, 1150°C, 1200°C and 1250°C. The data of $CaAl_2SiO_6$ are quoted from Hays (1967). Symbols are the same as in Fig. 3.

The pressure–temperature diagrams for three compositions ($Ac_{30}Di_{20}$–$CaTs_{50}$, $Ac_{21}Di_{14}CaTs_{65}$, and $Ac_{15}Di_{10}CaTs_{75}$) on this join were constructed (Figs. 4, 5 and 6). These diagrams show that the clinopyroxene-single-phase region appears at higher temperature in each composition, and also show that the stability fields of the clinopyroxene solid solutions of these compositions spread to a higher temperature and higher pressure sides. Fig. 7 shows that the solubility of $CaAl_2SiO_6$ is affected by temperature and increases with increasing temperature, and suggests that there is a complete series of solid solution between the clinopyroxene of the composition $Ac_{60}Di_{40}$ and $CaAl_2SiO_6$.

(2) Phase relations in the join $Ac_{20}Di_{80}$–CaTs at high pressures.

Fig. 8 shows an isothermal section of the join $Ac_{20}Di_{80}$ – CaTs at high

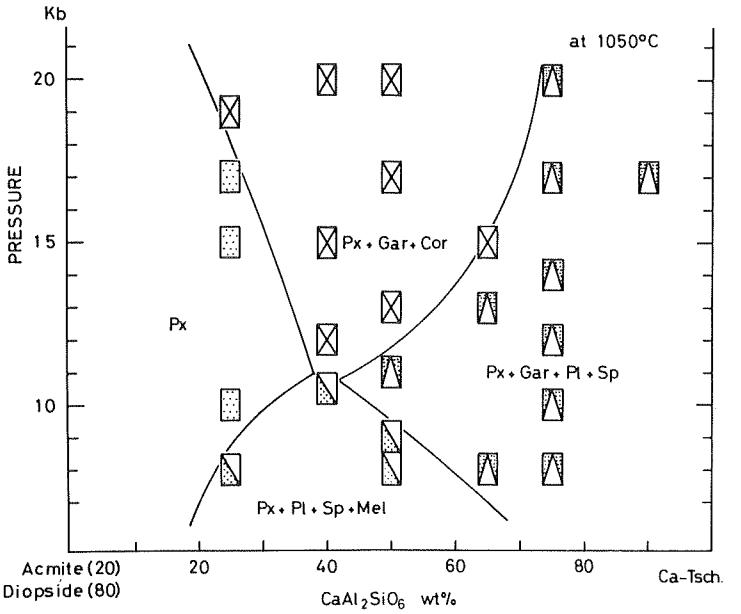


Fig. 8 Pressure-composition section for the join ($NaFe^{3+}Si_2O_6$ 20 wt% + $CaMgSi_2O_6$ 80 wt%)–$CaAl_2SiO_6$ at 1050°C. Px = pyroxene solid solution, Pl = plagioclase solid solution, Sp = spinel, Mel = melilite solid solution, Gar = garnet solid solution, Cor = corundum solid solution.

pressure from 8 to 20 kb at 1050°C, and the experimental data under the high pressure conditions are given in Table 1. It shows that $CaAl_2SiO_6$ solubility in the clinopyroxene of the composition $Ac_{20}Di_{80}$ increases with increasing pressure and the solubility attains to about 38 wt% at 1050°C and 11 kb. The phase assemblages under high pressure conditions change as follows with the increase of pressure: in the CaTs-poor region, $clinopyroxene_{ss}$ + $plagioclase_{ss}$ + $melilite_{ss}$ + spinel, $clinopyroxene_{ss}$, and $clinopyroxene_{ss}$ + $garnet_{ss}$ + $corundum_{ss}$, and in the CaTs-rich region, $clinopyroxene_{ss}$ + $plagioclase_{ss}$ + $melilite_{ss}$ + spinal, $clinopyroxene_{ss}$ + $garnet_{ss}$ + $plagioclase_{ss}$ + spinel, and $clinopyroxene_{ss}$ + $garnet_{ss}$ + $corundum_{ss}$.

(3) Phase relations in the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$ at high pressures.

Fig. 9 shows an isothermal section of the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$ at high pressures from 8 to 25 kb at 1050°C, and the experimental data at high pressure are given in Table 1. The phase assemblages under the high pressure conditions change as follows with the increase of pressure: in the acmite-rich region, $clinopyroxene_{ss}$ + $nepheline_{ss}$ + $plagioclase_{ss}$, $clinopyroxene_{ss}$ and $clinopyroxene_{ss}$ + $garnet_{ss}$ + $corundum_{ss}$, and in the diopside-rich region,

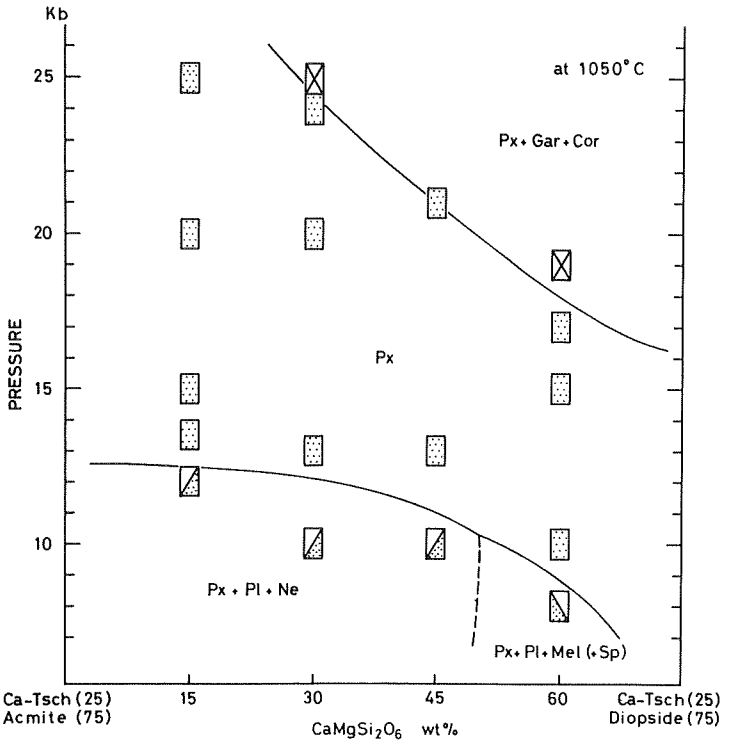


Fig. 9 Pressure-composition section for the join ($Na^{3+}FeSi_2O_6$ 75 wt% + $CaAl_2SiO_6$ 25 wt%)–($CaMgSi_2O_6$ 75 wt% + $CaAl_2SiO_6$ 25 wt%) at 1050°C. Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Mel = melilite solid solution, Sp = spinel, Gar = garnet solid solution, Cor = corundum solid solution.

clinopyroxene$_{ss}$ + plagioclase$_{ss}$ + melilite$_{ss}$ + spinel, clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$. It shows that with increasing diopside content in the bulk composition the stability field of the clinopyroxene$_{ss}$ becomes smaller and the clinopyroxene decomposes to Px, Gar and Cor at lower pressure.

(4) Phase relations in the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$ at high pressures.

