

CLINOPYROXENE SOLID SOLUTIONS FORMED BY REACTIONS BETWEEN DIOPSIDE AND PLAGIOCLASE AT HIGH PRESSURES

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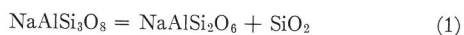
ABSTRACT

The subsolidus reactions between diopside and plagioclase have been studied on the joins diopside-albite, diopside-anorthite and diopside-plagioclase ($An_{48.5}Ab_{51.5}$) in the pressure range 8 to 36 kbar and in the temperature range 1050° to 1400°C. In the join diopside-albite, the field of omphacite + quartz increases continuously at the expense of albite-rich plagioclase, and omphacite becomes more jadeite-rich with increasing pressure at constant temperature or with decreasing temperature at constant pressure. It is likely that diopside and jadeite form a continuous series of solid solutions in the presence of quartz at temperatures at least higher than 1050°C and in the stability field of jadeite + quartz. Omphacite of composition diopside 50 jadeite 50 (mole %) coexisting with quartz is stable at pressures higher than about 27 and 31 kbar at 1150 and 1350°C, respectively. In the join diopside-anorthite, the field of clinopyroxene solid solution containing the $CaAl_2SiO_6$ component increases at the expense of anorthite, and clinopyroxene becomes more $CaAl_2SiO_6$ -rich with increasing pressure at constant temperature until garnet appears. At 1350°C, the field of clinopyroxene + quartz extends close to anorthite composition, whereas at 1150°C garnet appears at relatively low pressures and the clinopyroxene + quartz field does not extend beyond diopside 50 anorthite 50 (wt %). In the stability field of garnet, the range of the clinopyroxene solid solution is reduced with increasing pressure at constant temperature. In the join diopside-plagioclase ($An_{48.5}Ab_{51.5}$), the range of a clinopyroxene solid solution containing both jadeite and $CaAl_2SiO_6$ components increases with increase of pressure at constant temperature. The clinopyroxene solid solution coexisting with quartz, however, cannot dissolve more than 30 wt % of $CaAl_2SiO_6$ at 1150°C because of the appearance of garnet. Clinopyroxenes formed by the reaction between diopside and calcic plagioclase are relatively $CaAl_2SiO_6$ -rich and jadeite-poor in the granulite mineral assemblage, whereas they become jadeite-rich and $CaAl_2SiO_6$ -poor with increasing pressure, so that in the quartz-eclogite and kyanite-eclogite mineral assemblages, clinopyroxenes are jadeite-rich and poor in $CaAl_2SiO_6$. These results are consistent with the nature of the clinopyroxenes from quartz-bearing granulites and eclogites, and may be useful in making preliminary estimates of the physical conditions of their formation.

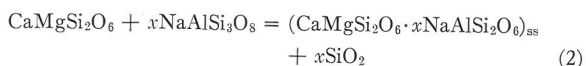
INTRODUCTION

Clinopyroxenes in eclogites, granulites and ultramafic inclusions in basaltic rocks and kimberlites often contain much more Al than that required to fill the tetrahedral position of the clinopyroxene structure and considerable amounts of Al exist in the octahedral position. On the other hand, most clinopyroxenes from common igneous rocks contain Al mostly in the tetrahedral position. The relative proportion of Al in the tetrahedral position and that in the octahedral position differs systematically among the clinopyroxenes from common igneous rocks, eclogites, and granulites and ultramafic inclusions in basaltic rocks (Kushiro, 1962; White, 1964; Aoki and Kushiro, 1968). The presence of Al in the octahedral position is associated with the presence of Al (and Fe^{3+}) in the tetrahedral position or the presence of Na in the position of eight-fold coordination in order to compensate the electrical charge. The former compensation is expressed as Tschermak's substitution (ignoring Fe^{3+}) and the latter as jadeite substitution. These two substitutions seem to be important for the clinopyroxenes formed at relatively high pressures.

The jadeite component can be formed by the breakdown of albite:



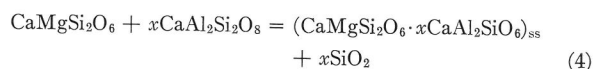
If diopside exists, the jadeite would form a solid solution with diopside at high pressures and the simplified reaction is written as follows:



The Tschermak's component can be formed by the breakdown of anorthite:



If diopside exists, the Ca-Tschermak's component would be included in diopside in solid solution depending on the P-T condition. The simplified reaction is as follows:



At atmospheric pressure, at temperatures near 1100°C, and with excess silica, diopside can dissolve in solid solution small amounts (less than 5 weight percent) of Ca-Tschermak's component (Hytönen and Schairer, 1961) and negligible amount of jadeite.

The jadeite and Tschermak's components (excluding ferri-Tschermak's component) are also formed by the reactions between plagioclase and various minerals such as forsterite, enstatite, nepheline, and melilite + corundum. The volume relations and the experimental results of these reactions (Robertson *et al.*, 1957; Yoder and Tilley, 1962, p. 501; Hays, 1966; Kushiro and Yoder, 1966) indicate that the higher pressure favors the formation of jadeite and Ca-Tschermak's components relative to albite and anorthite, respectively at constant temperature. The reactions involving formation of jadeite and Tschermak's components have important bearing on the transformation of basalts or gabbros to granulites and eclogites.

In the present experiments, reactions (2) and (4) have been studied at high pressures to show the ranges of diopside solid solutions containing jadeite and Ca-Tschermak's

components. The preliminary experiments have also been made on the reaction between diopside and plagioclase ($An_{48.5}Ab_{51.5}$ by mole) to approximate the reactions that occur in natural rock systems.

EXPERIMENTAL METHODS

All the experiments have been made with the solid-media, piston-cylinder apparatus similar to that designed by Boyd and England (1960) and the furnace assemblies are same as those described by Boyd and England (1961). The experimental method is the same as that described previously (Kushiro, 1969).

Starting materials of most of the runs were glasses, which were made by Schairer and Yoder (1960) on the join diopside-albite, by Osborn and Tait (1952) on the join diopside-anorthite, and by Lindsley and Emslie (1968) and Schairer and Kushiro (unpublished data) on the join diopside-plagioclase ($An_{50}Ab_{50}$ by weight or $An_{48.5}Ab_{51.5}$ by mole). Crystalline materials consisting of very fine-grained aggregates of clinopyroxene, plagioclase and quartz and of clinopyroxene and quartz were also used as starting materials for some of the runs made at temperatures above 1250°C. Several duplicate runs were made from both glass and crystalline materials under the same conditions to compare their results. The results of both the runs are in good agreement at temperatures above 1250°C. The phases after the runs were identified by microscope or by powder X-ray diffraction or by both. At temperatures 1150 and 1050°C, the phases are very fine-grained and identified only by their powder X-ray diffraction patterns.

EXPERIMENTAL RESULTS

The join diopside-albite. The runs on the join diopside-albite were made on five selected compositions $Di_{80}Ab_{20}$, $Di_{70}Ab_{30}$, $Di_{55}Ab_{45}$, $Di_{40}Ab_{60}$ and $Di_{25}Ab_{75}$ (weight percent) at 1350, 1250, 1150 and 1050°C. The results are summarized in Table 1. As shown in Table 1, two different assemblages Cpx+Pl+Qz and Cpx+Qz were obtained in the P-T range studied. Clinopyroxenes formed at temperatures below 1250°C are very fine-grained, whereas those formed at 1350°C are relatively coarse-grained (up to 0.020 mm across) and can be identified under the microscope. The clinopyroxene crystals are anhedral and usually contain thin irregular-shaped inclusions of quartz (and plagioclase where it exists). They do not show any exsolution or twinning. The clinopyroxene is believed to be a member of the diopside-jadeite solid solution series (omphacite), although slight deviation from this join may be possible as mentioned below. The powder X-ray diffraction patterns of the clinopyroxenes are those of omphacites and do not show any split reflections in the 2θ range at least between 20 and 60 degrees. This evidence suggests that the omphacites crystallized under the conditions of the present experiments are most likely single-phase omphacites. However, two omphacites having close d cannot be distinguished in the powder X-ray diffraction pattern and the presence of a

