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PHASE RELATIONS OF Ca-TSCHERMAK'S MOLECULE AT HIGH PRESSURES AND TEMPERATURES

by

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(with 4 Text-figures)

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Abstract

Phase relations of Ca-Tschermak's molecule have been investigated over the temperature range from 900°C to 1550°C and the pressure range from 9.5 kb to 25 kb with girdle type and modified girdle type high pressure apparatus. The charges were examined optically and by X-ray powder method.

The following three assemblages have been obtained with increasing pressure at a constant temperature: anorthite+gehlenite+corundum, clinopyroxene and grossularite+corundum. The maximum pressure and temperature of the stability field of the cliopyroxene is about 24 kb and 1480°C, respectively. The clinopyroxene phase changes to corundum+liquid with increasing temperature at a constant pressure. The incongruent melting point slightly increases with increasing pressure (1420°C at 13 kb, 1450°C at 20 kb).

The univariant curve for the reaction

$$\text{clinopyroxene} \rightleftharpoons \text{grossularite} + \text{corundum}$$

$$P = 0.028\,T - 17$$

where P is given in kb and T in degrees centigrade.

Lattice constants of the clinopyroxene are in good agreement with those obtained by CLARK et. al. (1962).

Some properties of the clinopyroxene have been discussed, with special reference to the behavior of Al atoms in silicates at high pressures and temperatures.

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1. *Introduction*

In recent years experimental studies of many silicate minerals under very high pressures and high temperatures have been made in connection with various problems of the upper mantle. Among them, behavior of Ca-Tschermak's molecule ($CaAl_2SiO_6$) at high pressures and temperatures is interesting, in view of the facts that many pyroxenes formed at the greater depth generally have high contents of this molecule. Diopside forms a solid solution with this molecule and the maximum degree of stable pyroxene solid solution was reported to be greater than 40 mole per cent Ca-Tschermak's molecule at 1 atmosphere (SAKATA, 1957; de NEUFVILLE, 1962). It is known that the Ca-Tschermak's molecule and diopside form a complete solid solution at 20 kb (CLARK, 1962). The stability field of the clinopyroxene of the Ca-Tschermak's molecule composition, however, has not yet been determined.

It has been pointed out that the amounts of Al_2O_3 in pyroxenes increase in general with increasing pressure and therefore the contents of Al_2O_3 in pyroxenes will indicate the pressures at which the pyroxenes were formed. CLARK (1962) has shown that the pyroxene of the composition $CaAl_2SiO_6$ has the same structure as that of diopside; that is, a half of Al atoms enters into 4-coordination sites and the other half enters into 6-coordination sites in the diopsidic structure.

THOMPSON (1947) has suggested that Al atoms 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.

It is expected from these reasons that pyroxene of Ca-Tschermak's molecule composition which should have Al atoms in both 4-and 6-coordination, may have a rather limited stability field in regard to temperature and pressure.

Present experimental studies have been made primarily to determine the stability field of this pyroxene and also to clarify the phase changes between the pyroxene and the other mineral assemblages at low or high pressures.

2. *Experimental method*

1) High pressure apparatus

The high pressure apparata used for the present experiments were both girdle type and modified girdle type. A schematic drawing of the girdle type apparatus is shown in Fig. 1. Two cone shaped pistons and a die insert of tungsten carbide were supported in compression by hardened steel binding rings. The cone

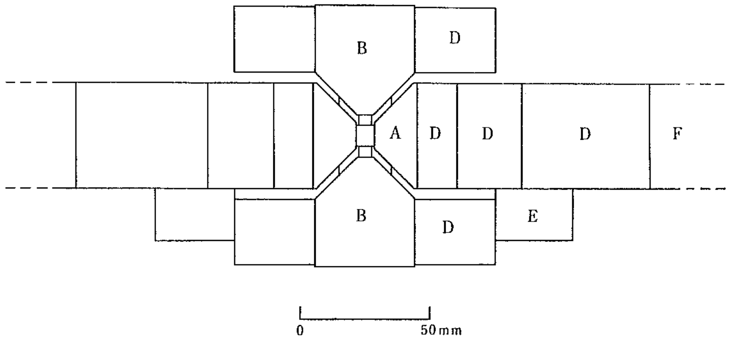

Fig. 1
Schematic drawing of the girdle type high pressure apparatus.
A: WC-cylinder, B: WC-anvil, D: steel binding ring, E: anvil guid,
F: steel safety ring.

