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PHASE RELATIONS IN THE SYSTEM $\text{CaMgSi}_2\text{O}_6 - \text{CaAl}_2\text{SiO}_6$
AT HIGH PRESSURES AND TEMPERATURES

by

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(with 3 Tables and 4 Figures)

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Abstract

Phase relations of the composition $(\text{CaMgSi}_2\text{O}_6)_{50}(\text{CaAl}_2\text{SiO}_6)_{50}$ and $(\text{CaMgSi}_2\text{O}_6)_{25}(\text{CaAl}_2\text{SiO}_6)_{75}$ (mol percent) have been investigated over the temperature range from 880°C to 1093°C and the pressure range from 3.0 kb to 13 kb with piston and cylinder high pressure apparatus.

For the composition of $(\text{CaMgSi}_2\text{O}_6)_{25}(\text{CaAl}_2\text{SiO}_6)_{75}$ the following assemblages have been obtained with increasing pressure at constant temperature: anorthite+melilite_{SS}+spinel, clinopyroxene_{SS}+anorthite+spinel, clinopyroxene_{SS}, clinopyroxene_{SS}+garnet_{SS}+anorthite+spinel.

Minimum temperature and pressure at which the clinopyroxene along the join $\text{CaMgSi}_2\text{O}_6 - \text{CaAl}_2\text{SiO}_6$ forms a complete series of solid solution have been found to be 1020°C and 11 kb.

Several properties of the clinopyroxenes have been discussed, with special reference to the behavior of Al and Fe^{3+} in silicates at high pressures and temperatures.

INTRODUCTION

In recent years experimental studies of many silicate minerals under very high pressures and temperatures have been made in connection with various problems of the upper mantle. Among them the behaviors of the Al-bearing clinopyroxene at high temperatures and pressures is interesting, in view of the fact that many clinopyroxenes formed at various conditions of pressures and temperatures have fairly high content of Al_2O_3 . Diopside forms a solid solution with $\text{CaAl}_2\text{SiO}_6$ molecule and the maximum degree of stable clinopyroxene solid solution was reported to be greater than 20 wt percent of $\text{CaAl}_2\text{SiO}_6$ molecule at 1 atmosphere (de NEUFVILLE and SCHAIRER, 1962),

while $\text{CaAl}_2\text{SiO}_6$ and diopside form a complete series of clinopyroxene solid solution at 20 kb (CLARK, 1962). The stability field and phase relations of the $\text{CaAl}_2\text{SiO}_6$ molecule were determined by HAYS (1966) and HIJIKATA and YAGI (1967), but those of the clinopyroxene solid solution along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ have not yet been determined.

THOMPSON (1947) has suggested that Al in silicates are generally found in 4-coordination at high temperatures and relatively low pressures and tend to take 6-coordination at high pressures and relatively low temperatures, based on the structural relations of the minerals obtained at various pressures and temperatures. Present experimental studies have been made to determine the stability field of the clinopyroxene solid solutions which have the compositions of $(\text{CaMgSi}_2\text{O}_6)_{50}(\text{CaAl}_2\text{SiO}_6)_{50}$ (henceforth $\text{CaAl}_2\text{SiO}_6$ will be abbreviated Ca-Ts), $\text{Di}_{25}\text{Ca-Ts}_{75}$ (mol percent), and also to clarify the phase relations between the clinopyroxenes and the other mineral assemblages at low or high pressures. The results obtained showed that the behavior of Al in these phases is consistent with the role of Al in silicates suggested by THOMPSON.

EXPERIMENTS

High pressure apparatus

The high pressure experiments on several compositions along the join $\text{CaMgSi}_2\text{O}_6$ (Di) - $\text{CaAl}_2\text{SiO}_6$ (Ca-Ts) were mainly carried out by means of a single stage piston and cylinder apparatus (Yagi, Hariya and Hijikata, 1967). High pressure reaction cell consisted of a talc tube (pressed talc powder), machined pyrophyllite rods and a short tube for sample holder, and fine stainless steel net for heater. Sample was enveloped by platinum foil (0.3 mm thick) and pressed by a small pressing mould.

Pressure was determined by measuring the load pressure on the piston face, with correction for the friction between cell surface and cylinder wall. The measured value of the friction at about 800°C and 3 - 13 kb was about 10 percent of the load on the piston face supplied by a 300 ton oil press. Heating power was supplied by a 5 kw low voltage transformer, and temperature was controlled manually by a valiac connected with input of a low voltage transformer. Temperature of the sample was measured by an chromel-alumel thermocouple connected to a potentiometer. The effect of pressure on the emf of a thermocouple was not considered.