TABLE 1. RESULTS OF EXPERIMENTS ON THE JOIN DIOPSIDE-ALBITE

Pressure (kbar)	Temperature (°C)	Time (min)	Starting material	Phases after run
$Di_{80}Ab_{20}$ (wt %)				
13	1150	90	Gl	Cpx+Qz, $d(311)=2.2858$
26	1350	40	Gl	Cpx+Qz, $d(311)=2.2856$
$Di_{70}Ab_{30}$				
10	1050	190	Gl	Cpx+Pl?, $d(311)=2.2892$
17	1150	90	Gl	Cpx+Qz+Pl?, $d(311)=2.2855$
17.5	1250		Cpx+Qz	Cpx+Pl+Qz
18.5	1150	90	Gl	Cpx+Pl+Qz
18.5	1250	90	Gl	Cpx+Pl+Qz, $d(311)=2.2878$
18.8	1150	120	Gl	Cpx+Pl+Qz
20	1250	90	Gl	Cpx+Qz, $d(311)=2.2833$
20	1250	240	Cpx+Pl+Qz	Cpx+Qz
23.5	1350	60	Gl	Cpx+(Pl?) + Qz?
25	1350	60	Gl	Cpx+Qz, $d(311)=2.2779$
$Di_{55}Ab_{45}$				
14	1050	180	Gl	Cpx+Pl, $d(311)=2.2821$
16	1150	90	Gl	Cpx+Pl+Qz?, $d(311)=2.2811$
20	1050	180	Gl	Cpx+Pl+Qz, $d(311)=2.2750$
20	1150	150	Gl	Cpx+Pl+Qz, $d(311)=2.2778$
20	1200	75	Gl	Cpx+Pl+Qz?
21	1250	80	Gl	Cpx+Pl+Qz, $d(311)=2.2794$
23	1150	120	Gl	Cpx+Pl+Qz, $d(311)=2.2701$
24	1100	456	Gl+Cpx+Pl+Qz	Cpx+Pl+Qz
24	1150	360	Gl+Cpx+Pl+Qz	Cpx+Pl+Qz
24	1250	90	Gl	Cpx+Pl+Qz, $d(311)=2.2737$
24	1350	60	Gl	Cpx+Pl+Qz, $d(311)=2.2766$
24.5	1150	360	Gl+Cpx+Pl+Qz	Cpx+Pl+Qz
24.5	1250	300	Gl+Cpx+Pl+Qz	Cpx+Pl+Qz
25	1150	90	Gl	Cpx+Qz
25	1250	300	Cpx+Qz	Cpx+Pl+Qz
25	1300	60	Gl	Cpx+Pl+Qz?
26	1200	360	Gl+Cpx+Pl+Qz	Cpx+Qz
26	1250	335	Cpx+Pl+Qz	Cpx+Pl+Qz
26	1350	300	Cpx+Pl+Qz	Cpx+Pl+Qz
26.5	1250	90	Gl	Cpx+Qz, $d(311)=2.2645$
27	1250	300	Cpx+Pl+Qz	Cpx+Qz
27	1350	60	Gl	Cpx+Pl+Qz, $d(311)=2.2717$
28	1350	320	Cpx+Pl+Qz	Cpx+Qz
28.5	1350	60	Gl	Cpx+Qz
29	1350	120	Gl	Cpx+Qz
29	1350	120	Cpx+Pl+Qz	Cpx+Qz
$Di_{40}Ab_{60}$				
17	1150	90	Gl	Cpx+Pl+Qz
24	1050	180	Gl	Cpx+Pl+Qz, $d(311)=2.2654$
27	1250	60	Gl	Cpx+Pl+Qz, $d(311)=2.2624$
27.5	1150	120	Gl	Cpx+Pl+Qz
28.5	1150	60	Gl	Cpx+Qz, $d(311)=2.2462$
28.5	1250	340	Cpx+Qz	Cpx+Pl+Qz
29	1250	90	Gl	Cpx+Pl+Qz
30	1250	330	Cpx+Pl+Qz	Cpx+Pl+Qz
30	1350	60	Gl	Cpx+Pl+Qz, $d(311)=2.2624$
30.5	1250	345	Cpx+Pl+Qz	Cpx+Pl+Qz
31	1250	135	Cpx+Pl+Qz	Cpx+Pl+Qz
31.5	1250	300	Cpx+Pl+Qz	Cpx+Pl+Qz
31.5	1350	60	Gl	Cpx+Qz, $d(311)=2.2510$
32.5	1250	240	Cpx+Pl+Qz	Cpx+Qz
$Di_{25}Ab_{75}$				
27.5	1250	80	Gl	Cpx+Pl+Qz
32	1250	120	Gl	Cpx+Pl+Qz, $d(311)=2.2451$
32.5	1250	330	Cpx+Pl+Qz	Cpx+Pl+Qz
33.5	1250	300	Cpx+Pl+Qz	Cpx+Pl+Qz
34	1150	180	Gl	Cpx+Qz+Pl?, $d(311)=2.2295$
34.5	1250	330	Cpx+Pl+Qz	Cpx+Pl+Qz

Abbreviations: Ab, albite; Cpx, clinopyroxene which is most probably a diopside-jadeite solid solution (omphacite); $d(311)$, spacing of 311 plane of clinopyroxene; Di, diopside; Gl, glass; Pl, albite-rich plagioclase; Qz, quartz.

TABLE 2. UNIT-CELL PARAMETERS OF CLINOPYROXENES (OMPHACITES) CRYSTALLIZED FROM THE MIXTURES ON THE JOIN DIOPSIDE-ALBITE

Composition of mixture (wt %) (Di, Jd ratio of clinopyroxene in mol. %)	Pressure (kbar)	Temperature (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	<i>V</i> (Å ³)
Di ₈₀ Ab ₂₀ (Di _{82.9} Jd _{17.1}) ^a	26	1350	9.697(2)	8.891(1)	5.251(1)	106.14(2)	434.86(19)
Di ₇₀ Ab ₃₀ (Di _{73.9} Jd _{26.1})	20	1250	9.695(3)	8.881(2)	5.254(2)	106.21(2)	434.39(25)
Di ₅₅ Ab ₄₅ (Di _{59.7} Jd _{40.3})	26.5	1250	9.637(6)	8.801(5)	5.256(4)	106.68(6)	427.03(62)
Di ₄₀ Ab ₆₀ (Di _{44.7} Jd _{55.3})	28.5	1150	9.558(11)	8.740(7)	5.252(6)	106.94(8)	419.66(93)
Di ₂₅ Ab ₇₅ (Di _{28.8} Jd _{71.2})	34	1150	9.495(21)	8.680(15)	5.238(13)	107.00(18)	412.8(2.1)
Pure Di (Clark <i>et al.</i> , 1962)			9.745(1)	8.925(1)	5.248(1)	105.87(1)	439.08(7)
Pure Jd (Prewitt and Burnham, 1966)			9.418(1)	8.562(2)	5.219(1)	107.58(1)	401.20(15)

Numbers in parentheses represent errors in final figures.

^a Diopside/jadeite ratio is calculated on the assumption that the omphacites crystallized on the join diopside-albite lie exactly on the join diopside-jadeite.

two-omphacite region cannot be entirely discarded, as discussed by Bell and Davis (1969) on the join diopside-jadeite. Plagioclase is also very fine-grained below 1250°C, but that formed above 1250°C can be identified under the microscope in some cases. The plagioclase should be close to albite but may not be pure albite on the basis of the results on the join diopside-albite at 1 atm (Schairer and Yoder, 1960). If plagioclase is not pure albite, the coexisting clinopyroxene cannot be on the join diopside-albite. Possible deviation may be toward enstatite and sodium-bearing component such as sodium metasilicate, although it could not be ascertained in the present experiments.

The unit-cell parameters have been measured for five omphacites crystallized in the Omph+Qz field from the mixtures Di₈₀Ab₂₀, Di₇₀Ab₃₀, Di₅₅Ab₄₅, Di₄₀Ab₆₀ and Di₂₅Ab₇₅. The least-squares refinement of data from the powder X-ray diffraction patterns was carried out on the basis of *C2/c* symmetry with a program for the IBM 7090 digital computer by Burnham (1962). The reflections measured against an internal silicon standard were $\bar{2}23$, $\bar{1}50$, $\bar{5}10$, $\bar{4}02$, $\bar{4}21$, $\bar{3}31$, $\bar{3}30$, $\bar{3}11$, $\bar{2}21$, 002 , $\bar{1}31$, $\bar{3}11$, $\bar{3}10$, $\bar{2}21$, $\bar{2}20$, 021 and 020 . However, some of these reflections could not be measured for omphacites crystallized from mixtures relatively rich in albite because of the interference of reflections of quartz and also of the overlapping of some of the above reflections. The amount of quartz increases with increase of albite content in the mixtures. The results are shown in Table 2 and their variations with composition of mixture are shown in Figure 1. As shown in Figure 2, cell constants *a*, *b* and unit-cell volume *V* de-

crease continuously, whereas β increases with increasing albite content of the mixture. The parameter *c* is almost constant throughout the compositional range studied. The change of *d* of the 311 reflection is also shown in the same figure. The error of the unit-cell parameters increases with decrease of diopside probably because of the decrease in number of reflections that can be measured precisely. The unit-cell parameters of omphacites from Kaminaljuyú, Guatemala (Na_{0.45}Ca_{0.56}Mg_{0.41}Fe²⁺_{0.04}Fe³⁺_{0.02}Al_{0.48}Si_{2.00}) and Tiburon Peninsula, California (Na_{0.48}Ca_{0.51}Mg_{0.44}Fe²⁺_{0.10}Fe³⁺_{0.10}Al_{0.43}Si_{1.96}) given by Clark and Papike (1968) are plotted in Figure 1 for comparison. The unit-cell parameters of these two natural omphacites plot very close to the variation curves of those for the synthetic omphacites, particularly the one from Kaminaljuyú, contain small amounts of Fe²⁺ and Fe³⁺ and are close to pure omphacites. On the basis of this evidence it is suggested that the compositions of the omphacites crystallized from the mixtures on the join diopside-albite lie on or very closely to the join diopside-jadeite, although slight deviation suggested previously may be possible. The variation of molar volume of omphacite with mole fraction of jadeite is not a straight line connecting the molar volumes of diopside and jadeite, but slightly deviates toward the larger volume side in the intermediate compositions. This evidence suggests that the diopside-jadeite solid solution is thermodynamically not ideal, although the deviation from the ideal solution may be small as suggested by Essene and Fyfe (1967).