portion of the opposing pistons has a 90-deg. cone angle, 7 mm. bore diameter and 10 mm. bore height. The steel piston nibs were machined to the size, 5 mm. in diameter and 4 mm. in height. The reaction cell, gaskets and thermocouple assembly are shown in Fig. 2. Pyrophyllite was used as pressure transmitting medium and gasket material, and graphite tube as heating element. The thermocouple wire was lead through the hole (1.0 mm. in diameter) of a cell and a gasket. Ceramics tube (1.0 mm. in outer diameter; 0.4 mm. in inner diameter) was used for insulating the thermocouple wire from the graphite tube. Platinum capsules made of thin foil (0.02 mm. in thickness) were used as sample containers for all experiments and were pressed by means of a small pressing mold. The head of thermocouple was fitted at the end of the sample. The calibration of pressure for the apparatus was carried out, using the transition points of Bi (I-II), Bi (II-III) and Tl (II-III). Load pressure was supplied by a 300-ton oil press which was modified from a universal testing machine with an automatic load holding mechanism.

Temperature of the sample was measured by a Pt-Pt. Rh 13 thermocouple. Heating power was supplied by a 5-kw low voltage transformer, and temperature was controled manually by a 5-kw variac connected with input of low voltage transformer. Accuracy of pressures is considered as ±1 kb and temperatures were maintained within 10°C at the control points, attaining an accuracy of ±20°C or higher.

Several runs at relatively low temperatures (from 900°C to 1125°C) and pressures (from 9.5 kb to 14 kb) were carried out mainly by the modified girdle type apparatus, because it was easy to control and to maintain the temperatures of the samples for 60–120 minutes within ±5°C at the controlled points, by means of a chromel-alumel thermocouple. Outline of the temperature control circuit

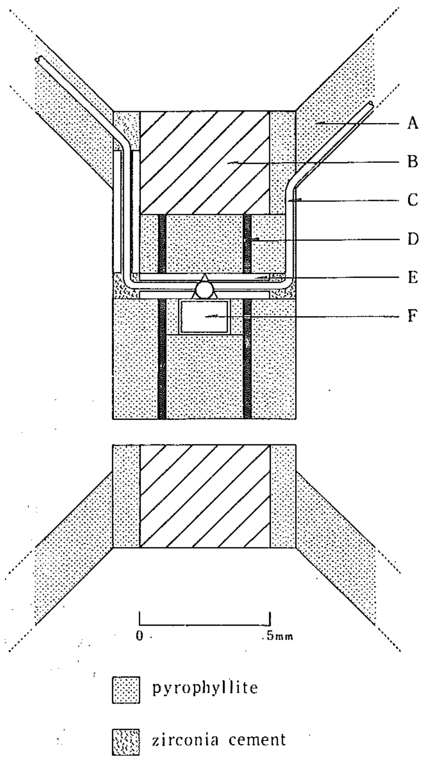

Fig. 2
Reaction cell, gaskets and thermocouple assembly for the girdle type high pressure apparatus.
A: gasket, B: steel piston nib, C: thermocouple D: graphite heater, E: ceramics tube, F: sample space.

of the apparatus is schematically shown in Fig. 3. Details of the apparatus are described elsewhere (YAGI, HARIYA and HIJIKATA, 1967). The effect of pressure on the emf of thermocouple (Pt-Pt. Rh 13 and Al-Ch) was not corrected.

2) Experimental technique of the girdle type high pressure apparatus.

After setting reaction cell assembly (Fig. 2), pressure was raised first to the desired value and then the temperature was raised. The time required to bring the sample to the desired pressure was about 15–30 minutes, and that for temperature was about 2–4 minutes. The time of the runs at the required condition of temperature and pressure ranged from 5 to 40 minutes, and then the sample was quenched by cutting off the heating power supply. In this way the temperature was dropped from 1500°C to 100°C within several seconds.

3) Preparation of starting materials.

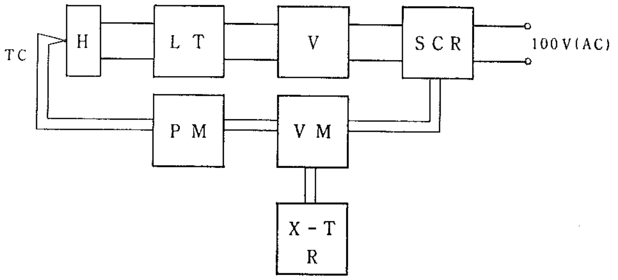

Fig. 3
Schematic drawing of the temperature control circuit for the modified girdle type high pressure apparatus.
H: graphite heater, TC: thermocouple, LT: low voltage transformer, V: variac, S.C.R.: S.C.R. control unit, PM: potentio meter, VM: μ-volt meter, X-TR: x-t recorder.