Fig. 10 shows an isothermal section of the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$ at high pressures from 8 to 20 kb at 1050°C, and the experimental data at high pressure are given in Table 1. The phase assemblages under the high pressure conditions change as follows with the increase of pressure: in the acmite-rich region, clinopyroxene$_{ss}$ + nepheline$_{ss}$ + plagioclase$_{ss}$, clinopyroxene$_{ss}$, and clinopyroxene$_{ss}$ + garnet$_{ss}$ + corundum$_{ss}$, and in the diopside-rich region, clinopyroxene$_{ss}$ + plagioclase$_{ss}$ + spinel, clinopyroxene$_{ss}$, clinopyroxene$_{ss}$ +

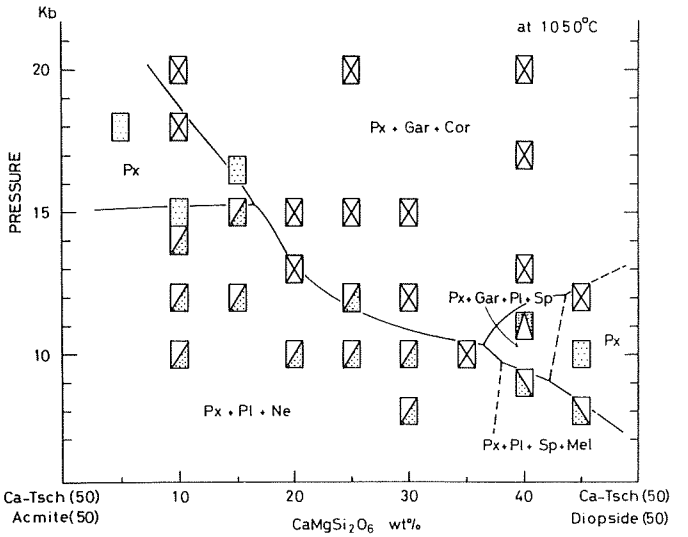


Fig. 10 Pressure-composition section for the join ($NaFe^{3+}Si_2O_6$ 50 wt% + $CaAl_2SiO_6$ 50 wt%)–($CaMgSi_2O_6$ 50 wt% + $CaAl_2SiO_6$ 50 wt%) at 1050°C. Px = pyroxene solid solution, Ne = nepheline solid solution, Pl = plagioclase solid solution, Sp = spinel, Mel = melilite solid solution, Gar = garnet solid solution, Cor = corundum solid solution.

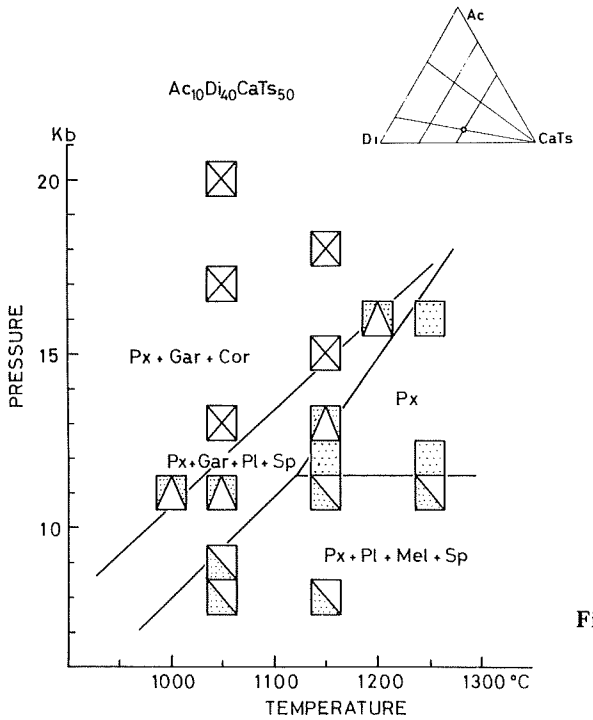


Fig. 11 Temperature-pressure plane of the composition $Ac_{10}Di_{40}CaTs_{50}$. Symbols are the same as in Fig. 10.

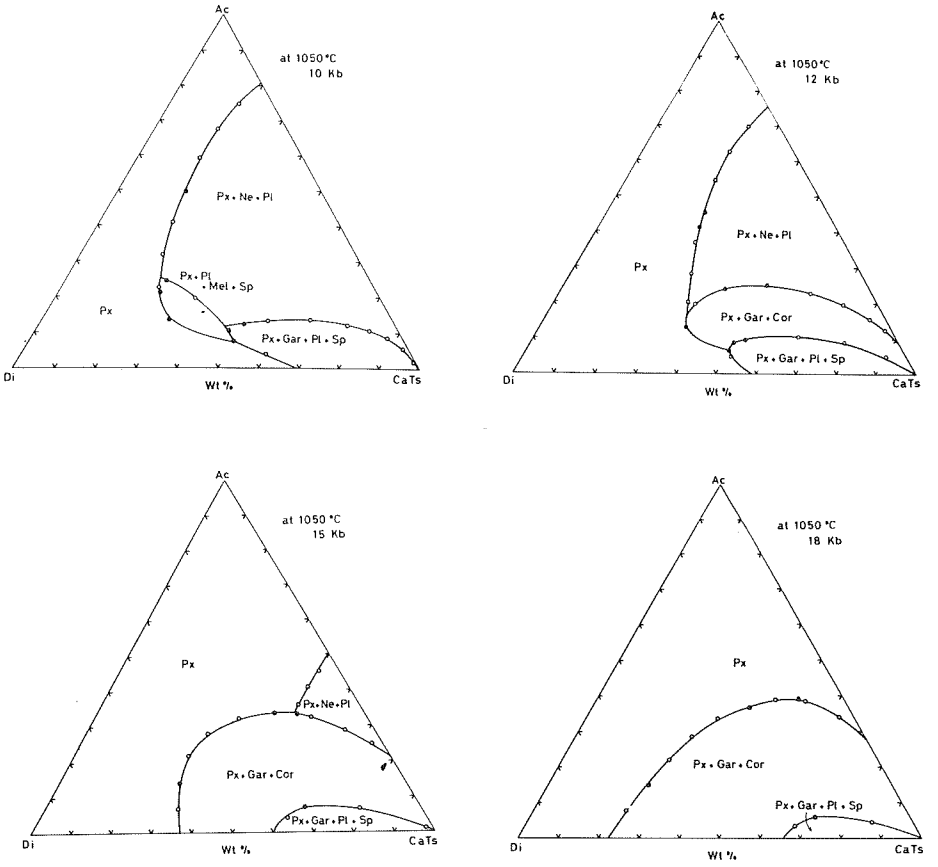


Fig. 12 (top left) Isobaric section for 10 kb at 1050°C.
Fig. 13 (top right) Isobaric section for 12 kb at 1050°C.
Fig. 14 (bottom right) Isobaric section for 15 kb at 1050°C.
Fig. 15 (bottom left) Isobaric section for 18 kb at 1050°C. Symbols are the same as in Fig. 10.

garnet$_{SS}$ + plagioclase$_{SS}$ + spinel, and clinopyroxene$_{SS}$ + garnet$_{SS}$ + corundum$_{SS}$.

Fig. 11 shows a pressure–temperature diagram of the composition $Ac_{1\,0}\,Di_{4\,0}\,CaTs_{5\,0}$. It shows that the clinopyroxene of this composition is stable at higher pressures and higher temperatures.

(5) The isothermal and isobaric sections in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$.

Figs. 12, 13, 14 and 15 show the isothermal (at 1050°C) and isobaric (10 kb, 12 kb, 15 kb, and 18 kb, respectively) sections in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$. Each phase boundary was determined

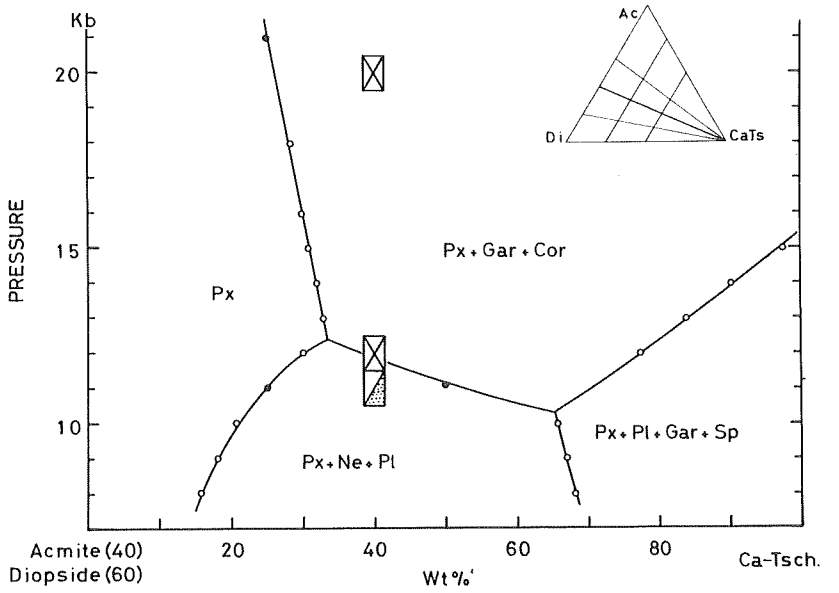


Fig. 16 Pressure-composition section for the join $Ac_{40}Di_{60}$–CaTs. Symbols are the same as in Fig. 10.

on the basis of four sections (Figs. 3, 8, 9 and 10), considering the pressure-composition diagram in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 950°C (Fig. 2) and the pressure-temperature diagrams of the composition $Di_{50}CaTs_{50}$ and $Di_{25}CaTs_{75}$ determined by Hijikata (1969). Black dots indicate compositions on the join $Ac_{60}Di_{40}$–CaTs, the join $Ac_{20}Di_{80}$–CaTs, the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$, or the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$. Fig. 16 shows the pressure-composition diagram (at 1050°C) or the join $Ac_{40}Di_{60}$–CaTs which is estimated from the phase diagrams mentioned above. The experimental data of a composition $Ac_{24}Di_{36}CaTs_{40}$ on this join indicates that this estimated phase diagram is reasonable.