A series of mixtures consisting of two different omphacites in different proportions could show an apparent shift

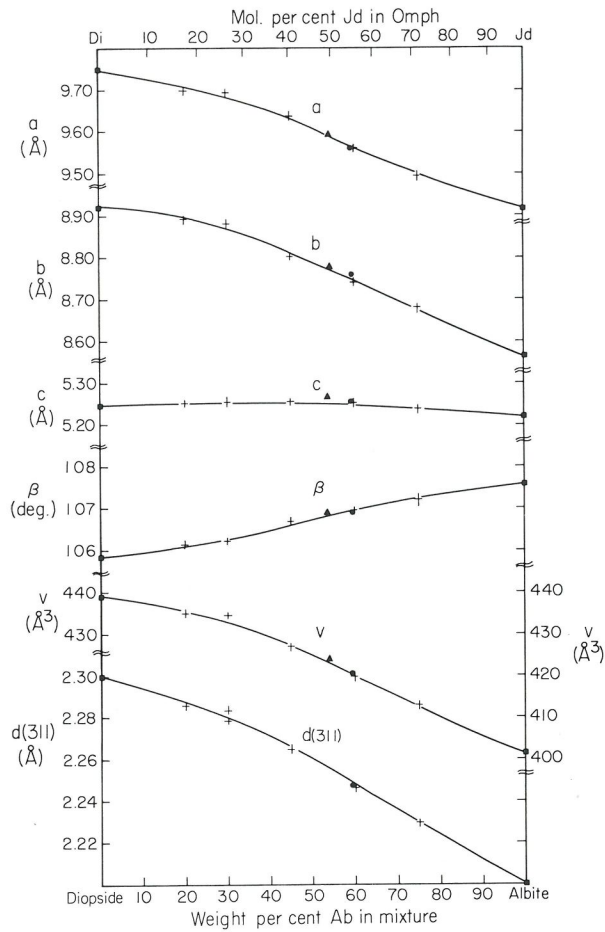


FIG. 1. Unit-cell parameters and $d(311)$ of omphacites crystallized in the Omph + Qz field from the mixtures on the join diopside-albite. P - T conditions of the formation of these omphacites are as follows: $\text{Di}_{50}\text{Ab}_{20}$, 26 kbar — 1350°C; $\text{Di}_{70}\text{Ab}_{30}$, 20 kbar — 1250°C; $\text{Di}_{55}\text{Ab}_{45}$, 26.5 kbar — 1250°C; $\text{Di}_{40}\text{Ab}_{60}$, 28.5 kbar — 1150°C; $\text{Di}_{25}\text{Ab}_{75}$, 34 kbar — 1150°C. Solid circles are the unit-cell parameters of omphacite from Kaminaljuyú, Guatemala, and solid triangles are those of omphacite from Tiburon Peninsula, California (Clark and Papike, 1968). Mole percent of jadeite in omphacite is calculated on the assumption that the omphacites crystallized on the join diopside-jadeite.

of d and probably of unit-cell parameters. However, the shift of such reflections as those of 150, 510 and 311 is large and mixtures of two omphacites different from one another by more than 20 percent jadeite would show split peaks at least between $\sim\text{Di}_{83}\text{Jd}_{17}$ and $\sim\text{Di}_{29}\text{Jd}_{71}$ (mole percent). It is unlikely, therefore, that the shift of reflection and the change of unit-cell parameters shown in Figure 1 are due to the mixing of two different omphacites in different proportions, although the possibility of a relatively narrow miscibility gap (less than 20 percent jadeite interval) cannot be entirely discarded at temperatures even above 1050°C.

The Omph + Pl + Qz assemblage was obtained at pres-

ures lower than the Omph + Qz assemblage at constant temperature for any of the compositions studied. The amount of plagioclase relative to those of omphacite and quartz in the Omph + Pl + Qz assemblage decreases with increase of pressure at constant temperature, indicating that the reaction (2) takes place. The pressure at which plagioclase disappears is higher for the more albite-rich compositions at constant temperature. These relations are shown in the isothermal sections on the join diopside-albite at 1350, 1250 and 1150°C (Fig. 2), which are constructed on the basis of the data in Table 1. At 1250°C the boundary curve between the two different assemblages has been determined by the reversed reactions for three compositions $\text{Di}_{70}\text{Ab}_{30}$, $\text{Di}_{55}\text{Ab}_{45}$ and $\text{Di}_{40}\text{Ab}_{60}$. The results obtained by crystallizing glass are nearly the same as those obtained by the reversed reactions for compositions $\text{Di}_{70}\text{Ab}_{30}$ and $\text{Di}_{55}\text{Ab}_{45}$. The results obtained from glass and crystalline materials are also the same for the composition $\text{Di}_{55}\text{Ab}_{45}$ at 1350°C. The boundary curves at 1150 and 1350°C are drawn on the basis of the runs made with glass as starting materials. These boundary curves are believed to be reliable on the basis of the duplicate runs made from both

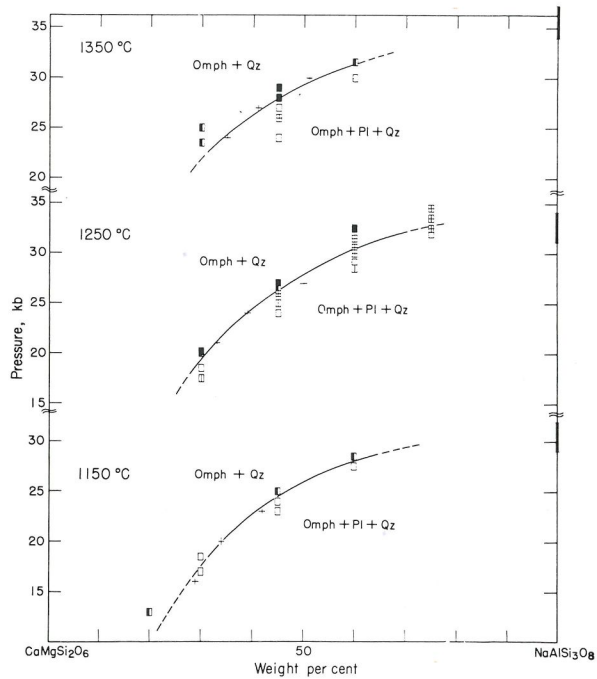


FIG. 2. Isothermal sections of the join diopside-albite at 1350, 1250 and 1150°C. Abbreviations: Omph, omphacite; others as in Table 1. Symbols: solid rectangle, Omph + Qz formed from Omph + Pl + Qz; half solid rectangle, Omph + Qz formed from glass; open rectangle, Omph + Pl + Qz formed from glass; open rectangle with vertical line, Omph + Pl + Qz formed from Omph + Qz; open rectangle with cross, Omph + Pl + Qz unchanged; cross, the limit of the Omph + Qz field determined by the composition of Omphacite, which was estimated by the $d(311)$. Thick lines on the ordinate at $\text{NaAlSi}_3\text{O}_8$ indicate the uncertainty of pressure for the reaction albite = jadeite + quartz.

glass and crystalline mixtures at 1250 and 1350°C. In the reversal experiments using the Omph+Pl+Qz assemblage as a starting material, plagioclase diminished in several runs for compositions $Di_{40}Ab_{60}$ and $Di_{25}Ab_{75}$. However, the decrease in amount of plagioclase cannot be used to locate the boundary curve, because plagioclase in the starting materials diminishes both in the Omph+Qz field and Omph+Pl+Qz field if the pressure is higher than that for making the starting material. Disappearance of plagioclase is, therefore, required to ascertain the Omph+Qz field. Disappearance of plagioclase was judged mainly by the powder X-ray diffraction pattern. The plagioclase less than about 5 percent, however, cannot be detected by this method and the position of the boundary curves may be shifted slightly to the higher pressure side.

The subsolidus phase relations obtained on the join diopside-albite can be illustrated in the system diopside-jadeite-quartz (Fig. 3) in which plagioclase is projected to albite composition and omphacite is assumed to lie on the join diopside-jadeite. The boundary curves between the Omph+Qz and the Omph+Pl+Qz assemblages shown in Figure 2 indicate the shift with pressure and temperature of the point B, which is a projection of A onto the join diopside-albite from the quartz apex. The boundary curves between the Omph+Qz and Omph+Pl+Qz fields can also be determined by the composition of clinopyroxene coexisting with plagioclase and quartz, since the point B is a projection of the point A as shown in Figure 3. The composition of the omphacite is estimated by the d of the 311 plane given in Figure 1. Points of determination by this method are also shown by + symbols in Figure 2. The boundary curves estimated by the d of the 311 plane are in good agreement with those determined by the phase assemblage method.

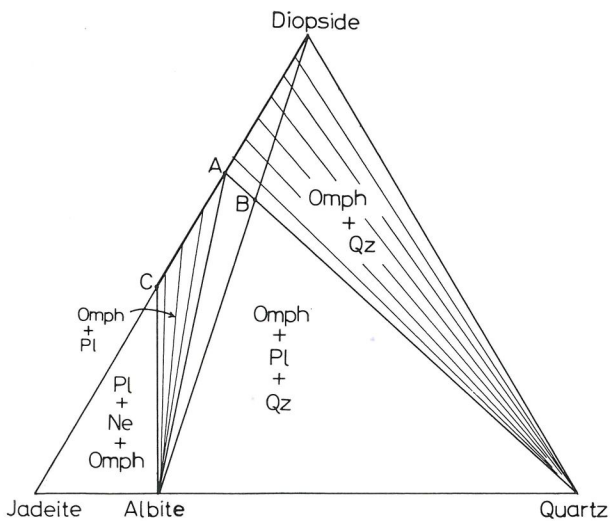


FIG. 3. Isothermal and isobaric section of the system diopside-jadeite-quartz showing the subsolidus phase relations. It is assumed that composition of plagioclase is pure albite and those of omphacite lie on the join diopside-jadeite.