Glass of Ca-Tschermak's molecule composition was prepared by melting reagent grade chemicals, $CaCO_3$, Al_2O_3 and pure quartz at 1600°C for 3 hrs. Refractive index of the glass was 1.597. The glass was then completely crystallized by heating at 1200°C for 4 days and the final products were identified optically or by X-ray powder pattern to be composed of fine aggregates of anorthite, gehlenite and corundum. Fine-grained powder of these crystalline aggregates was used as starting materials for all experiments.

3. *Experimental results*

In total 39 effective runs were carried out, among which 27 were with the girdle type apparatus and 12 with the modified girdle type. The results of those experiments are summarized in Table 1 and Table 2, respectively and are shown graphically in Fig. 4. Large squares and small rectangles indicate the results of experiments which were carried out by the girdle type high pressure apparatus and by the modified girdle type, respectively.

The stable crystalline phase of Ca-Tschermak's molecule under the condition of 1 atmosphere is anothite+gehlenite+corundum (de Neufville, 1962), whereas both grossularite+corundum assemblage and clinopyroxene phase are the stable crystalline phases at higher pressures according to the results obtained by the present experiments. No other crystalline phases have been found over the temperature range from 900°C to 1550°C and the pressure range from 9.5 kb to 25 kb. The clinopyroxene has a relatively limitted stability field, and the upper limit of the pressure is about 24 kb. On the higher pressure side of the boundary curve of the clinopyroxene field, grossularite+corundum assemblage is stable.

The time required for formation of grossularite+corundum assemblage or clinopyroxene from the starting materials was only 5–8 minutes at about 1180°C–

Table 1. Results of the high pressure experiments obtained by a girdle type high pressure apparatus.

press. kb±1	temp. °C±20	time min.	results
10	900	40	Gross+Cor
13	1030	35	Gross+Cor
13	1080	20	Gross+Cor+Cpx
13	1130	20	Cpx
13	1180	25	Cpx
13	1230	25	Cpx
13	1350	15	Cpx
13	1440	10	Cor+Gl
16	1200	30	Gross+Cor+Cpx
16	1410	5	Cpx
18	1180	20	Gross+Cor
*18	1180	20	Gross+Cor+small amount of Cpx
*18	1180	30	Gross+Cor
18	1230	20	Gross+Cor
18	1280	15	Cpx
**18	1280	15	Cpx+small amount of Gross & Cor
**18	1280	25	Cpx
18	1400	12	Cpx
18	1470	10	Cor+Gl
20	1470	15	Cor+Cpx+Gl
21	1530	15	Cor+Gl
22	1300	20	Gross+Cor
22	1350	15	Gross+Cor
22	1400	15	Gross+Cor+Cpx
22	1470	15	Cor+Cpx+Gl
24	1550	10	Cor+Gl
25	1430	10	Gross+Cor

Symbols: Cor, corundum; Cpx, clinopyroxene; Gross, grossularite; Gl, glass.

* Temperature was first raised to 1280°C, where the sample was held long enough for the formation of clinopyroxene from the starting materials, and them temperature was reduced at 1180°C, and held for 20–30 minutes.

** Temperature was first raised to 1180°C, where the sample was held long enough for the formation of grossularite and corundum from the starting materials, and then temperature was raised to 1280°C, and held for 15–25 minutes.

1280°C and 18 kb, and nonreacted starting materials (anorthite, gehlenite or corundum) were not found. The reaction between grossularite+corundum assemblage and clinopyroxene, however, was not so rapid as the formation of both grossularite+corundum assemblage and clinopyroxene directly from the starting materials. For instance, a sample was first heated at 1180°C and 18 kb, and was held at this condition long enough to complete the formation of grossularite+corundum from starting materials. The grossularite+corundum assemblage obtained was further

Table 2. Results of the high pressure experiments obtained by a modified girdle type high pressure apparatus.

press. kb±0.5	temp. °C±10	time min.	results
9.5	975	120	An+Geh+Cor
*9.5	975	120	Gross+Cor
9.5	1025	120	An+Geh+Cor
**9.5	1125	120	Cpx
10.0	1125	120	An+Geh+Cor
10.5	1075	120	An+Geh+Cor
11.5	975	120	Gross+Cor
11.5	1025	120	Gross+small amount of Cpx & Cor
11.5	1125	60	Cpx+small amount of An, Geh & Cor
12.0	1060	120	Gross+Cor+Cpx
14.0	1125	60	Cpx+small amount of Gross & Cor
9.5	1125	120	An+Geh+Cor

Symbols: An, anorthite; Cor, corundum; Cpx, clinopyroxene; Geh, gehlenite; Gross, grossularite; Gl, glass.