(6) Crystalline phases

In the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$, clinopyroxene$_{ss}$, nepheline$_{ss}$, plagioclase$_{ss}$, melilite$_{ss}$, spinel, $(CaO.6Al_2O_3)_{ss}$, hematite, magnetite, garnet$_{ss}$, and corundum$_{ss}$ were encountered.

Clinopyroxene: Clinopyroxene forms euhedral and subhedral crystals, light bluish green or light yellowish green in color. The size of clinopyroxene becomes smaller with the increase of the content of $CaAl_2SiO_6$ molecule. In the three-phase assemblage region (Px + Gar + Cor) of the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ the refractive indices of clinopyroxene$_{ss}$ tend to decrease slightly with increasing pressure (Yoshikawa, 1976). Fig. 17 shows the unit-cell

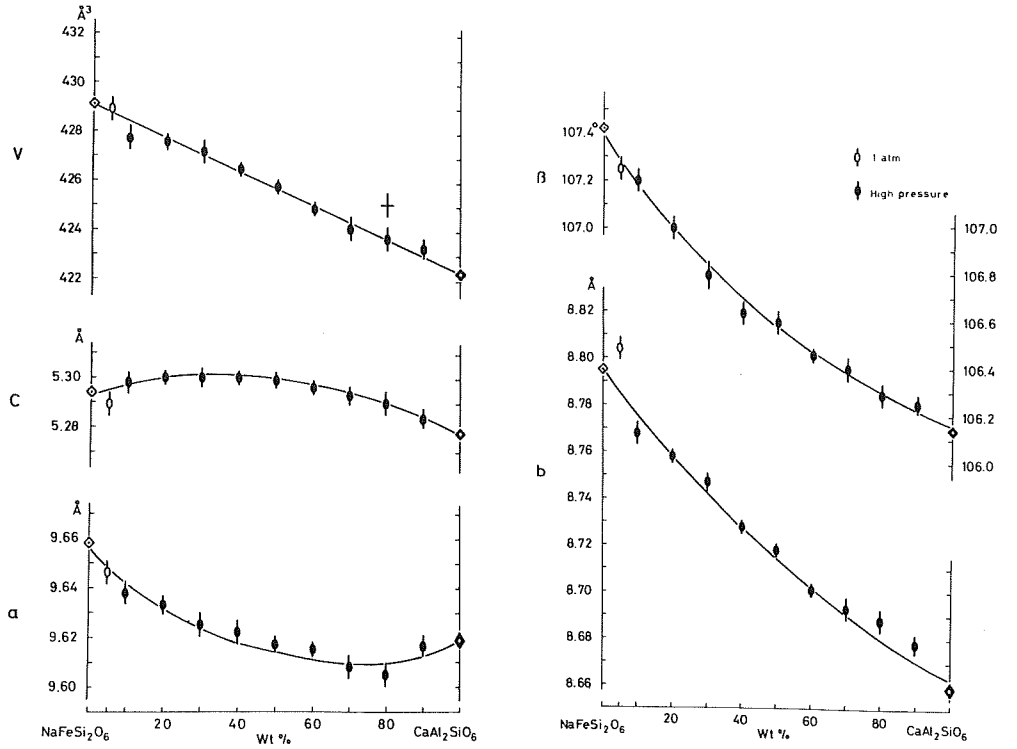


Fig. 17 Unit-cell parameters of the pyroxene solid solution along the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$. Open circle: the data at 1 atm. Solid circle: the data at high pressure and high temperature. A cross: the datum of pyroxene synthesized from the glass of the composition $Ac_{20}CaTs_{80}$. The data of $NaFe^{3+}Si_2O_6$, and $CaAl_2SiO_6$ are quoted from Nolan and Edgar (1963), and Clark et al. (1962), respectively.

parameters of clinopyroxene$_{SS}$ along the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$. The cell edge 'a' gradually decreases to about 80 wt % and then increases slightly. The cell edge 'b' and 'β' decrease with increasing $CaAl_2SiO_6$. The cell edge 'c' increases slightly up to a maximum at about 40 wt % $CaAl_2SiO_6$ and then decreases. As the result, the unit-cell volumes of clinopyroxene$_{SS}$ decrease almost linearly with increasing $CaAl_2SiO_6$ content. The lattice spacing (233) of clinopyroxene$_{SS}$ in the products synthesized from $Ac_{30}CaTs_{70}$ decreases continuously with increasing pressure (Table 3). Unit-cell volumes of clinopyroxene$_{SS}$ in the field of Px + Ne + Pl are larger than those of clinopyroxene solid solutions along the join acmite-Ca-Tschermak's molecule (Table 4). Table 2 and Fig. 18 show the unit-cell parameters of clinopyroxene solid solutions along the join $Ac_{60}Di_{40}$–CaTs. The cell edge 'a' and 'b' show negative deviation, while 'c' shows positive deviation from linearity. The unit-cell volume as well as 'β' decreases almost linearly with increasing $CaAl_2SiO_6$

Table 2 Unit-cell parameters of pyroxene solid solutions in the system $NaFe^{3+}Si_2O_6$-$CaMgSi_2O_6$-$CaAl_2SiO_6$

Composition (wt %) Ac	Di	CaTs	Temp. (°C)	Press. (kb)	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
60	15	25	1050	25	9.639 (3)	8.767 (3)	5.291 (3)	106.73 (3)	428.2 (3)
45	30	25	1050	20	9.655 (3)	8.794 (3)	5.285 (3)	106.51 (3)	430.2 (3)
30	45	25	1050	21	9.662 (3)	8.811 (3)	5.276 (3)	106.39 (3)	430.9 (3)
15	60	25	1050	15	9.682 (3)	8.835 (3)	5.274 (3)	106.23 (3)	433.2 (3)
36	24	40	1050	18	9.640 (3)	8.765 (3)	5.290 (3)	106.45 (3)	428.7 (3)
45	5	50	1050	18	9.626 (3)	8.729 (3)	5.299 (3)	106.57 (3)	426.8 (3)
35	15	50	1050	17	9.636 (3)	8.742 (3)	5.294 (3)	106.43 (3)	427.8 (3)
30	20	50	1150	17	9.636 (3)	8.747 (3)	5.291 (3)	106.31 (4)	428.0 (4)
20	30	50	1250	17	9.641 (3)	8.758 (3)	5.288 (3)	106.30 (3)	428.5 (3)
10	40	50	1250	12	9.652 (3)	8.771 (3)	5.284 (3)	106.22 (3)	429.6 (3)
21	14	65	1250	16	9.632 (3)	8.723 (3)	5.293 (3)	106.29 (3)	426.8 (3)
7	28	65	1350	13	9.639 (3)	8.740 (4)	5.284 (3)	106.20 (3)	427.5 (3)
15	10	75	1250	18	9.619 (3)	8.701 (3)	5.287 (3)	106.25 (3)	424.8 (3)
5	20	75	1350	16	9.629 (3)	8.718 (3)	5.283 (3)	106.24 (3)	425.8 (3)
6	4	90	1350	15	9.618 (3)	8.682 (3)	5.283 (3)	106.18 (3)	423.7 (3)

Table 3 The lattice spacing (223) of the pyroxene in the products synthesized from $NaFe^{3+}SiO_6$ 30 wt% + $CaAl_2SiO_6$ 70 wt% at 10 kb, 18 kb, 20 kb, and 30 kb, at 950°C.