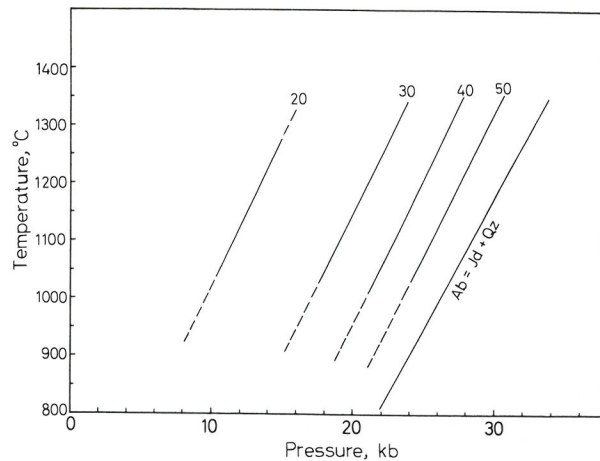


FIG. 4. P-T diagram showing the stability field of omphacite coexisting with quartz. Omphacite of each composition is stable on the higher pressure side of each curve. Numbers indicate mole percent of jadeite in omphacite.

Each boundary curve between the Omph+Qz and Omph+Pl+Qz fields in Figure 2 terminates at the composition of albite where reaction albite = jadeite + quartz takes place. The univariant curve for this reaction has been determined by Birch and LeComte (1960) (temperature range, 700–1000°C), R. C. Newton and Smith (1967) (500–600°C) and M. S. Newton and Kennedy (1968) (500–800°C). Extrapolation of their univariant curves gives different pressure values at a fixed temperature; the pressure uncertainty is 29–32 kbar at 1150°C, 31–34 kbar at 1250°C and 33–37 kbar at 1350°C.

Comparing the three isothermal sections at 1150, 1250 and 1350°C in Figure 2, it is evident that the boundary curve shifts toward the higher pressure side with increasing temperature. The shift is 3–4 kbar between 1150 and 1350°C. On the basis of these isothermal sections, the stability field of omphacite coexisting with quartz can be shown in the P-T diagram (Fig. 4). The stability field of omphacite more jadeite-rich than $Di_{50}Jd_{50}$ (mole percent) is not shown in this diagram because of the uncertainty of the boundary curves on the albite-rich portion of the join diopside-albite. As shown in Fig. 4, omphacite of the composition $Di_{50}Jd_{50}$, is stable at pressures higher than about 27 and 31 kbar at 1150 and 1350°C, respectively.

The join diopside-anorthite. The runs on the join diopside-anorthite have been made on six selected compositions $Di_{80}An_{20}$, $Di_{70}An_{30}$, $Di_{60}An_{40}$, $Di_{50}An_{50}$, $Di_{40}An_{60}$ and $Di_{35}An_{65}$ (weight percent) at 1150 and 1350°C in the pressure range 8 to 37 kbar. The results are summarized in Table 3. Following assemblages have been obtained at subsolidus temperatures: $Cpx + An \pm Qz$, $Cpx \pm Qz$, $Cpx + Gar + An + Qz$ and $Cpx + Gar \pm Qz$. Clinopyroxenes formed at 1150°C are very fine-grained, whereas those formed at 1350°C are relatively coarse-grained (up to 0.03 mm across) and can be identified under the microscope. The

clinopyroxenes do not show any exsolution or twinning, and often contain thin, irregular-shaped inclusions of quartz and anorthite where they exist. Anorthite, believed to be pure, is small in amount and very fine-grained and could not be observed in detail. The powder X-ray diffraction patterns of all the clinopyroxenes did not show any split reflections in the 2θ range at least between 20 and 60

TABLE 3. RESULTS OF EXPERIMENTS ON THE JOIN DIOPSIDE-ANORTHITE

Pres- sure (kbar)	Tempera- ture (°C)	Time (min)	Starting material	Phases after run
Di ₈₀ An ₂₀ (wt %)				
8	1150	120	Gl	Cpx+An
8	1350	30	Cpx+An	Cpx+Gl?
10	1150	120	Gl	Cpx
10	1300	90	Cpx+An	Cpx+An
20	1150	120	Gl	Cpx
Di ₇₀ +An ₃₀				
8	1350	30	Cpx+An	Cpx+Gl+An?
10	1150	120	Gl	Cpx+An
11	1300	85	Cpx+An	Cpx
12	1150	60	Gl	Cpx+An
13	1350	60	Cpx+An	Cpx+An?
14	1150	120	Gl	Cpx+An+Qz
15	1300	70	Cpx+An	Cpx
18	1150	120	Gl	Cpx+Qz?
20	1150	120	Gl	Cpx+Gar+Qz
28	1350	60	Cpx+An	Cpx+Qz?
35	1350	60	Gl	Cpx+Qz
36.5	1350	60	Gl	Cpx+Gar
Di ₆₀ +An ₄₀				
10	1150	120	Gl	Cpx+An
10	1200	120	Cpx+An	Cpx+An
10	1350	60	Gl	Cpx+Gl
15	1150	120	Gl	Cpx+An+Qz?
15	1350	60	Cpx+An	Cpx+An+Qz?
17	1150	120	Gl	Cpx+An+Qz?
18	1350	60	Cpx+An	Cpx+An
18.5	1150	120	Gl	Cpx+An+Gar+Qz
20	1150	120	Gl	Cpx+Qz+Gar
20	1350	60	Cpx+An	Cpx
25	1150	120	Gl	Cpx+Gar+Qz
35	1350	15	Gl	Cpx+Gar
Di ₅₀ An ₅₀				
15	1150	120	Gl+Cpx+Gar	Cpx+An+Qz
15	1350	60	Cpx+An	Cpx+An
19.5	1350	80	Cpx	Cpx+An
20	1350	60	Gl	Cpx+An+Qz?
22	1350	60	Gl	Cpx+Qz?
22	1400	60	Gl	Cpx
23	1350	120	Cpx+An+Qz?	Cpx+Qz?+An?
27	1350	100	Cpx	Cpx
30	1350	60	Gl+Cpx+Gar	Cpx+Qz
32.5	1350	60	Gl+Cpx+Gar	Cpx+Qz
35	1350	60	Gl	Cpx+Gar+Qz?

TABLE 3—(Continued)

Pres- sure (kb)	Tempera- ture (°C)	Time (min)	Starting material	Phases after run
Di ₄₀ An ₆₀				
15	1150	120	Gl	Cpx+An+Qz
20	1150	120	Gl	Cpx+An+Gar+Qz
20	1350	60	Gl	Cpx+An+Qz
25	1150	120	Gl	Cpx+An+Gar+Qz
28	1350	60	Gl	Cpx+Qz+An?
30	1350	60	Gl	Cpx+Qz
30	1350	120	Cpx+An	Cpx+Qz
32.5	1350	60	Gl	Cpx+Gar+Qz
Di ₃₅ An ₆₅				
20	1350	60	Cpx+An	Cpx+An
25	1350	78	Cpx+An	Cpx+An+Qz
28	1350	60	Cpx+An	Cpx+An+Qz?
35	1350	60	Cpx+An	Cpx+Qz

Abbreviations: An, anorthite; Cpx, clinopyroxene which is probably diopside—Ca-Tschermak's pyroxene solid solution; Gar, garnet of the pyrope-grossular series; Gl, glass; Qz, quartz.

degrees. The clinopyroxenes are considered to be members of the diopside-Ca-Tschermak's pyroxene ($\text{CaAl}_2\text{SiO}_6$) solid solution series, the content of the $\text{CaAl}_2\text{SiO}_6$ component varying with the composition of starting material and P - T conditions. However, clinopyroxenes may dissolve excess silica over the ideal clinopyroxene composition because of the reason that the amount of quartz relative to clinopyroxene is often far less than that expected from the composition of the starting materials, and moreover, only clinopyroxene was obtained in some cases (Table 3).

The unit-cell parameters have been calculated for four clinopyroxenes crystallized from the mixtures $\text{Di}_{80}\text{An}_{20}$, $\text{Di}_{70}\text{An}_{30}$, $\text{Di}_{50}\text{An}_{50}$ and $\text{Di}_{40}\text{An}_{60}$ in the Cpx+Qz field. The reflections measured and the method of calculation are the same as those described in the previous section. The results are shown in Table 4 and the variations of the unit-cell parameters with composition are shown in Figure 5. As shown in Figure 5, a , b and unit-cell volume V decrease, whereas c and β increase slightly with increasing anorthite content of the mixtures from which clinopyroxenes have crystallized. The slight increase in c may be explained by the substitution of Si by Al. The trends of variations of the unit-cell parameters are the same as those given by Clark *et al.* (1962) for the clinopyroxenes on the join diopside- $\text{CaAl}_2\text{SiO}_6$, which are shown by dashed curves in Figure 5 for comparison. However, the absolute values are slightly different from each other in a relatively anorthite-rich part: a , b and V of the present clinopyroxenes are smaller than those of the clinopyroxenes on the join diopside- $\text{CaAl}_2\text{SiO}_6$. The difference may be due to the presence of excess silica or Al_2SiO_5 molecule in solid solution as mentioned previously. In this case vacant sites would exist

TABLE 4. UNIT-CELL PARAMETERS OF CLINOPYROXENES CRYSTALLIZED FROM THE MIXTURES ON THE JOIN DIOPSIDE-ANORTHITE

Composition of mixture (wt %)	Pressure (kbar)	Temperature (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	<i>V</i> (Å ³)
Di ₈₀ An ₂₀	20	1150	9.699(4)	8.880(2)	5.261(2)	106.11(3)	435.34(31)
Di ₇₀ An ₃₀	18	1150	9.696(2)	8.861(1)	5.267(2)	106.21(2)	434.54(20)
Di ₅₀ An ₅₀	30	1350	9.632(2)	8.784(1)	5.265(3)	106.36(2)	427.45(26)
Di ₄₀ An ₆₀	30	1350	9.614(2)	8.746(3)	5.272(1)	106.44(2)	425.19(22)
Ca-Tschermak's pyroxene (Clark <i>et al.</i> , 1962)			9.615(3)	8.661(2)	5.272(3)	106.12(3)	421.79(28)

in the eight-fold coordination. Schairer and Kushiro (1964) have suggested a possibility that a small amount (<5 weight percent) of excess silica may be dissolved in diopside crystallized on the join diopside-silica at 1 atm. O'Hara and Yoder (1967) and Sobolev *et al.* (1968) also suggested this possibility for clinopyroxenes in kyanite eclogites and grosopydites.