Accuracy of pressures is considered to be ± 0.5 kb and temperatures were maintained within $\pm 7^\circ\text{C}$ at the control points, attaining an accuracy of $\pm 15^\circ\text{C}$ or higher.

Preparation of starting materials

Homogeneous glasses of the compositions and $\text{Di}_{50}\text{Ca-Ts}_{50}$ and $\text{Di}_{25}\text{Ca-Ts}_{75}$ (mol percent) were prepared by melting reagent grade chemicals CaCO_3 , Al_2O_3 , MgO and pure quartz at temperatures from 1400°C to 1600°C . Refractive indices of these glasses were 1.648, 1.605 and 1.602, respectively. These glasses were then completely crystallized by heating at temperatures from 900°C to 1200°C for 4 to 7 days and the final products were identified optically or by X-ray powder patterns to be composed of fine-grained crystalline aggregates. Identified crystals for each composition are as follows;

$\text{Di}_{50}\text{Ca-Ts}_{50}$: anorthite, melilite solid solution, forsterite.

$\text{Di}_{25}\text{Ca-Ts}_{75}$: spinel, anorthite, melilite solid solution.

For the composition $\text{Di}_{25}\text{Ca-Ts}_{75}$ sintering technique was employed instead of melting because of high melting point. The mixture of the chemicals and quartz for the composition $\text{Di}_{25}\text{Ca-Ts}_{75}$, was ground well in an agate mortar with pure ethyl alcohol, ignited at 1200°C for 3 hours in a platinum crucible to form sintered cake, and this was crushed and then was ground again. The well-mixed powder was heated again at 1200°C for 3 hours. After repeating the treatment of sintering for three times, stable crystalline phases of the composition $\text{Di}_{25}\text{Ca-Ts}_{75}$, that is, anorthite+melilite solid solution+spinel (de Neufville and Schairer, 1962) was obtained. Identification of the sintered materials was carried out optically or by X-ray powder method. In addition the products synthesized from the crystalline aggregates of both compositions $\text{Di}_{50}\text{Ca-Ts}_{50}$ and $\text{Di}_{25}\text{Ca-Ts}_{75}$ under hydrothermal conditions (700°C , 1 kb, for 4 days) were also used as starting materials for some high pressure experiments. These crystalline aggregates were identified optically or by X-ray powder data to be composed of garnet solid solution, clinopyroxene solid solution, anorthite and trace of spinel for $\text{Di}_{50}\text{Ca-Ts}_{50}$. Some products obtained at high pressures and temperatures were used again as starting materials for other high pressure experiments at different conditions of pressures and temperatures.

EXPERIMENTAL RESULTS

$\text{Di}_{25}\text{Ca-Ts}_{75}$

The results of the high pressure experiments for the composition $\text{Di}_{25}\text{Ca-Ts}_{75}$ are summarized in Table 1 and shown graphically in Fig. 1. All experiments of this composition were carried out by the piston and cylinder apparatus.

As outlined in Fig. 1, there are five different stability fields in which the

Table 1. Results of high pressure experiments of the composition $(\text{CaMgSi}_2\text{O}_6)_{25}(\text{CaAl}_2\text{SiO}_6)_{75}$.

press. kb \pm 0.5	temp. °C \pm 15	time min.	starting materials	results
3.0	950	60	An+Garn+Sp	An+Garn+Sp+Cpx
3.0	1075	40	Cpx+An+Sp	Cpx+An+Mel+Sp
5.0	880	300	An+Garn+Sp	An+Garn+Sp
5.0	925	60	Cpx	Cpx+Garn+An+Sp
5.0	1015	60	An+Sp+Mel	Cpx+An+Sp
6.5	950	60	Cpx	An+Garn+Cpx+Sp
6.5	1000	60	Garn+An+Sp	An+Garn+Sp+Cpx
6.5	1078	40	An+Sp+Mel	An+Sp+Cpx
8.0	900	60	Cn+Cpx+Garn+Sp	Garn+An+Sp
8.0	950	60	Garn+An+Sp	An+Garn+Cpx+Sp
8.0	1000	60	Garn+An+Sp	Cpx+Garn+An+Sp
8.0	1050	60	Cpx	Cpx+An+Sp
10.0	975	60	Garn+An+Sp	Cpx+Garn+An+Sp
10.0	1000	60	Garn+An+Sp	Cpx+Garn+An+Sp
10.0	1000	40	An+Sp+Mel	Cpx+Garn+An+Sp
10.0	1025	60	Garn+An+Sp	Cpx
10.0	1050	60	An+Sp+Mel	Cpx
10.0	1093	50	An+Sp+Mel	Cpx
13.0	950	60	Garn+An+Sp	Cpx+Garn+An+Sp
13.0	1030	40	An+Garn+Sp	Garn+An+Sp+Cpx
13.0	1075	60	Cpx+Garn+An+Sp	Cpx