Pressure	d_{223} (Å)	Phase assemblages
30 kb	1.627 ± 0.001	Px + Gar + Cor
20 kb	1.630 ± 0.001	Px + Gar + Cor
18 kb	1.630 ± 0.001	Px
10 kb	1.640 ± 0.001	Px + Ne + Pl

Table 4 Unit-cell parameters of pyroxene solid solutions in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$

Composition (wt %) Ac	CaTs	Temp. (°C)	Press. (kb)	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
100	0	750	1 kb	9.658 (5)	8.795 (5)	5.294 (5)	107.42 (5)	429.1 (5)
95	5	860	1 atm.	9.646 (5)	8.804 (5)	5.289 (5)	107.25 (5)	428.9 (5)
93	7*	910	1 atm.	9.656 (3)	8.808 (4)	5.292 (3)	107.22 (4)	429.9 (4)
90	10*	900	1 atm.	9.667 (5)	8.815 (5)	5.301 (3)	107.15 (5)	431.6 (5)
90	10	950	10 kb	9.638 (5)	8.768 (5)	5.298 (5)	107.20 (5)	427.7 (5)
80	20	950	20 kb	9.633 (4)	8.758 (3)	5.300 (3)	107.00 (5)	427.6 (3)
0	100		20 kb	9.615 (3)	8.661 (2)	5.272 (3)	106.12 (3)	421.79 (28)
$CaFe^{3+}AlSiO_6$		1250	1 atm.	9.783 (3)	8.787 (2)	5.372 (3)	105.82 (3)	444.3 (4)

(*): the data of pyroxene coexisting with nepheline and plagioclase. The data of acmite, Ca-Tschermak's molecule, $CaFe^{3+}AlSiO_6$ are quoted from Nolan and Edgar (1963), Clark et al. (1962), Hijikata (1968), respectively.

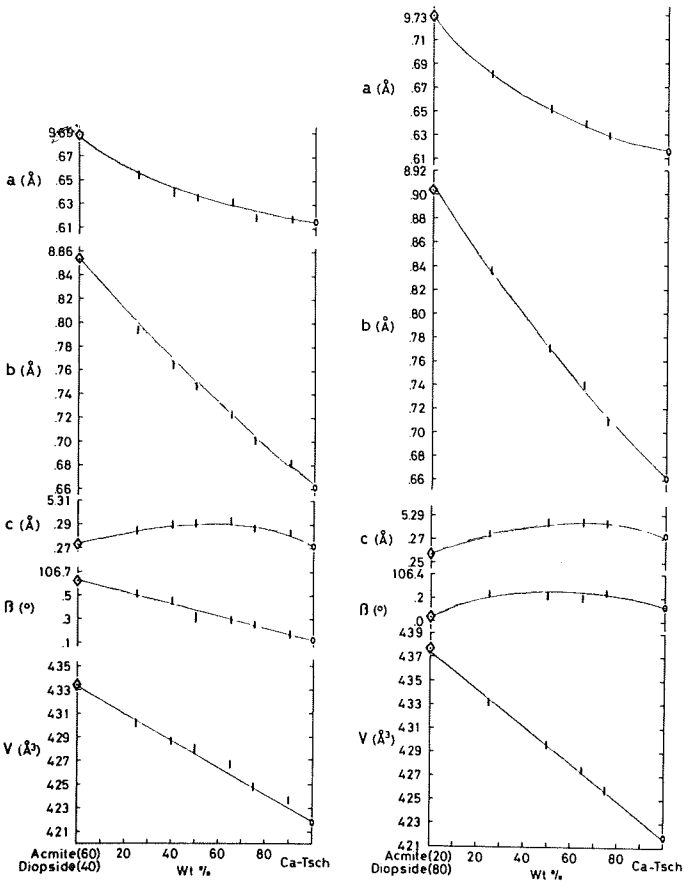


Fig. 18 (left) Unit-cell parameters of the pyroxene solid solutions along the join $Ac_{60}Di_{40}$ –CaTs. The data of $Ac_{60}Di_{40}$ and $CaAl_2SiO_6$ are quoted from Nolan and Edgar (1963), and Clark et al. (1962), respectively.

Fig. 19 (right) Unit-cell parameters of the pyroxene solid solutions along the join $Ac_{20}Di_{80}$–CaTs. . The data of $Ac_{20}Di_{80}$ and $CaAl_2SiO_6$ are quoted from Nolan and Edgar (1963), and Clark et al. (1962), respectively.

solubility. The unit-cell parameters of clinopyroxene solid solutions along the join $Ac_{20}Di_{80}$–CaTs are not a linear function of composition (Table 2 and Fig. 19). The cell edges 'a' and 'b' show negative deviation from linearity, while 'c' and 'β' show positive deviation from linearity. As the result, the unit-cell volumes of these clinopyroxenes decrease almost linearly with increasing $CaAl_2SiO_6$ content. Table 2 and Fig. 20 show the unit-cell parameters of the clinopyroxene solid solutions along the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$. Table 2 and Fig. 21 show the unit-cell parameters of the clinopyroxene solid solutions along the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$. The cell edges 'a', 'b' and

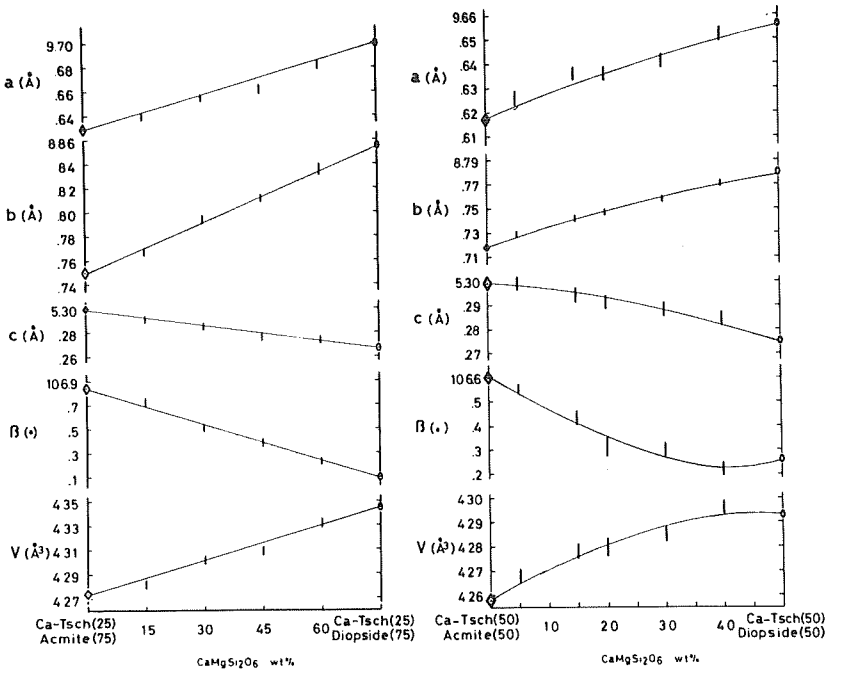


Fig. 20 (Left) Unit-cell parameters of the pyroxene solid solutions along the join $Ac_{75}CaTs_{25}$–$Di_{75}CaTs_{25}$. The data of $Di_{75}CaTs_{25}$ are quoted from Clark et al. (1962).

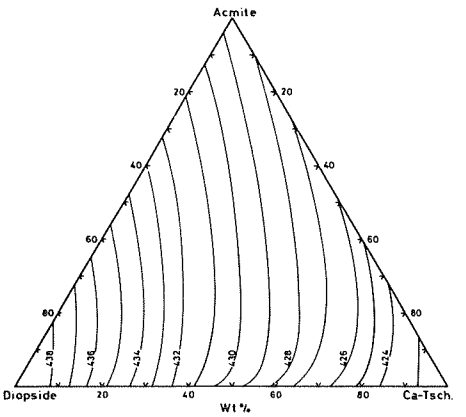
Fig. 21 (Right) Unit-cell parameters of the pyroxene solid solutions along the join $Ac_{50}CaTs_{50}$–$Di_{50}CaTs_{50}$. The data of $Di_{50}CaTs_{50}$ are quoted from Clark et al. (1962).