The fields for the four different assemblages are shown in the preliminary isothermal sections of the join diopside-anorthite at 1350 and 1150°C (Fig. 6), which are constructed on the basis of the data in Table 3. The boundary curves at 1350°C have been determined on the basis of the runs made with both glass and crystalline mixtures. The boundary between the Cpx+Qz and Cpx+An+Qz assemblages was checked by the reversed reactions $\text{Cpx} + \text{An} + \text{Qz} \rightleftharpoons \text{Cpx} + \text{Qz}$ at composition Di₅₀An₅₀. The boundary obtained by the reversal reactions agrees with that obtained by the crystallization of glass. The boundary curves at 1150°C have been drawn on the basis of the runs made with glass as starting materials, because complete reaction of crystalline mixtures did not take place at 1150°C. Moreover, decrease or increase in relative amount of anorthite or clinopyroxene cannot be used to locate the boundary curve because anorthite diminishes relative to clinopyroxene both in the Cpx+Qz and the Cpx+An+Qz fields.

At 1350°C the Cpx+Qz field expands relative to the Cpx+An+Qz field with increasing pressure up to about 30 kbar, where the former field attains at least Di₄₀An₆₀. Above 32 kbar the Cpx+Qz field is directly bounded by the field of the garnet-bearing assemblage Cpx+Gar+Qz in the higher pressure side, the former field being reduced

relative to the latter with increasing pressure. Kyanite may appear in the anorthite side of the dashed curve in Figure 6. The Cpx+Qz field may extend close to anorthite at 1350°C at about 31 kbar. Hariya and Kennedy (1968) found that anorthite breaks down to Ca-Tschermak's pyroxene (CaAl₂SiO₆) and quartz in a small pressure-temperature range, which is a triangular field with apices 31 kbar-1350°C, 31.5 kbar-1400°C and 40 kbar-1540°C in the

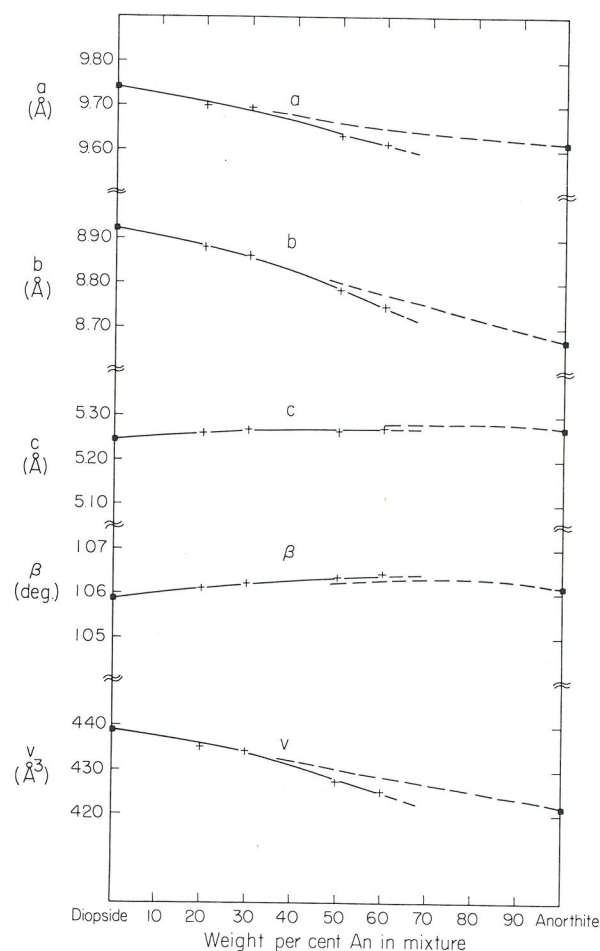


FIG. 5. Unit-cell parameters of clinopyroxenes crystallized in the Cpx + Qz field from the mixtures on the join diopside-anorthite. P-T conditions of their crystallization are as follows: Di₈₀An₂₀, 20 kbar — 1150°C; Di₇₀An₃₀, 18 kbar — 1150°C; Di₅₀An₅₀, 30 kbar — 1350°C; Di₄₀An₆₀, 30 kbar — 1350°C. Dashed curves are variation curves of unit-cell parameters for the clinopyroxenes crystallized on the join diopside — CaAl₂SiO₆ (Clark *et al.*, 1962). Their compositions are projected onto the join diopside-anorthite from the SiO₂ composition.

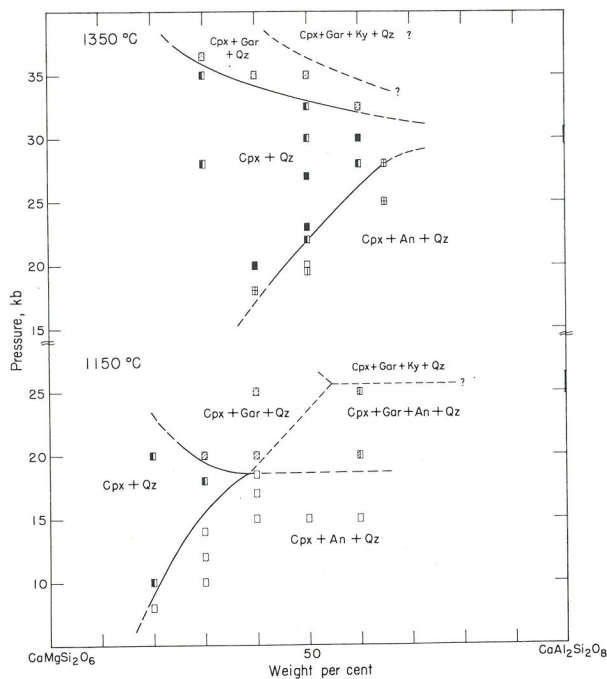
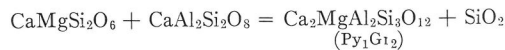


FIG. 6. Isothermal sections of the join diopside-anorthite at 1350 and 1150°C. Abbreviations: Ky, kyanite; others as in Table 3. Symbols: solid rectangle, Cpx + Qz formed from Cpx + An + Qz; half solid rectangle, Cpx + Qz formed from glass; shaded rectangle, Cpx + Gar + Qz formed from glass; half shaded rectangle, Cpx + Gar + An + Qz formed from glass; open rectangle, Cpx + An + Qz formed from glass; rectangle with vertical line, Cpx + An + Qz formed from Cpx + Qz; rectangle with cross, Cpx + An + Qz unchanged. Although all the fields are shown to have quartz, some runs do not show quartz in their powder X-ray patterns. Thick lines on the ordinate at $\text{CaAl}_2\text{Si}_2\text{O}_8$ indicate the uncertainty of pressure for the breakdown if anorthite.

P-T projection.¹ If anorthite breaks down to Ca-Tschermak's pyroxene and quartz and if this assemblage is a stable assemblage, the Cpx+Qz field would be expected to extend continuously from diopside to anorthite on the join diopside-anorthite in the stability field of the Ca-Tschermak's pyroxene + quartz assemblage.

At 1150°C the Cpx+Qz field also expands relative to the Cpx+An+Qz field with increasing pressure, but does not exceed $\text{Di}_{60}\text{An}_{40}$ since the fields of garnet-bearing assemblages appear at about 18 kbar, much lower than that at 1350°C. Above 18 kbar the Cpx+Gar+Qz field expands with increasing pressure at the expense of the Cpx+Qz field. The Cpx+An+Qz assemblage is replaced by the gar-

net-bearing assemblages, Cpx+Gar+Qz and Cpx+Gar+An+Qz at about 18 kbar. This replacement may be explained by the reaction of diopside with anorthite to form garnet of the pyrope-grossular series and quartz. The simplified reaction is written as follows:



However, the existence of the Cpx+Gar+An+Qz assemblage indicates that the garnet would be actually more grossular-rich than Py_1Gr_2 (pyrope 1 grossular 2 by mole) and clinopyroxene contains some excess enstatite molecule over diopside. The composition of garnet was estimated from the unit-cell parameter with the use of the unit-cell—composition relations for the pyrope-grossular garnet (e.g., Winchell, 1958). The unit-cell parameter a of garnet formed from the mixture $\text{Di}_{70}\text{An}_{30}$ at 36.5 kbar and 1350°C is $11.820 (\pm 0.005) \text{ \AA}$, that of garnet formed from the mixture $\text{Di}_{60}\text{An}_{40}$ at 25 kbar and 1150°C is 11.828 \AA , and those of garnets formed from the mixture $\text{Di}_{40}\text{An}_{60}$ at 20 kbar and 1150°C, at 25 kbar and 1150°C, and at 32.5 kbar and 1350°C are 11.823 , 11.828 , and 11.820 \AA , respectively. These unit-cell parameters correspond to those of garnets of compositions pyrope 8–12 grossular 92–88 (by mole), considerably more grossular-rich than Py_1Gr_2 . As a consequence, the composition of clinopyroxene coexisting with the garnet must also contain excess enstatite component in addition to Ca-Tschermak's component at least under the above conditions. The Cpx+Gar+An+Qz assemblage at 1150°C would be replaced by the Cpx+Gar+Ky+Qz assemblage and the Gar+An+Ky+Qz assemblage (near anorthite) in a narrow pressure interval between 25 kbar and the pressure at which anorthite breaks down to grossular+kyanite+quartz. This replacement may be explained by the reaction of clinopyroxene with anorthite to form garnet, kyanite and quartz. The Gar+An+Ky+Qz assemblage is replaced by the Gar+Ky+Qz assemblage when anorthite breaks down. This occurs at about 26 kbar at 1150°C (Hayes, 1966; Hariya and Kennedy, 1968).