Symbols: Cpx, clinopyroxene solid solution; Garn, garnet solid solution (grossularite-pyrope); An, anorthite; Sp, spinel; Mel, melilite solid solution (akermanite-gehlenite).

different mineral assemblages are stable. The assemblage of anorthite+melilite_{SS}+spinel is stable up to curve A from atmospheric pressure. On the higher pressure side of curve A and the higher temperature side of curve C, clinopyroxene_{SS}+anorthite+spinel assemblage is stable. On the higher pressure side of curve B and the higher temperature side of curve D, clinopyroxene_{SS} of the composition $\text{Di}_{25}\text{Ca-Ts}_{75}$ is stable. Between curve A and B the relative amounts of anorthite and spinel to clinopyroxene_{SS} decrease with increasing pressures. The compositions of the clinopyroxene_{SS} in this area were not determined. It is clear, however, that they have compositions different from $\text{Di}_{25}\text{Ca-Ts}_{75}$ and changing with pressures, since the peak of (531) for clinopyroxene_{SS} shifts to lower angle with decreasing pressures in X-ray powder patterns. The variation of 2θ (531) for $\text{Cu}_{K\alpha}$ radiation of the clinopyroxene solid solutions along the join $\text{CaMgSi}_2\text{O}_6 - \text{CaAl}_2\text{SiO}_6$, it is possible to determine the composition of the clinopyroxene_{SS} using the diagram shown in

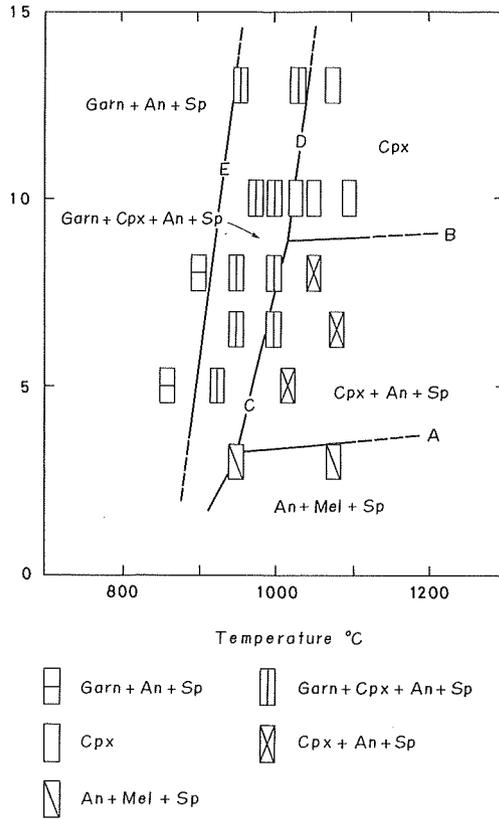


Fig. 1. Pressure-temperature plane for the composition $(\text{CaMgSi}_2\text{O}_6)_{25}(\text{CaAl}_2\text{SiO}_6)_{75}$. Cpx, clinopyroxene solid solution; Garn, garnet solid solution, An anorthite, Sp, spinel; Mel, melilite.

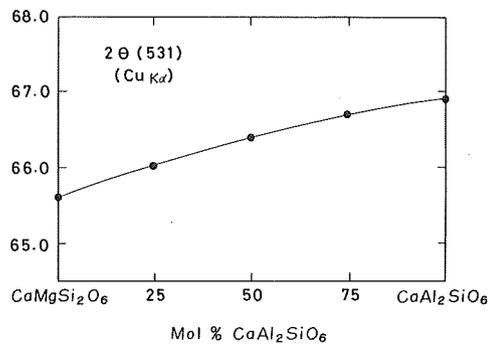


Fig. 2. The variation of $2\theta (531)$ for the clinopyroxene solid solutions along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$.