'c' show positive deviation, while 'β' shows negative deviation from linearity. The unit-cell volume of the clinopyroxene in this join changes with a positive deviation from linearity. The unit-cell parameters of the clinopyroxene solid solutions in the field of Px + Gar + Cor in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ are given in Table 5. This shows that the unit-cell volume of the clinopyroxene synthesized at higher pressure is smaller than that of the clinopyroxene synthesized from the same composition at lower pressure. The change of the unit-cell volume in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ is shown in Fig. 22. The data used to construct this diagram are given in Table 2 with those of Clark et al. (1962), Nolan and Edgar (1963), and Yoshikawa (1976). Fig. 23 shows the change of the cell edge 'b' and 'β' in the system acmite–diopside–Ca-Tschermak's molecule. It suggests that combining the cell edge 'b' and β, it is possible to determine the composition of synthetic clinopyroxenes in this system.

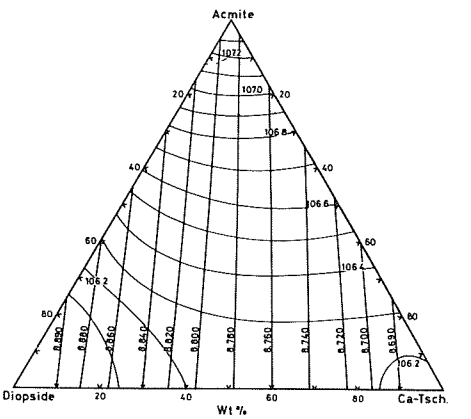
Other phases: Nepheline occurs as colorless prismatic crystals and has

Table 5 Unit-cell parameters of pyroxene solid solutions in the field of Px + Gar + Cor in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$

Composition (wt %) Ac	Di	CaTs	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)	Phase Assemblages
10	40	50	9.652 (3)	8.771 (3)	5.284 (3)	106.22 (3)	429.6 (3)	Px
			9.647 (3)	8.762 (3)	5.284 (3)	106.27 (3)	428.7 (3)	Px + Gar + (Cor) (20 kb)
21	14	65	9.632 (3)	8.723 (3)	5.293 (3)	106.29 (3)	426.8 (3)	Px
			9.616 (3)	8.714 (3)	5.288 (3)	106.37 (5)	425.1 (3)	Px + Gar + (Cor) (15 kb)
15	10	75	9.619 (3)	8.701 (3)	5.287 (3)	106.25 (3)	424.8 (3)	Px
			9.619 (4)	8.702 (3)	5.283 (4)	106.26 (4)	424.6 (4)	Px + Gar + (Cor) (15 kb)
			9.603 (3)	8.718 (5)	5.282 (3)	106.43 (3)	424.2 (4)	Px + Gar + Cor (25 kb)



Volume



b and ß

Fig. 22 (Left) Variation of the unit-cell volume for synthetic pyroxenes in the system acmite–diopside–Ca-Tschermak's molecule.

Fig. 23 (Right) Relationship between chemical composition and the combined 'b' and 'β' for synthetic pyroxenes in the system acmite–diopside–Ca-Tschermak's molecule.

somewhat higher refractive indices than pure nepheline. Bailey and Schairer (1963) and Onuma et al. (1972) showed that the refractive indices of nepheline become higher with the increase of $NaFe^{3+}SiO_4$. Probably this is also the case of the present nepheline and $NaFe^{3+}SiO_4$ could be formed by the following reaction.

$$NaFe^{3+}Si_2O_6 + CaAl_2SiO_6 = NaFe^{3+}SiO_4 + CaAl_2Si_2O_8$$

acmite CaTs iron-nepheline anorthite

Plagioclase is colorless and generally subhedral. At higher temperature in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ at 1 atm plagioclase occurs as

tabular crystals (Yoshikawa and Onuma, 1975). Hematite is reddish brown in color, but is black in very small grain. It occurs as hexagonal or granular crystals. Melilite is colorless and stout prismatic or rounded in shape. Refractive indices of melilite become higher with increasing $CaAl_2SiO_6$ content in liquid, indicating that this melilite is a solid solution, probably containing gehlenite molecule. Magnetite was identified optically and in the X-ray powder diffraction pattern of the run products of $Ac_{80}CaTs_{20}$ at 1370°C and those of $Ac_{70}CaTs_{30}$ at 1390°C, at 1 atm , but below these temperatures magnetite was not observed. Garnet usually forms rounded grains and is colorless or pale green in color. Table 6 gives the unit-cell parameters of the garnet solid solutions in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$. Some of them have smaller values than that of grossular (11.855 Å: Prandl, 1966). This indicates that the garnets in this system form solid solution series among andradite, grossular and pyrope. These data also show that the garnet synthesized at higher pressure has a larger unit-cell parameter than that synthesized at lower pressure from the same starting material at the same temperature. In the garnet solid solution in this system andradite molecule increases with increasing pressure as that in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ (Yoshikawa, 1976). Corundum is light yellowish green in color and appears generally as rounded form. The value of (012) spacing of the corundum synthesized from $Ac_{30}CaTs_{70}$ at 30 kb and 950°C is 3.489 (±0.002) Å and that from

Table 6 Unit-cell parameters of garnet solid solutions in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$

Composition wt % Ac	Di	CaTs	Temp. (°C)	Press. (kb)	a (Å)
12	48	40	1050	20	11.845 (3)
30	20	50	1050	15	11.885 (3)
25	25	50	1050	20	11.867 (3)
20	30	50	1050	15	11.858 (3)
10	40	50	1050	20	11.833 (3)
21	14	65	1050	15	11.848 (3)
15	10	75	950	15	11.849 (3)
			950	20	11.860 (3)
			1050	15	11.845 (3)
			1050	20	11.846 (3)
			1050	25	11.854 (3)
6	4	90	1050	13	11.848 (3)

Andradite	(Quareni and Pieri, 1966)	12.061 Å
Grossular	(Prandl, 1966)	11.855 Å
Pyrope	(Gibbs and Smith, 1965)	11.459 Å

$Ac_{40}CaTs_{60}$ at 30 kb and 950°C is 3.486 (±0.002) Å. These values indicate that the amount of Fe_2O_3, if present at all, must be less than 5–6 mole %. Spinel was detected by X-ray diffraction. In this experiment, it could not be confirmed whether it is solid solution, or not.

Discussion

In this section the nature of clinopyroxenes in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ is discussed with the present experimental data and the data by Yoshikawa and Onuma (1975) and Yoshikawa (1976).

(1) Tschermak's substitution in clinopyroxenes

In the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ clinopyroxene has its stability field over the wide pressure range, from 1 atm to 30 kb. The solubility of $CaAl_2SiO_6$ in the clinopyroxene in the join $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$ is controlled not only by pressure but also by temperature. Thompson (1947) pointed out that high pressure condition favors octahedrally coordinated aluminum and high temperature condition favors tetrahedrally coordinated aluminum in silicate minerals. The present investigation indicates that the solubility of $CaAlAlSiO_6$ in pyroxene, which has one half of aluminum atoms in tetrahedral site and the other half in octahedral site, is facilitated under the relatively high pressure and the relatively high temperature condition.