The system diopside-anorthite-albite. The reaction of diopside and plagioclase has been studied on three compositions $\text{Di}_{70}\text{An}_{15}\text{Ab}_{15}$, $\text{Di}_{50}\text{An}_{25}\text{Ab}_{25}$ and $\text{Di}_{30}\text{An}_{35}\text{Ab}_{35}$ (weight percent) at 1150 and 1350°C in the pressure range 15 to 31 kbar. The composition of plagioclase in these mixtures is $\text{An}_{48.5}\text{Ab}_{51.5}$ (mole percent). The results are shown in Table 5. Four different assemblages Cpx+Qz, Cpx+Pl+Qz, Cpx+Gar+Qz and Cpx+Gar+Pl+Qz have been obtained.

Clinopyroxenes formed at 1150°C are very fine grained, whereas those formed at 1350°C are relatively coarse-grained (up to 0.03 mm across) and can be identified under the microscope. The clinopyroxenes are homogeneous and show no exsolution or twinning, although they often contain very fine-grained, irregular-shaped inclusions of quartz and/or plagioclase. The clinopyroxenes presumably

¹ Roseboom (oral commun.) pointed out the discrepancy in that the field of Ca-Tschermak's pyroxene + quartz by Hariya and Kennedy (1968) lies mostly outside the P-T range of the field of pure Ca-Tschermak's pyroxene by Hays (1966), and suggested that one set of data is wrong, or Ca-Tschermak's pyroxene by Hariya and Kennedy is not a pure $\text{CaAl}_2\text{Si}_2\text{O}_8$ but may be a solid solution containing some anorthite component or excess silica.

contain both the jadeite and Ca-Tschermak's components.

The unit-cell parameters of two clinopyroxenes crystallized from the mixtures $\text{Di}_{70}\text{An}_{15}\text{Ab}_{15}$ and $\text{Di}_{50}\text{An}_{25}\text{Ab}_{25}$ at 1350°C in the $\text{Cpx} + \text{Qz}$ field have been determined. The reflections measured and the method of calculation are the same as those described in the section of the join diopside-albite. The results are shown in Table 6. The unit-cell parameters of these clinopyroxenes are very close to, but slightly different from, those of the clinopyroxenes crystallized from the mixtures of the same diopside/plagioclase ratio along the joins diopside-albite and diopside-anorthite. The parameter c of these two clinopyroxenes is larger than those of omphacites and close to those of the clinopyroxenes crystallized on the join diopside-anorthite.

The preliminary isothermal section of the join diopside-plagioclase ($\text{An}_{50}\text{Ab}_{50}$ by weight) at 1150°C is shown in Figure 7, which is constructed on the basis of the runs made with glass as starting materials. Crystalline mixtures were also used, but reaction was very slow at 1150°C and the products could not be used to determine the boundary curves. At 1350°C reaction was relatively fast and could be used for the determination of the boundary. For composition $\text{Di}_{50}\text{An}_{25}\text{Ab}_{25}$, the boundary between the $\text{Cpx} + \text{Qz}$ and $\text{Cpx} + \text{Pl} + \text{Qz}$ fields could be determined at 1350°C by the reversed reaction $\text{Cpx} + \text{Pl} + \text{Qz} \rightleftharpoons \text{Cpx} + \text{Qz}$. Glass was also crystallized under the same conditions as those of the reversal reactions and identical results were obtained.

As shown in Figure 7 at 1150°C the $\text{Cpx} + \text{Qz}$ field ex-

TABLE 6. UNIT-CELL PARAMETERS OF CLINOPYROXENES CRYSTALLIZED FROM THE MIXTURES IN THE SYSTEM DIOPSIDE-ALBITE-ANORTHITE

$\text{Di}_{70}\text{An}_{15}\text{Ab}_{15}$ (wt %) (25 kbar, 1350°C)	$\text{Di}_{50}\text{An}_{25}\text{Ab}_{25}$ (30 kbar, 1350°C)
$a = 9.672(5) \text{ \AA}$	$a = 9.622(7) \text{ \AA}$
$b = 8.855(4)$	$b = 8.787(4)$
$c = 5.263(4)$	$c = 5.267(4)$
$\beta = 106.28(6)^\circ$	$\beta = 106.52(6)^\circ$
$V = 432.67(53) \text{ \AA}^3$	$V = 426.93(55) \text{ \AA}^3$

pands relative to the $\text{Cpx} + \text{Pl} + \text{Qz}$ field with increasing pressure up to about 26 kbar, above which garnet-bearing assemblages appear. In the presence of garnet, the $\text{Cpx} + \text{Qz}$ field would be reduced relative to the $\text{Cpx} + \text{Gar} + \text{Qz}$ field with increasing pressure as in the case of the join diopside-anorthite. The phase assemblage and the general features of the field boundaries in the present system at 1150°C are similar to those in the system diopside-anorthite at the same temperature. However, garnet appears at considerably higher pressures in the present system than in the system diopside-anorthite because of the presence of albite component, which delays the formation

TABLE 5. RESULTS OF EXPERIMENTS IN THE SYSTEM DIOPSIDE-ANORTHITE-ALBITE

Pressure (kbar)	Temperature ($^\circ\text{C}$)	Time (min)	Starting material	Phases after run
$\text{Di}_{70}\text{An}_{15}\text{Ab}_{15}$ (wt %)				
15	1150	270	Gl	$\text{Cpx} + \text{Pl} + \text{Qz}$
17.5	1150	275	Gl	$\text{Cpx} + \text{Pl} + \text{Qz}$
20	1150	290	Gl	$\text{Cpx} + \text{Qz}$
21	1150	300	$\text{Cpx} + \text{Pl}$	$\text{Cpx} + \text{Pl} + \text{Qz}$ (Pl diminished)
23	1350	120	Gl	$\text{Cpx} + \text{Qz}$
23	1350	120	$\text{Cpx} + \text{Pl}$	$\text{Cpx} + \text{Qz}$?
25	1350	120	Gl	$\text{Cpx} + \text{Qz}$
25	1350	120	$\text{Cpx} + \text{Pl}$	$\text{Cpx} + \text{Qz}$
31	1150	190	Gl	$\text{Cpx} + \text{Qz}$
$\text{Di}_{50}\text{An}_{25}\text{Ab}_{25}$				
23.5	1150	250	Gl	$\text{Cpx} + \text{Pl} + \text{Qz}$
25.5	1150	260	Gl	$\text{Cpx} + \text{Pl} + \text{Qz} + \text{Gar}$?
27.5	1150	285	Gl	$\text{Cpx} + \text{Pl} + \text{Gar} + \text{Qz}$
28	1350	120	$\text{Cpx} + \text{Qz}$	$\text{Cpx} + \text{Pl} + \text{Qz}$
28.5	1350	120	Gl	$\text{Cpx} + \text{Pl} + \text{Qz} + \text{Gar}$?
28.5	1350	120	$\text{Cpx} + \text{Pl}$	$\text{Cpx} + \text{Pl} + \text{Qz} + \text{Gar}$?
29.5	1150	270	Gl	$\text{Cpx} + \text{Gar} + \text{Qz} + \text{Pl}$?
30	1350	120	Gl	$\text{Cpx} + \text{Qz}$
30	1350	120	$\text{Cpx} + \text{Pl}$	$\text{Cpx} + \text{Qz}$
31	1150	190	Gl	$\text{Cpx} + \text{Gar} + \text{Qz}$
$\text{Di}_{30}\text{An}_{35}\text{Ab}_{35}$				
25.5	1150	255	Gl	$\text{Cpx} + \text{Pl} + \text{Qz}$
26.5	1150	290	Gl	$\text{Cpx} + \text{Gar} + \text{Pl} + \text{Qz}$

Abbreviations: Cpx, clinopyroxene solid solution containing both jadeite and Ca-Tschermak's component; Gar, garnet of the pyrope-grossular series; Gl, glass; Pl, plagioclase; Qz, quartz.