Fig. 2. In the present join, however, these clinopyroxene solid solution should include CaSiO_3 molecule, judging from the relation between the total composition $\text{Di}_{25}\text{Ca-Ts}_{75}$ and the assemblage of clinopyroxene_{SS}+anorthite+spinel. Therefore, it is impossible to determine the composition of these clinopyroxene_{SS}. The assemblage garnet_{SS}+clinopyroxene_{SS}+anorthite+spinel is stable up to curve E on the higher pressure side of curves C and D. The relative amount of clinopyroxene solid solution to anorthite and spinel decreases whereas the amount of garnet_{SS} increases with lowering temperatures from curves C and D, until on the higher pressure side of curve E, clinopyroxene_{SS} disappears completely and garnet_{SS}+anorthite+spinel assemblage is stable. Though the compositions of clinopyroxene_{SS} coexisting with garnet_{SS} were not measured, they may be the same series of solid solutions as described in the case of clinopyroxene_{SS}+anorthite+spinel assemblage. The garnet_{SS} may be the

Table 2. Results of high pressure experiments of the composition $(\text{CaMgSi}_2\text{O}_6)_{50}(\text{CaAl}_2\text{SiO}_6)_{50}$.

press. kb \pm 0.5	temp. $^{\circ}\text{C} \pm 15$	time min.	starting materials	results
3.0	950	60	Cpx+Garn+An+Sp	Cpx+Garn+An+Sp
3.0	1030	60	Cpx	Cpx+An+Sp
5.0	880	60	An+Fo+Mel	Cpx+Garn+An+Sp
5.0	980	60	Cpx+Garn+An+Sp	Cpx+An+Garn+Sp
5.0	1020	60	Cpx+Garn+An+Sp	Cpx+An+Sp
5.0	1040	60	An+Fo+Mel	Cpx+An+Sp
5.0	1040	60	Cpx	Cpx+An+Sp
5.0	1090	40	An+Fo+Mel	Cpx+An+Sp
6.5	950	60	Cpx	Cpx+Garn+An+Sp
6.5	1000	60	Cpx+Garn+An+Sp	Cpx+Garn+An+Sp
6.5	1070	60	Cpx+Garn+An+Sp	Cpx
6.5	1075	60	An+Fe+Mel	Cpx
8.0	900	60	Cpx+Garn+An+Sp	Cpx+Garn+An+Sp
8.0	950	60	Cpx+Garn+An+Sp	Cpx
8.0	1000	60	Cpx+Garn+An+Sp	Cpx
10.0	950	60	Cpx	Cpx+Garn+An+Sp
10.0	975	60	Cpx+Garn+An+Sp	Cpx+Garn+An+Sp
10.0	1000	60	An+Fo+Mel	Cpx+Garn+An+Sp
10.0	1025	60	Cpx+Garn+An+Sp	Cpx
10.0	1050	60	An+Fo+Mel	Cpx
10.0	1090	40	An+Fo+Mel	Cpx+Garn+An+Sp
13.0	1030	60	Cpx+Garn+An+Sp	Cpx+Garn+An+Sp

Symbols: Cpx, clinopyroxene solid solution; Garn, garnet solid solution (grossularite-pyrope); An, anorthite; Sp, spinel; Fo, forsterite; Mel, melilite solid solution (akermanite-gehlenite).

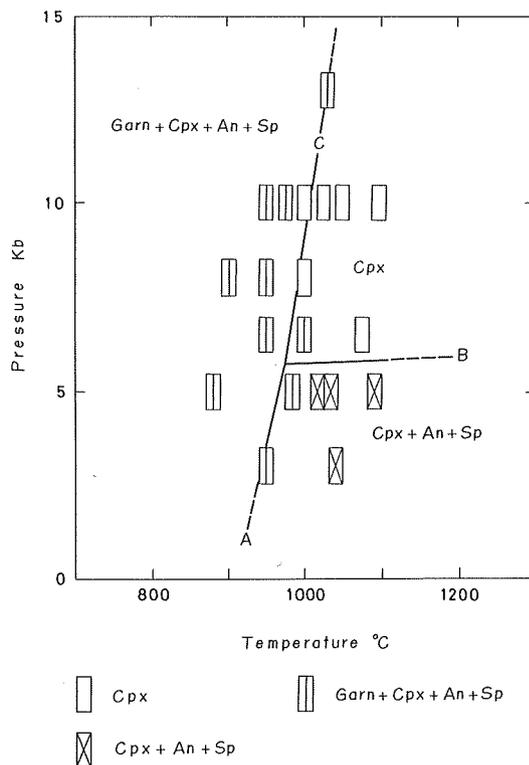
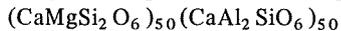


Fig. 3. Pressure-temperature plane for the composition



Cpx, clinopyroxene solid solution; Garn, garnet solid solution; An, anorthite; Sp, spinel.

solid solutions between $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (grossularite) and $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (pyrope), though their compositions could not be determined because the amount of garnet_{SS} coexisting with anorthite, spinel and clinopyroxene_{SS} is too small to measure the lattice constant a of these garnet_{SS}.