Fig. 24 shows the solubility limit of $CaAl_2SiO_6$ in clinopyroxene at various pressure at 1050°C in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$. The solubility limit of $CaAl_2SiO_6$ in clinopyroxene at 1 atm is estimated on the basis of the following studies: There is a complete series of solid solutions between acmite and diopside (Yagi, 1966); diopside incorporates $CaAl_2SiO_6$ up to about 12 wt % at 1 atm (Schairer and Yoder, 1970); and the solubility limit of $CaAl_2SiO_6$ in acmite is about 6 wt % at 1 atm (Yoshikawa and Onuma, 1975). This diagram shows that near the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ the solubility of $CaAl_2SiO_6$ in acmite increases with increasing pressure up to about 16 kb at 1050°C and decreases with increasing pressure above this pressure, and that near the join $CaMgSi_2O_6$–$CaAl_2SiO_6$ the solubility of $CaAl_2SiO_6$ in diopside increases with increasing pressure up to 9 kb at 1050°C, and decreases with increasing pressure above this pressure. These facts indicate that the clinopyroxene solid solution between $NaFe^{3+}Si_2O_6$ and $CaAl_2SiO_6$ is more stable than that between $CaMgSi_2O_6$ and $CaAl_2SiO_6$ at higher pressure. In other words, the substitution of $CaAl^{VI}Al^{IV}$ for $NaFe^{3+}Si$ requires higher

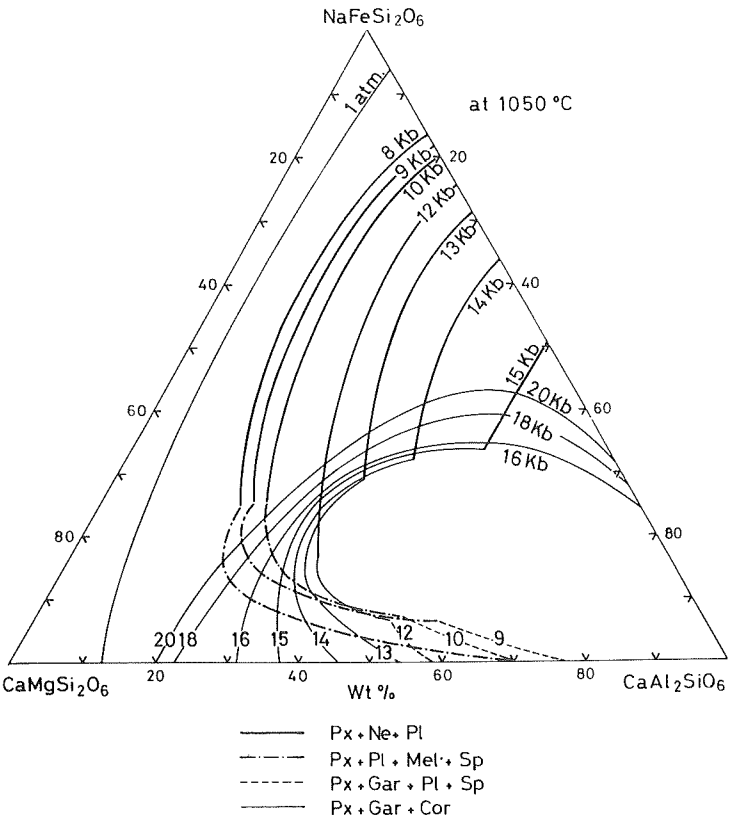


Fig. 24 The solubility limit of $CaAl_2SiO_6$ in clinopyroxenes against pressure at 1050°C in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$. Symbols are the same as in Fig. 10.

pressure condition than that of $Al^{VI}Al^{IV}$ for MgSi. Therefore, the former substitution is more difficult than the latter coupled substitution at upper crust condition. This may be one of the reasons why the solubility of $CaAl_2SiO_6$ in Na-rich clinopyroxene is small, comparing to that in Ca-rich clinopyroxene (Fig. 25). Fig. 24 also shows that the presence of a small amount of acmite molecule in the clinopyroxene gives significant effect on the solubility of $CaAl_2SiO_6$ in diopside under lower pressure (below about 10 kb); for example, the solubility of $CaAl_2SiO_6$ in diopside decreases from about 70 wt % to about 30 wt % with the presence of 10 wt % acmite at 8 kb.

(2) Clinopyroxene solid solutions in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$

The solubility of $CaAl_2SiO_6$ in acmite increases with increasing pressure up to 18 kb at 950°C and decreases with increasing pressure above this pressure. The $clinopyroxene_{ss}$ between acmite and Ca-Tschermak's molecule decomposes

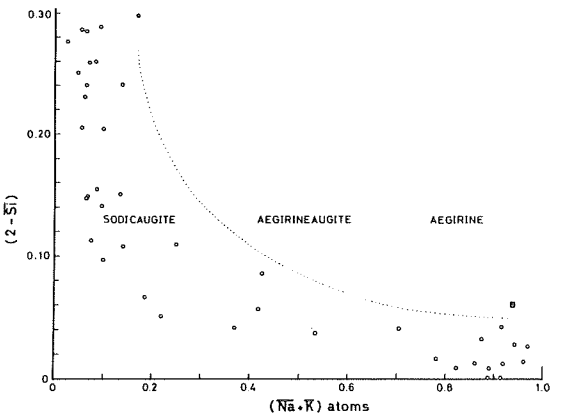


Fig. 25 Number of (Na + K) versus that of (2-Si) per formula unit based on 6 oxygens for natural clinopyroxenes quoted from Deer et al. (1963), Carmichael (1962), Huckenholz (1970), and Binns (1969).

to clinopyroxene, nepheline, and plagioclase at lower pressure, while to clinopyroxene, garnet, and corundum at higher pressure.

In the three-phase assemblage region (Px + Ne + Pl) the following reaction is expected and $CaFe^{3+}AlSiO_6$ would be incorporated into the clinopyroxene$_{ss}$ together with $CaAl_2SiO_6$.

$$\underset{\text{acmite}}{m(NaFe^{3+}Si_2O_6)} + \underset{\text{CaTs}}{2n(CaAl_2SiO_6)} = \underset{\text{nepheline}}{n(NaAlSiO_4)} + \underset{\text{albite}}{(m-n)(NaAlSi_3O_8)}$$

$$+ \underset{\text{anorthite}}{(2n-m)(CaAl_2Si_2O_8)} + \underset{\text{pyroxene}}{m(CaFe^{3+}AlSiO_6)} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

The difference of molar volume in reaction (1) is + (1.9 m + 28.3 n) cm^3. $CaFe^{3+}AlSiO_6$ (ferri-aluminum Tschermak's molecule) is a stable compound having clinopyroxene structure at 1 atm and its unit-cell volume is larger than that of acmite (Hijikata, 1968; Hijikata and Onuma, 1969). Therefore, when this molecule is incorporated in acmite, the unit-cell volume of the clinopyroxene is increased. The unit-cell volumes of the clinopyroxene in this three-phase assemblage region are plotted near the line connecting the unit-cell volume of acmite and $CaFe^{3+}AlSiO_6$ (Yoshikawa and Onuma, 1975). $CaAl_2SiO_6$ has clinopyroxene structure only at high pressure and has a smaller unit-cell volume than acmite (Clark et al., 1962; Hays, 1966; Hijikata and Yagi, 1967). If the clinopyroxene$_{ss}$ contains $CaAl_2SiO_6$, the unit-cell volume would become smaller. Actually, the clinopyroxene$_{ss}$ crystallized at high pressure containing more than 10 wt % $CaAl_2SiO_6$ are plotted near the line connecting the unit-cell volume of acmite and $CaAl_2SiO_6$ (Fig. 17). Consequently, clinopyroxene$_{ss}$ in this field may consist of $NaFe^{3+}Si_2O_6$, $CaAl_2SiO_6$ and $CaFe^{3+}AlSiO_6$.

Huckenholz (1973) stated that the content of $CaFe^{3+}_2SiO_6$ is small or absent in aegirine-augite of the alkalic rocks with sodium in excess of potassium in the bulk composition of rocks, while the clinopyroxenes of sodium-poor alkalic rocks contain $CaFe^{3+}_2SiO_6$. The results of the present study suggests that clinopyroxene$_{ss}$ changes from the solid solution between acmite and $CaAl_2SiO_6$ to that consisting of $NaFe^{3+}Si_2O_6$, $CaAl_2SiO_6$ and $CaFe^{3+}AlSiO_6$, but not $CaFe^{3+}_2SiO_6$ with the decrease of sodium content in the liquid. This indicates that $CaFe^{3+}AlSiO_6$ can be incorporated into acmite if the liquid from which acmite crystallizes becomes poor in sodium and rich in calcium.