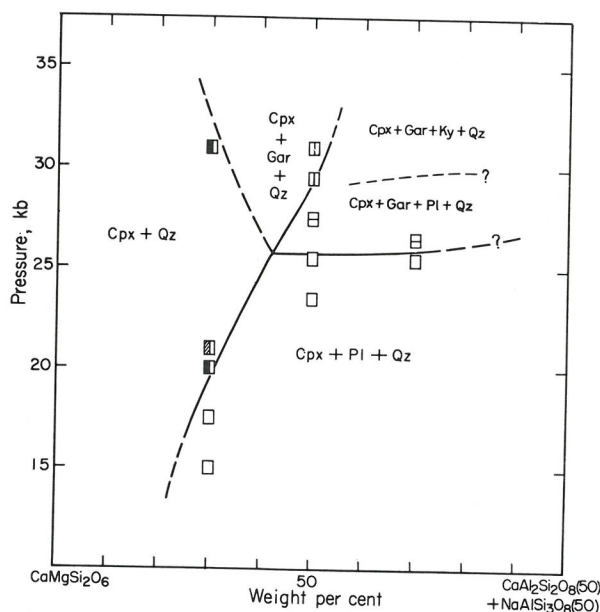


FIG. 7. Preliminary isothermal section of the join diopside-plagioclase ($\text{An}_{50}\text{Ab}_{50}$ by weight or $\text{An}_{54.5}\text{Ab}_{51.5}$ by mole) at 1150°C . Abbreviations as in Table 5. Symbols: half solid rectangle, $\text{Cpx} + \text{Qz}$ formed from glass; half shaded rectangle, $\text{Cpx} + \text{Pl} + \text{Qz}$ unchanged; open rectangle, $\text{Cpx} + \text{Pl} + \text{Qz} + \text{Gar}$ formed from glass; open rectangle with vertical line, $\text{Cpx} + \text{Gar} + \text{Qz}$ formed from glass; open rectangle with horizontal line, $\text{Cpx} + \text{Gar} + \text{Pl} + \text{Qz}$ formed from glass. There may be narrow fields of $\text{Cpx} + \text{Gar} + \text{Pl} + \text{Ky} + \text{Qz}$ and $\text{Gar} + \text{Ky} + \text{Pl} + \text{Qz}$ between the fields of $\text{Cpx} + \text{Gar} + \text{Pl} + \text{Qz}$ and $\text{Cpx} + \text{Gar} + \text{Ky} + \text{Qz}$.

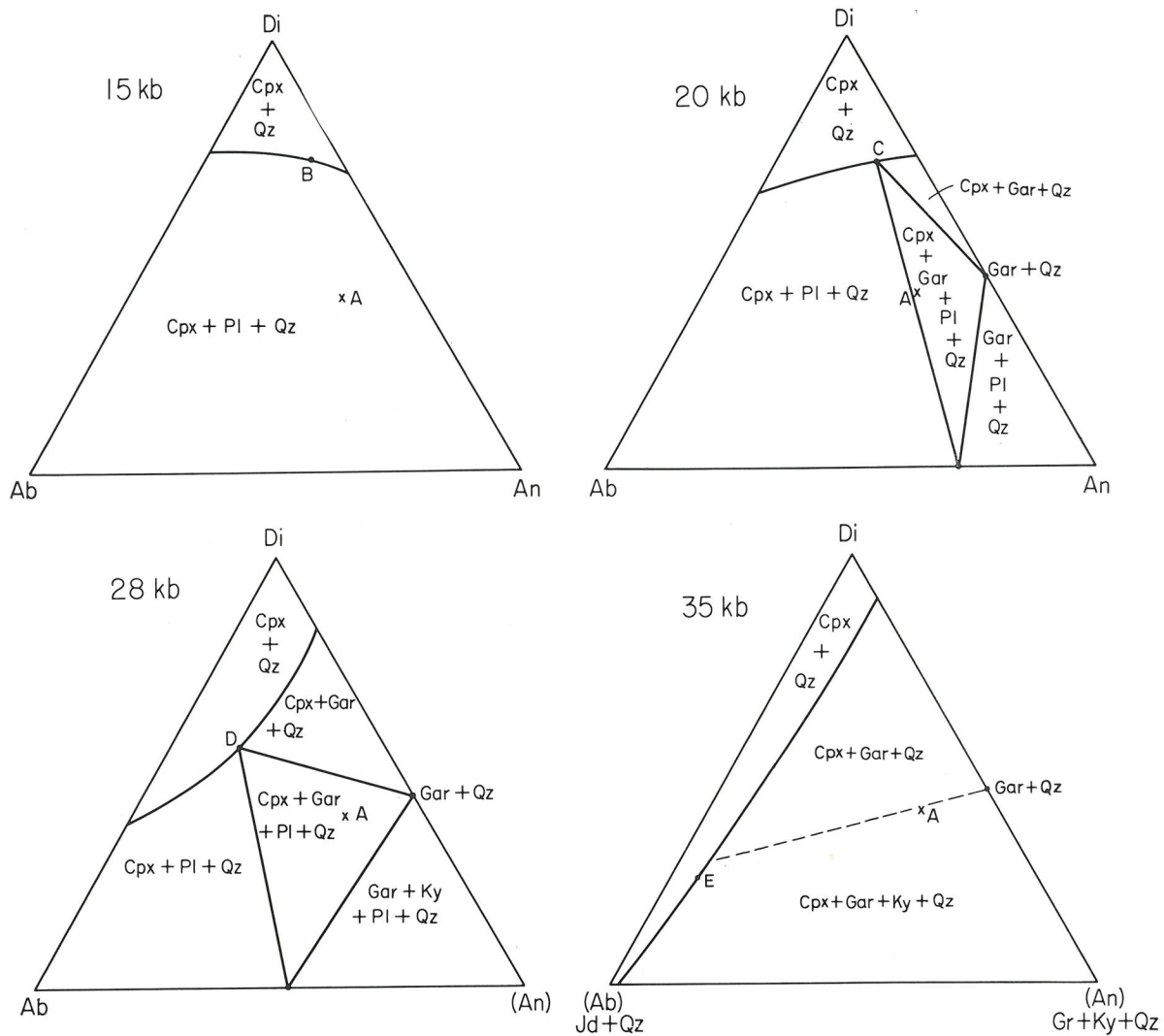


FIG. 8. Simplified isothermal and isobaric projections in the system $\text{CaMgSi}_2\text{O}_6\text{-NaAlSi}_3\text{O}_8\text{-CaAl}_2\text{Si}_2\text{O}_8$ at 15, 20, 28 and 35 kbar at 1150°C . Abbreviations: Ky, kyanite; Gr, grossular; others as in Table 5. Composition of garnet is assumed to be Py_1Gr_2 for the simplicity of illustration. A is a mixture of 40 weight percent diopside and 60 percent plagioclase ($\text{An}_{75}\text{Ab}_{25}$ by mole).

of garnet by the reaction between plagioclase and clinopyroxene.

DISCUSSION AND APPLICATION OF THE EXPERIMENTAL RESULTS

Change with P-T conditions of the range of clinopyroxene solid solution formed by the reaction between diopside and plagioclase. On the basis of the results on the join diopside-albite, diopside-anorthite and diopside-plagioclase ($\text{An}_{48.5}\text{Ab}_{51.5}$ by mole), subsolidus phase relations and change of the range of the clinopyroxene solid solution series formed by the reaction between diopside and plagioclase can be outlined. Figure 8 shows the simplified subsolidus phase relations at 1150°C in the system diopside-jadeite- $\text{CaAl}_2\text{Si}_2\text{O}_8$ -silica (or ' enstatite-wollastonite-jadeite- $\text{Al}_2\text{O}_3\text{-SiO}_2$), which are projected from the silica apex onto the plane diopside-albite-anorthite. The Cpx+Qz field in this

figure is a projected solid solution range of clinopyroxene coexisting with quartz. The range of omphacite solid solution (and clinopyroxene solid solution with $\text{CaAl}_2\text{Si}_2\text{O}_8$ when garnet is absent) is wider in the absence of quartz than that in the presence of quartz under the same P-T conditions.

As shown in Figure 8, the Cpx+Qz field is limited near diopside composition and is slightly wider toward anorthite than toward albite at 15 kbar. At 20 kbar, however, the Cpx+Qz field is expanded more toward albite, but not toward anorthite because of appearance of garnet. It is assumed to simplify the diagram that the garnet has the composition Py_1Gr_2 , although the actual composition of the garnet is more grossular-rich than Py_1Gr_2 as shown before. With increasing pressure, the Cpx+Qz field expands more toward albite but is more reduced along the join diopside-anorthite, and the Cpx-Pl-Qz join (plane)

of the Cpx+Gar+Pl+Qz field moves toward albite. At 28 kbar the Cpx+Qz field is expanded to about $Di_{40}Ab_{60}$ (clinopyroxene is about $Di_{45}Jd_{55}$ by mole) along the join diopside-albite and may be reduced to about $Di_{15-20}An_{85-80}$ along the join diopside-anorthite. Anorthite is broken down to grossular+kyanite+quartz at about 26 kbar at 1150°C, but albite and intermediate plagioclase are still stable at 28 kbar. The actual phase relations at or near 28 kbar are more complicated; for example, the Cpx+Gar+Qz field in Figure 8 is divided into the Cpx+Gar+Qz and the Cpx+Gar+Ky+Qz fields, and the Cpx+Gar+Pl+Qz field is also divided into the Cpx+Gar+Pl+Qz and the Cpx+Gar+Pl+Ky+Qz fields.

At 35 kbar albite is not stable and intermediate plagioclase would also not be stable. The Cpx+Qz field extends continuously across diopside-albite, whereas it is considerably reduced along the join diopside-anorthite, and there are two fields of the Cpx+Gar+Qz and the Cpx+Gar+Ky+Qz assemblages. The compositions of clinopyroxenes in this stage are close to the join diopside-jadeite and essentially omphacite. It is evident from the sequence shown in Figure 8 that the range of clinopyroxene solid solution formed by the reaction of diopside with plagioclase attains jadeite but cannot extend beyond a certain limit along the diopside- $CaAl_2SiO_6$ join in the presence of quartz at least at 1150°C. At temperatures lower than 1150°C, garnet would appear at lower pressures and the solid solution toward $CaAl_2SiO_6$ would be more restricted. Above 1350°C, however, clinopyroxene solid solution may attain $CaAl_2SiO_6$ composition (the Cpx+Qz field may attain anorthite composition) before garnet appears, and consequently, the range of clinopyroxene solid solution in the system diopside-jadeite- $CaAl_2SiO_6$ must be much wider than that at 1150°C and all the assemblages are very rich in clinopyroxene.