$\text{Di}_{50}\text{Ca-Ts}_{50}$

The results of the high pressure experiments for the composition $\text{Di}_{50}\text{Ca-Ts}_{50}$ are summarized in Table 2, and are shown graphically in Fig. 3. All experiments of this composition were carried out by the piston and cylinder apparatus.

The stable assemblage of the composition $\text{Di}_{50}\text{Ca-Ts}_{50}$ at atmospheric pressure is anorthite+mellilite_{SS}+forsterite (de Neufville and Schairer, 1962). On the high temperature side of curve A, clinopyroxene_{SS}+anorthite+spinel assemblage is stable at pressures from 3 kb up to curve B. On the higher

temperature side of curve C and the higher pressure side of curve B, clinopyroxene_{SS} of the composition Di₅₀ Ca-Ts₅₀ is stable. The relative amount of anorthite to clinopyroxene_{SS} increases with decreasing pressure from curve B. The composition of clinopyroxene_{SS} may be of the same series as clinopyroxene solid solutions mentioned in the case of Di₂₅ Ca-Ts₇₅. On the higher pressure side of curves A and C, garnet_{SS}+clinopyroxene_{SS}+anorthite+spinel assemblage is stable. The amounts of garnet_{SS} and spinel are very small, so that the composition of garnet_{SS} could not be measured. The clinopyroxene_{SS} coexist with garnet_{SS} may be the same kind of clinopyroxene solid solution as described above. The boundary curve between the two assemblages clinopyroxene_{SS}+anorthite+spinel and anorthite+melilite+forsterite should exist at pressures less than 3 kb, but was not determined experimentally.

DISCUSSION

The minimum temperature and pressure in each of the stability fields for the three different clinopyroxene solid solution of the compositions Di₀ Ca-Ts₁₀₀, Di₂₅ Ca-Ts₇₅ and Di₅₀ Ca-Ts₅₀ are 1020°C and 11 kb, 1010°C and 9 kb, and 970°C and 6 kb, respectively. The stability field of the clinopyroxene solid solution extends to lower temperatures and lower pressures systematically with the change of composition from Di₀ Ca-Ts₁₀₀ to Di₅₀ Ca-Ts₅₀. The refractive indices of these three clinopyroxene solid solutions together with clinopyroxene CaAl₂SiO₆ are given in Table 3 and are shown in Fig. 4. The linear change of the refractive indice indicates that these clinopyroxenes are the solid solutions along the join CaMgSi₂O₆-CaAl₂SiO₆. Therefore this join forms a complete binary solid solution of clinopyroxene at 1020°C and 11 kb.

The behavior of Al in silicate minerals is an important clue for the elucidation of many transformation phenomena observed at high pressures and temperatures. In general, Al have a dual role in the structures of silicate minerals; i.e., they can play a role of network former in 4-coordination site,

Table 3. Refractive indices of the clinopyroxene solid solutions along the join CaMgSi₂O₆-CaAl₂SiO₆.

composition CaMgSi ₂ O ₆	mol percent CaAl ₂ SiO ₆	α (± 0.005)	γ
75	25	1.676	1.702
50	50	1.682	1.714
25	75	1.696	1.721
0	100	1.710	1.735

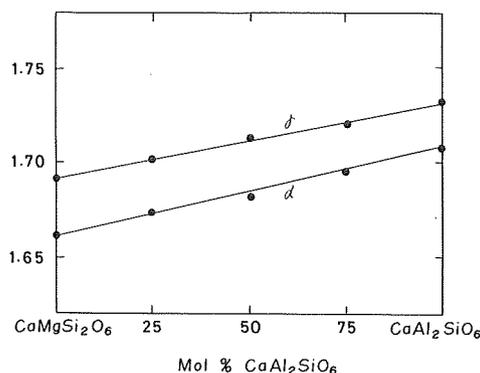


Fig. 4. Refractive indices of the clinopyroxene solid solutions along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$.