In the field of Px + Gar + Cor garnet is considered to be solid solution between andradite and grossular on the basis of the data of the unit-cell parameter (Yoshikawa, 1976). Therefore, in this field it is expected that the following chemical reaction takes place.

$$\underset{\text{acmite}}{2m(NaFe^{3+}Si_2O_6)} + \underset{\text{CaTs}}{3n(CaAl_2SiO_6)} = (n-m)\underset{\text{grossular}}{(Ca_3Al_2Si_3O_{12})} +$$

$$\underset{\text{andradite}}{m(Ca_3Fe^{3+}_2Si_3O_{12})} + \underset{\text{jadeite}}{2m(NaAlSi_2O_6)} + \underset{\text{corundum}}{2n(Al_2O_3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where $NaAlSi_2O_6$, jadeite, is stable only under the high pressure conditions. The refractive indices of clinopyroxene$_{ss}$ in this field become somewhat low with increasing pressure and the lattice spacing (223) becomes much smaller than that of the clinopyroxene$_{ss}$ in the clinopyroxene-single-phase region (Table 3). These facts seem to support the view that clinopyroxene$_{ss}$ in this field incorporates $NaAlSi_2O_6$ molecule. The difference of molar volume in reaction (2) is $-(2.1\,m + 14.1\,n)\ cm^3$. Consequently, clinopyroxene$_{ss}$ in this region contains three pyroxene molecules of $NaFe^{3+}Si_2O_6$, $CaAl_2SiO_6$ and $NaAlSi_2O_6$. Table 3 shows that the lattice spacing (223) of clinopyroxene$_{ss}$ tends to decrease continuously with increasing pressure. This indicates that the chemical composition of clinopyroxene in this join changes continuously with increasing pressure. With increasing pressure, $CaFe^{3+}AlSiO_6$ molecule decreases in clinopyroxene$_{ss}$ when it coexists with nepheline and plagioclase, while jadeite molecule tends to be richer in the clinopyroxene$_{ss}$ when it coexists with garnet and corundum. On the basis of the data mentioned above, it is estimated that the nature of the pyroxene$_{ss}$ in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$ changes as follows with increasing pressure: $NaFe^{3+}Si_2O_6$ + $CaAl_2SiO_6$ + $CaFe^{3+}AlSiO_6$ (in the field of Px + Ne + Pl), $NaFe^{3+}Si_2O_6$ + $CaAl_2SiO_6$ (in the field of Px), $NaFe^{3+}Si_2O_6$ + $CaAl_2SiO_6$ + $NaAlSi_2O_6$ (in the field of Px + Gar + Cor).

In addition to the change of the nature of the clinopyroxene solid solutions, the amount of garnet in the run products and andradite molecule in the garnet$_{ss}$ increase with increasing pressure. Sodium is unlikely to enter into

garnet and corundum under these experimental conditions. Therefore, Ca and Fe^{3+} move from clinopyroxene into garnet with increasing pressure, and as a result, both Na/Ca ratio and Al/Fe^{3+} ratio in clinopyroxene become gradually larger and Na and Al are concentrated in clinopyroxene. When sodium content in the liquid decreases, clinopyroxene$_{ss}$ crystallized from this liquid tends to incorporate more $CaFe^{3+}AlSiO_6$ and less sodium, although sodium content in clinopyroxene$_{ss}$ increases with increasing pressure.

(3) Clinopyroxene solid solutions in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$.

At lower pressure, clinopyroxene coexists with nepheline and plagioclase in the acmite-rich region, and with plagioclase, melilite, and spinel in the diopside-rich region. In these regions the following reactions are expected.
In the field of Px + Ne + Pl:

$$\underset{\text{acmite}}{x(NaFe^{3+}Si_2O_6)} + \underset{\text{diopside}}{y(CaMgSi_2O_6)} + \underset{\text{CaTs}}{z(CaAl_2SiO_6)}$$

$$= \underset{\text{nepheline}}{\frac{z}{2}(NaAlSiO_4)} + \underset{\text{albite}}{(x-\frac{z}{2})(NaAlSi_3O_8)} + \underset{\text{anorthite}}{(z-x)(CaAl_2Si_2O_8)}$$

$$+ \underset{\text{clinopyroxene}}{x(CaFe^{3+}AlSiO_6)} + \underset{\text{diopside}}{y(CaMgSi_2O_6)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\Delta V = +(1.9\,x + 28.3\,z)\ cm^3$$

In the field of Px + Pl + Mel + Sp:

$$\underset{\text{acmite}}{x(NaFe^{3+}Si_2O_6)} + \underset{\text{diopside}}{y(CaMgSi_2O_6)} + \underset{\text{CaTs}}{z(CaAl_2SiO_6)}$$

$$= \underset{\text{albite}}{x(NaAlSi_3O_8)} + \underset{\text{anorthite}}{\frac{1}{7}(3y+3z-7x)(CaAl_2Si_2O_8)} + \underset{\text{spinel}}{\frac{1}{7}(y+z)(MgAl_2O_4)}$$

$$+ \underset{\text{gehlenite}}{\frac{1}{7}(3z-4y)(Ca_2Al_2SiO_7)} + \underset{\text{åkermanite}}{\frac{1}{7}(6y-z)(Ca_2MgSi_2O_7)} + \underset{\text{clinopyroxene}}{x(CaFe^{3+}AlSiO_6)} \ldots (4)$$

$$\Delta V = +(1.2\,x + 10.8\,y + 10.9\,z)\ cm^3$$

The clinopyroxene$_{ss}$ in these regions may consist of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$, $CaAl_2SiO_6$, and $CaFe^{3+}AlSiO_6$.

At higher pressure, the clinopyroxene$_{ss}$ consisting of acmite, diopside and Ca-Tschermak's molecule decomposes to three phases, clinopyroxene, garnet

and corundum, and the following reaction is expected:

$$2x(NaFe^{3+}Si_2O_6) + y(CaMgSi_2O_6) + z(CaAl_2SiO_6)$$
acmite diopside CaTs

$$= x(Ca_3Fe^{3+}_2Si_3O_{12}) + \frac{1}{3}(y + z - 3x)(Ca_3Al_2Si_3O_{12}) +$$
andradite grossular

$$\frac{y}{3}(Mg_3Al_2Si_3O_{12}) + \frac{2}{3}(z - y)(Al_2O_3) + 2x(NaAlSi_2O_6) \quad \ldots\ldots (5)$$
pyrope corundum jadeite

$$\Delta V = -(3.9\,x + 3.6\,y + 4.7\,z)\ cm^3$$

Table 5 shows the unit-cell parameters of clinopyroxene solid solutions in the field of Px + Gar + Cor. The unit-cell volume of clinopyroxene$_{ss}$ in this field is smaller than that of the clinopyroxene$_{ss}$ in the clinopyroxene-single-phase region. This fact seems to support the above reaction indicating that the clinopyroxene$_{ss}$ in this field incorporates $NaAlSi_2O_6$ molecule. The clinopyroxene$_{ss}$ in this field may consist of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$, $CaAl_2SiO_6$, and $NaAlSi_2O_6$. It is expected that the variation of aluminous clinopyroxene molecules in the clinopyroxene solid solutions in the system $NaFe^{3+}Si_2O_6$–$CaMgSi_2O_6$–$CaAl_2SiO_6$ against pressure is the same trend as that in the join $NaFe^{3+}Si_2O_6$–$CaAl_2SiO_6$.