* Grossularite+corundum was used for the starting material.

** Ca-Tschermak's molecule clinopyroxene was used for the starting material.

heated at 1280°C under the same pressure to form clinopyroxene. Runs of at least 20 or 25 minutes were necessary for the complete formation of the clinopyroxene. The time required for the reverse reaction from clinopyroxene to grossularite+corundum was about 30 minutes at the temperature of 1180°C under the same pressure. The results support that the reaction is reversible.

The fact that the direct formation of grossularite+corundum or clinopyroxene from the starting materials was rapid may have been caused by the decrease in stability of starting materials at these conditions and also by the acceleration of the reactions due to water liberated by the dehydration of the pyrophyllite sample holder.

The boundary curve has been determined for the reaction as shown in Fig. 4.

$$Ca_3Al_2Si_3O_{12}+2Al_2O_3=3CaAl_2SiO_6$$

The equation for the curve is given as:

$$P=0.028T-17,$$

where P is given in kilobars and T in degree centigrade.

Lattice constants of the clinopyroxene listed in Table 3 are in good agreement with those obtained by Clark et. al. (1962).

Crystals of clinopyroxene are usually found as aggregates of fine-grained granular crystals under the microscope, usually too small for the determination of the optical properties. Refractive indices obtained on relatively well-developed crystals are: γ 1.735 and α 1.710.

On the higher temperature side of the stability fields of clinopyroxene phase

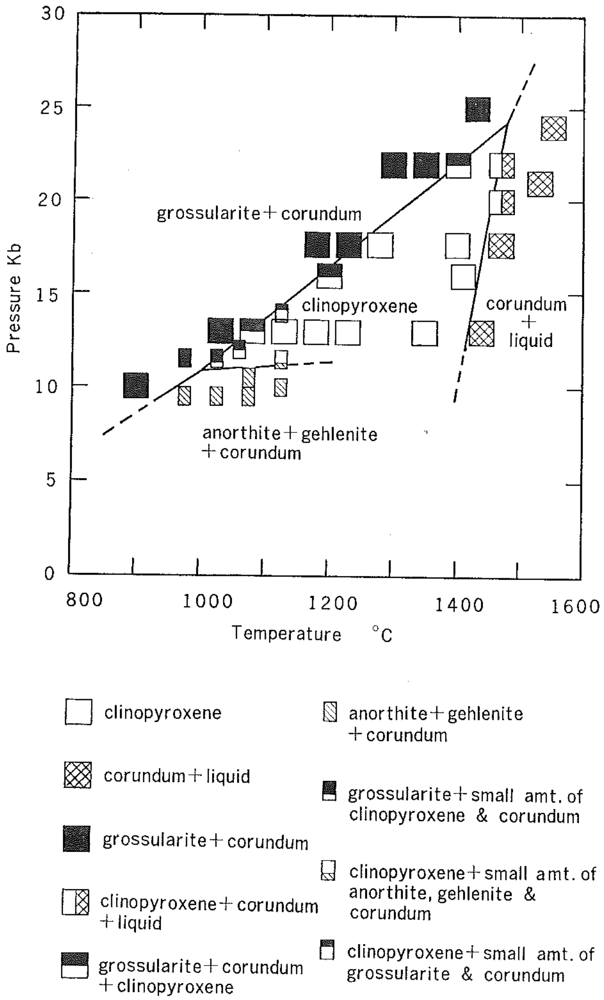

Fig. 4
Pressure-temperature plane for Ca-Tschermak's molecule composition.

Table 3. Unit cell parameters of Ca-Tschermak's molecule clinopyroxene

	Present study	Clark et. al. (1962)
a_0 (Å)	9.613±0.005	9.615±0.003
b_0 (Å)	8.664±0.005	8.661±0.002
c_0 (Å)	5.275±0.005	5.272±0.003
ß (deg.)	73.81±0.05	73.88±0.03

and grossularite+corundum assemblages, both of them melt incongruently to corundum+liquid. Corundum crystals formed tabular or dendritic crystals in the glassy matrix. The curve for the beginning of melting, however, may exist at higher temperature side than that shown in Fig. 4, when the effect of water liberated from the pyropyllite sample holder on the melting of clinopyroxene or grossularite+corundum assemblage is taken into consideration.