replacing Si, as well as a role of normal cations in 6-coordination site. THOMPSON (1947) has suggested that Al in silicates are generally found in 4-coordination at high temperatures and relatively low pressures and tend to take 6-coordination at high pressures and relatively low temperatures. For instance, in the reactions albite ($\text{NaAlSi}_3\text{O}_8$) = jadeite ($\text{NaAlSi}_2\text{O}_6$) + quartz (SiO_2) and albite + nepheline (NaAlSiO_4) = jadeite, all Al in albite and nepheline are in 4-coordination, whereas all Al in jadeite are in 6-coordination, and the chains of pyroxene structure consist of only SiO_4 tetrahedron. In the following reactions (Hariya and Kennedy, 1968) anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) = grossularite ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) + kyanite (Al_2SiO_5) + quartz, anorthite = clinopyroxene ($\text{CaAl}_2\text{SiO}_6$) + quartz and clinopyroxene + quartz = grossularite + kyanite + quartz, all Al of 4-coordination in anorthite change to 6-coordination in grossularite and kyanite, and a half of 4-coordination Al ions in anorthite change to 6-coordination in clinopyroxene and a half of 4-coordination in clinopyroxene change to 6-coordination in grossularite and kyanite. In these reactions, it is noticed that albite, albite+nepheline and anorthite are stable at low pressure side, and jadeite, jadeite+quartz and grossularite+kyanite+quartz are stable at high pressure side, whereas clinopyroxene+quartz are stable at relatively limited intermediate areas of high pressures and high temperatures.

In the case of the composition $\text{Di}_{10}\text{Ca-Ts}_{100}$, anorthite and gehlenite have all Al only in 4-coordination site, but clinopyroxene have one half of Al in 4-coordination site, and the other half in 6-coordination site, whereas all Al in garnet are in 6-coordination sites. It is evident, therefore, that the amount of Al in 6-coordination site increase with increasing pressures, whereas Al in 4-coordination site decrease. The same behavior of Al ions is observed in the

case of $Di_{25} Ca-Ts_{75}$ or $Di_{50} Ca-Ts_{50}$. Melilite_{SS} and anorthite include all Al in 4-coordination site, and the assemblages bearing anorthite and melilite_{SS} are stable at relatively low pressure and high temperature. At higher pressure the assemblages bearing clinopyroxene_{SS} which includes Al in both sites of 4- and 6-coordination as mentioned before are stable, and at still higher pressures than that of the stability field of clinopyroxene garnet_{SS} appears and number of Al in 6-coordination sites increases. Minerals such as anorthite and clinopyroxene_{SS} which include all or a half of Al in 4-coordination sites, however still coexist stably with garnet_{SS}. Judging from "role of coordination of Al in silicates", the assemblages bearing some minerals which include Al only in 4-coordination site, will disappear and the assemblages of the minerals, in which all Al are in 6-coordination site will be stable at higher pressure and/or lower temperatures than those of the present experiments. Under these conditions of pressures and temperatures, it is expected, therefore, that garnet_{SS}+anorthite+spinel assemblage for $Di_{25} Ca-Ts_{75}$ will change to a more dense assemblage of garnet_{SS}+corundum, and garnet_{SS}+clinopyroxene_{SS}+spinel+anorthite assemblage for $Di_{50} Ca-Ts_{50}$ will also change to a more dense phase of garnet_{SS} through an intermediate phase assemblage of garnet_{SS}+anorthite+spinel.

The role of coordination of Al suggested by THOMPSON can be applied well to the estimation and explanation of many transformation phenomena observed in silicate minerals including Al. Judging from the role of coordination Al, stability field of natural clinopyroxene with a large amount of $CaAl_2SiO_6$ is expected to exist at relatively higher temperatures and lower pressures than that of the clinopyroxenes including $NaAlSi_2O_6$. Therefore, attention should be paid to the fact that the total Al_2O_3 contents in pyroxenes do not always indicate the pressures and temperatures at which the pyroxenes were formed. The stability field of the pyroxenes will be largely changed by the partial substitution of Fe^{3+} for Al (HIRAKATA., 1968).

The clinopyroxene including a large amount of $CaAl_2SiO_6$ type molecule (so-called fassaite) are usually found in limestone content formed at high temperatures, whereas the clinopyroxene including a large amount of $NaAlSi_2O_6$ type molecule (so-called omphacite) are usually found in eclogite formed at high pressures. The distinct difference of these two type of clinopyroxenes can be well explained by the role of coordination of Al or Fe^{3+} in the structure of clinopyroxenes.

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