(4) On aluminous clinopyroxene molecules

It is well known that clinopyroxenes in nature contain mainly $CaFe^{3+}AlSiO_6$, $CaAl_2SiO_6$, $NaAlSi_2O_6$, and $CaTiAl_2O_6$ as aluminous clinopyroxene molecule. In addition to these molecules, Flower (1974) indicated that $NaTiAlSiO_6$ molecule is able to be incorporated in acmite up to about 18 mole % at 1000 bars under Mn_2O_3–Mn_3O_4 buffer condition. Judging from the Mössbauer spectragraph (Ohashi and Hariya, 1970, 1973), most of aluminum in $CaFe^{3+}AlSiO_6$ seem to occupy the tetrahedral site in clinopyroxene structure. Okamura et al. (1974) reported that a half of aluminum atoms in $CaAlAlSiO_6$ molecule occupies the octahedral site and the other half occupies the tetrahedral site. All aluminum atoms are coordinated by six oxygens in jadeite (Prewitt and Burnham, 1966). All aluminum in nepheline, plagioclase, and melilite occupies tetrahedral sites in each structure, while aluminum atom is coordinated by six oxygens in garnet. In view of the change of coordination number of aluminum in pyroxene structure with change of pressure, the change of the nature of pyroxene solid solutions mentioned above also indicates that aluminum atoms in clinopyroxene concentrate from tetrahedral sites into octahedral sites with increasing pressure; that is, the content of Tschermak's molecule in clinopyroxene decreases and most of tetrahedral sites become to be

occupied by Si^{4+} with increasing pressure. The results of the present work indicate that when clinopyroxene coexists with such silicate minerals in which all aluminum atoms occupy the tetrahedral sites, clinopyroxene incorporates more $CaAl_2SiO_6$ and less $CaFe^{3+}AlSiO_6$ with increasing pressure. On the other hand, when clinopyroxene coexists with silicate minerals containing six-coordinated aluminum, $CaAl_2SiO_6$ solubility in clinopyroxene$_{ss}$ decreases with increasing pressure. This is clearly shown in Fig. 24. When clinopyroxene coexists with nepheline and plagioclase, or plagioclase and melilite, the solubility of $CaAl_2SiO_6$ in clinopyroxene increases with increasing pressure. However, when clinopyroxene coexists with garnet, the solubility of $CaAl_2SiO_6$ decreases with increasing pressure. Kushiro (1962) reported that an increase of pressure has an important effect on the solubility of $CaAl_2SiO_6$ and $NaAlSi_2O_6$ in natural clinopyroxenes and that the clinopyroxene formed at higher pressure contains more jadeite molecule than Ca-Tschermak's molecule. The present experimental results agree with his result. However, the present study also indicates that the relative amount of these two molecules in pyroxene is controlled not only by pressure but also by temperature.

Al and/or Ti entry into clinopyroxene is controlled greatly by silica concentration (Carmichael et al., 1970; Gupta et al., 1973). Ohashi and Hariya (1975 a, 1975 b) show that the stability of $CaFe^{3+}AlSiO_6$ clinopyroxene is controlled by the oxygen fugacity. Yagi and Onuma (1967) reported that perovskite exsolves from Ti-rich diopside at high pressure in the system $CaMgSi_2O_6$–$CaTiAl_2O_6$. Verhoogen (1962) discussed from theoretical aspects that high oxygen fugacity favors the concentration of titanium in silicates. Flower (1974) also indicated that the oxygen fugacity is the most important factor on titanium entry into clinopyroxene. These suggest that the solubility of $CaFe^{3+}AlSiO_6$, $CaTiAl_2O_6$, and $NaTiAlSiO_6$ in clinopyroxene is controlled not only by pressure and temperature but also by the composition of the liquid (especially, Na, K, and Si content) and the oxygen fugacity.

(5) Calculation scheme for pyroxene end-members

Calculation scheme for pyroxene end-members have been suggested by Kushiro (1962), Yoder and Tilley (1962), White (1964), Essen and Fyfe (1967), and Cawthorn and Collerson (1974). Yoder and Tilley (1962) and White (1964) did not give the order of calculation among the Tschermak's molecules. Essen and Fyfe (1967) and Cawthorn and Collerson (1974) proposed the method for electron microprobe data in which Fe_2O_3 content is not given. Ca-Tschermak's molecule is the first end-member to be calculated in the method by Essen and Fyfe. The possibility of Al^{VI} being less than Al^{IV}, thus making the value for jadeite negative in the method by Essen and Fyfe, is

fairly common and Essen and Fyfe ignored TiO_2 and K_2O content. The method by Cawthorn and Collerson (1974) is somewhat similar to that by Kushiro (1962) except that jadeite is calculated before acmite and the theoretical end-member $CaFe^{3+}AlSiO_6$ is not calculated. In their method $CaFe^{3+}AlSiO_6$ is never calculated and both of $CaFe^{3+}_2SiO_6$ and $CaAl_2SiO_6$ are likely to be calculated in the same pyroxene. Hijikata and Onuma (1969) reported that $CaFe^{3+}AlSiO_6$ is stable compound with clinopyroxene structure at 1 atm. This fact leads to the conclusion that $CaFe^{3+}_2SiO_6$ is not able to co-exist with $CaAl_2SiO_6$ in the same pyroxene. The present investigation shows that Na-Rich and Al-rich clinopyroxene does not always contain jadeite molecule, because clinopyroxene$_{ss}$ between acmite and Ca-Tschermak's molecule also is stable under higher pressure. Therefore, without determination of Fe_2O_3 content or SiO_2 content, jadeite content in the pyroxene cannot be calculated. It also shows that $NaAlSi_2O_6$ molecule cannot coexist with $CaFe^{3+}AlSiO_6$ molecule in a clinopyroxene$_{ss}$. From the present experimental aspect, Kushiro's method (1962) is more reasonable for most of calcium clinopyroxenes. Since Na-rich clinopyroxene is not so deficient in SiO_2 as Ca-rich pyroxene (Fig. 25), it is more reasonable that $NaTiAlSiO_6$ molecule (Flower, 1974) is calculated as titanium-aluminum pyroxene molecule rather than $CaTiAl_2O_6$ in Na-rich pyroxene. The present study indicates that the clinopyroxene solid solutions crystallized in the system $NaFeSi_2O_6-CaMgSi_2O_6-CaAl_2SiO_6$ are composed not only of three pyroxene molecules of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$ and $CaAl_2SiO_6$, but five pyroxene molecules of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$, $NaAlSi_2O_6$, $CaAl_2SiO_6$ and $CaFe^{3+}AlSiO_6$, and that the combination of these five molecules is changed by the physical condition under which the clinopyroxene$_{ss}$ crystallized. In a strict sense, therefore, in the order of calculation of pyroxene end-members the assemblage of coexisting minerals and the mutual stability among the end-members at physical condition in question must be carefully considered.

Conclusion

1. The solubility of $CaAl_2SiO_6$ in clinopyroxene is controlled not only by pressure but also by temperature, and is facilitated at high pressure and high temperature. When pyroxene coexists with such silicate minerals in which all aluminum atoms occupy the tetrahedral site, the solubility of $CaAl_2SiO_6$ in clinopyroxene increases with increasing pressure. However, when clinopyroxene coexists with such silicate minerals in which all aluminum atoms occupy the octahedral site, the solubility of $CaAl_2SiO_6$ decreases with increasing pressure.

2. The clinopyroxene$_{ss}$ between acmite–Ca-Tschermak's molecule is more stable than that between diopside–Ca-Tschermak's molecule at high pressure.
3. The presence of a small amount of acmite molecule in the clinopyroxene affects significantly on the solubility of $CaAl_2SiO_6$ in diopside at lower pressure (below about 10 kb).
4. The clinopyroxene solid solutions crystallized in the system $NaFe^{3+}Si_2O_6$ – $CaMgSi_2O_6$ –$CaAl_2SiO_6$ are composed not only of three pyroxene molecules of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$ and $CaAl_2SiO_6$ but five pyroxene molecules of $NaFe^{3+}Si_2O_6$, $CaMgSi_2O_6$, $NaAlSi_2O_6$, $CaAl_2SiO_6$ and $CaFe^{3+}AlSiO_6$, and the combination of these five molecules is changed by the physical condition under which the clinopyroxene$_{ss}$ crystllized. Aluminous clinopyroxene molecules in the clinopyroxene solid solutions in the system $NaFe^{3+}Si_2O_6$ –$CaMgSi_2O_6$ – $CaAl_2SiO_6$ change as follows with the increase of pressure: ($CaFe^{3+}AlSiO_6$ + $CaAl_2SiO_6$), ($CaAl_2SiO_6$), and ($CaAl_2SiO_6$ + $NaAlSi_2O_6$). This change indicates that aluminum atoms in clinopyroxene concentrate from tetrahedral site into octahedral site with increasing pressure; that is, the content of Tschermak's molecule in clinopyroxene decreases and most of tetrahedral site become to be occupied by Si^{4+} with increasing pressure.
5. When sodium content in the liquid decreases, clinopyroxene$_{ss}$ crystallized from this liquid tends to contain less sodium, although sodium content in clinopyroxene$_{ss}$ increases with increasing pressure.
6. The unit-cell parameters of clinopyroxene solid solutions between $NaFe^{3+}Si_2O_6$, and $CaAl_2SiO_6$ change continuously with the change of the composition.

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