The determination of the melting curves for clinopyroxene and grossularite+corundum under completely dry condition is therefore necessary to obtain true equilibrium. It would be desireable to determine the melting curve for the low pressure assemblage of Ca-Tschermak's molecule, i.e., anorthite+gehlenite+corundum. Unfortunately, our high pressure apparatus is not suited for use in this range of relatively high temperatures and low pressures.

The boundary between grossularite+corundum and anorthite+gehlenite+corundum assemblage, and that between clinopyroxene and anorthite+gehlenite+corundum assemblage could not be determined accurately, because these reactions proceeded from low pressure assemblage to high pressure assemblage, but the reverse reactions did not occur within the limit of time of experiment (60–120 min.) at temperatures from 900°C to 1125°C, and at pressures from 9.5 kb to 11.5 kb. X-ray powder data indicate that the high pressure assemblages changed partially to low pressure assemblages as the results of heating experiments of high pressure assemblages 1100°C for 6 days under atmospheric pressure, but no change has been observed on the high pressure assemblages in the experiments at temperatures lower than 1000°C for 6 days under atmospheric pressure. Probably the reactions are reversible and considerably longer runs should be required to determine the true phase boundaries under dry condition.

Therefore the two boundary curves shown in Fig. 4. were drawn from the results of one-way reactions from the starting material to high pressure assemblages. High pressure experiments under hydrothermal conditions will probably accelerate the reactions to make the determination of the phase boundaries possible within the limit of time of experiment.

4. *Discussion*

The behavior of Al atoms in silicate minerals is an important clue for the elucidation of many transformation phenomena observed at high pressures and temperatures. In general, Al atoms play a dual role in silicate minerals; i.e., they construct the framework of silicate structure, replacing Si atoms, and also occupy the sites of normal cations together with Mg^{2+}, Fe^{2+}, Fe^{3+}, etc. As mentiond before, coordination number of Al atoms in silicates is usually six at relatively high pressures and low temperatures and four at relatively low pressures and high temperatuers (THOMPSON, 1947).

For instance, in the reaction albite ($NaAlSi_3O_8$) $\rightleftharpoons$ jadeite ($NaAlSi_2O_6$)+

quartz, all the Al atoms in albite are in 4-coordination and contribute to construct the framework of the structure similarly to Si atoms, whereas all Al atoms in jadeite are in 6-coordination, and the chains of pyroxene structure are formed only by SiO_4 tetrahedrons.

It has been reported that anorthite transforms to grossularite+kyanite (Al_2SiO_5)+quartz assemblage at high pressures (Boyd, 1961; Hariya, 1966). In this case the coordination number of Al atoms changes from four in the low pressure phase (anorthite) to six in both grossularite and kyanite of the high pressure assemblage.

In the polymorphic transformation of Al_2SiO_5 (andalusite, sillimanite and kyanite) change of coordination number of Al atoms occures. It is of interest to note that sillimanite has a half of Al atoms in 4-coordination and the other half in 6-coordination, whereas 4-coordination Al atoms in sillimanite change to 6-coordination in kyanite in the transformation of sillimanite to kyanite at high pressures. This relation is regarded as almost the same as that between clinopyroxene ($CaAl_2SiO_5$) and grossularite+corundum assemblage. A half of Al atoms of clinopyroxene are in 4-coordination and the other half are in 6-coordination, whereas grossularite and corundum have all the Al atoms in 6-coordination sites only.

Stability relations of these minerals would be determined by the free energy values of those minerals at high pressures and temperatures, but it may be true that these thermodynamical values are controlled by the properties of ions or atoms, which construct the minerals. Among them the behavior of Al atoms is especially important. Studies on the factors which control the behavior of Al atoms in many silicates at various conditions of pressures and temperatures are expected to throw much light on the phase relations of silicate minerals.

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POSTSCRIPT

After the manuscript was submitted, the following paper on the $CaAl_2SiO_6$ pyroxene appeared in American Mineralogist.

HAYS, J. F. (1966): Stability and properties of the synthetic pyroxen $CaAl_2SiO_6$. Am. Min. 51, 1524–1529.

His data on the optical properties and unit cell parameters are in agreement with ours within the experimental errors. Although the p-t plane for the pyroxene of $CaAl_2SiO_6$ composition is not given in his paper, each mineral assemblage obtained in his experiments (Table 5) falls within the corresponding field in the p-t plane of Fig. 4 of this paper.