The change of composition of clinopyroxene solid solution formed by the reaction between diopside and calcic plagioclase is considered here in order to understand the behavior of basaltic or gabbroic rocks at high pressures. As an example, a mixture consisting of 40 weight percent of diopside and 60 percent of plagioclase ($An_{75}Ab_{25}$ by mole) is considered. The bulk composition of this mixture is shown by point A in Figure 8. At 15 kbar this mixture is in the Cpx+Pl+Qz field and the projection of the clinopyroxene formed from this mixture onto the plane diopside-albite-anorthite is B. This clinopyroxene has a composition approximately Jd 5.3, Ca-Tsch 17.8 and Di 76.9 mole percent. At 20 kbar the mixture is within the four-phase field Cpx+Gar+Pl+Qz ('garnet-granulite' and 'plagioclase-eclogite') and the composition of clinopyroxene solid solution is estimated to be Jd 7.9 and Ca-Tsch 17.0 mole percent (projection is C). At 28 kbar the mixture is still in the Cpx+Gar+Pl+Qz field, but the coexisting clinopyroxene contains more jadeite and less $CaAl_2SiO_6$ (projection is D). Its composition is estimated to be Jd 27.0 and Ca-Tsch 11.9 mole percent. At 35 kbar the mixture is in the Cpx+Gar+Ky+Qz (kyanite-eclogite) field or possibly in

the Cpx+Gar+Qz (quartz-eclogite) field and the composition of clinopyroxene would be more jadeite-rich and less $CaAl_2SiO_6$ -rich. Projection of a possible composition is shown by E. Thus, the composition of clinopyroxene formed by the reaction between diopside and bytownite ($An_{75}Ab_{25}$) changes from relatively $CaAl_2SiO_6$ -rich and jadeite-poor to relatively $CaAl_2SiO_6$ -poor and jadeite-rich with increasing pressure at constant temperature or with change of phase assemblage from granulite through garnet-granulite (or plagioclase-eclogite) to quartz-eclogite and quartz-kyanite-eclogite.

Even in the absence of quartz, the same change in the range of clinopyroxene solid solution would be expected. In the absence of quartz, however, omphacite and clinopyroxene containing Ca-Tschermak's component become stable at lower pressures than those of the same compositions in the presence of quartz, and garnet becomes stable also at lower pressures. Comparing the isothermal section of the join diopside-albite at 1150°C (Fig. 2) and that of the join diopside-jadeite at the same temperature given by Bell and Kalb (1969), it is found that the lower stability limit of omphacite in the absence of quartz is 7–10 kbar lower than that of the omphacite of the same composition in the presence of quartz at 1150°C and at least in the composition range between $Di_{60}Jd_{40}$ and $Di_{30}Jd_{70}$. In the absence of quartz, continuous solid solution is expected at pressures higher than about 23 kbar between diopside and jadeite at 1150°C, and nearly complete solid solution may be expected at pressures near 11 kbar between diopside and Ca-Tschermak's pyroxene at the same temperature on the basis of the stability field of Ca-Tschermak's pyroxene by Hays (1966). It is expected, therefore, that clinopyroxene makes a solid solution more toward Ca-Tschermak's pyroxene than toward jadeite at relatively low pressures (*e.g.*, near 11 kbar or less at 1150°C), as in the system diopside-anorthite-albite. In the presence of a grossular-rich garnet of the pyrope-grossular series, however, content of the Ca-Tschermak's component would decrease with increase of pressure. Pressure for the appearance of garnet is also lower in the absence of quartz. Pure grossular is stable at pressures higher than about 8 kbar and grossular+quartz is stable at pressures higher than about 17 kb at 1150°C (Hays, 1966). On the basis of the above experimental results, it is suggested that even in the absence of quartz, clinopyroxenes are relatively $CaAl_2SiO_6$ -rich and jadeite-poor at lower pressures (*e.g.*, near and a little less than 11 kbar at 1150°C), and $CaAl_2SiO_6$ -poor and jadeite-rich at higher pressures (*e.g.*, above 15 kbar at 1150°C), although the absolute pressure values are much lower than those in the presence of quartz. This conclusion as well as that for excess silica conditions is consistent with the natural clinopyroxenes from granulites and eclogites. That is, clinopyroxenes from granulites are relatively rich in Tschermak's component and poor in jadeite, whereas those from eclogites are relatively poor in Tschermak's component and rich in jadeite (Kushiro, 1962; White, 1964; Aoki and Kushiro, 1968; Lovering and White, 1968).

Application to the conditions of formation of natural clinopyroxenes. The present experimental results are applicable to the physical conditions of formation of natural omphacites and aluminous clinopyroxenes (with the Tschermak's component) which coexist with quartz and contain only small amounts of other elements such as Fe^{2+} , Fe^{3+} and Ti. Omphacites coexisting with quartz are found in quartz-eclogites in various metamorphic terrains and in some glaucophane schists. Aluminous clinopyroxenes coexisting with quartz are found in granulites in some metamorphic terrains. However, many of these omphacites and aluminous clinopyroxenes contain considerable amounts of iron, Ti and other elements, and the present results may not be wholly satisfactorily applied to the conditions of their formation. Omphacites which coexist with quartz and have only small amounts of Fe^{2+} , Fe^{3+} and Ti are, for example, those from kyanite eclogites in Silberbach, Münchgebirge Massif, and those from some glaucophane schists in California.

Omphacites from kyanite eclogite in Silberbach (one may be from Weissenstein), of which analyses were given by Tilley (1936), Yoder and Tilley (1962, Table 39) and Essene and Fyfe (1967), contain 19 to 25 mole percent jadeite, depending on the specimen and method of calculation, and 1 percent acmite (calculations based on Yoder and Tilley, 1962, and Essene and Fyfe, 1967). On the basis of the stability curves shown in Figure 4, these omphacites would be stable at pressures higher than 10–14 kb at 1000°C. If the curves in Figure 4 could be extrapolated linearly to much lower temperatures, the above omphacites would be stable at pressures higher than 2–6 kbar at 600°C. Since kyanite is stable at pressures higher than about 5 kbar at 600°C (Richardson, Bell and Gilbert, 1968), the omphacites in kyanite-eclogites in Silberbach would have been equilibrated at pressures higher than 5–6 kbar, if temperature is assumed to be 600°C. It should be noted that the sillimanite-kyanite transition curve given by the above authors is very close to the lower stability limit of omphacite of composition $\text{Di}_{75}\text{Jd}_{25}$ (by mole) in the presence of quartz. It is suggested, therefore, that omphacites which coexist with sillimanite and quartz and have compositions on or close to the join diopside-jadeite must be more diopside-rich than $\text{Di}_{75}\text{Jd}_{25}$.

In the Franciscan metamorphic rocks, metagraywackes, metacherts and some metabasalts contain omphacite or jadeite with quartz (McKee, 1962; Coleman and Lee, 1963; Ernst, 1965; Coleman *et al.*, 1965; Coleman and Clark, 1968). Omphacites from metagraywackes contain 70 to 90 mole percent jadeite, those from metacherts appear to contain less than 20 percent, and those from metabasalts contain about 35 percent (Coleman and Clark, 1968). However, among these omphacites, those whose compositions are close to the join diopside-jadeite are relatively

few. The omphacites (and jadeitic pyroxene) to which the present experimental results may be applicable are, for example, an omphacite from metabasalt (glaucophane-pumpellyite schist) from Ward Creek (15-cz-59 by Coleman *et al.*, 1965) and a jadeitic pyroxene from metagraywackes from Angel Island (B-48 by Coleman and Clark, 1968). The former contains 37 mole percent jadeite, 41 percent diopside and 7 percent acmite and the latter contains 87.5 percent jadeite, 5.9 percent diopside and 3.7 percent acmite. If the stability curves of omphacite shown in Figure 4 could be extrapolated linearly to the temperatures of the metamorphism of Franciscan formation (*e.g.*, 270–315°C for the schist in Ward Creek given by Taylor and Coleman, 1968, on the basis of oxygen isotope analyses), the omphacite from Ward Creek and the jadeitic pyroxene from Angel Island would have been formed at pressures higher than 7–8 kbar and 9–10 kbar, respectively. The former value is consistent with the value at Ward Creek estimated by Ernst and Seki (1967) and Taylor and Coleman (1968) on the basis of the calcite-aragonite transition. It is noted that the stability field of omphacite containing more than 70 percent jadeite is essentially the same as that of jadeite in the presence of quartz.

Newton and Smith (1967) have shown that the lower limit of the stability field of a jadeitic pyroxene (jadeite 82, acmite 14, diopside 4 by mole), which is considered by them as an average jadeitic pyroxene in the metasediments of the Franciscan formation, is almost parallel to the univariant curve albite = jadeite + quartz in the temperature range 0 to 400°C, the former being located on the lower pressure (less than 1 kbar) side of the latter (Newton and Smith, 1967, Fig. 7). This jadeitic pyroxene is stable at pressures higher than 9–10 kbar at temperatures 270–315°C. Their experimental data (Newton and Smith, 1967, Fig. 5) also show that the presence of acmite in amounts less than 15 percent affects only slightly (less than 0.5 kbar) the stability field of jadeite at 600°C. It is expected that the stability fields of omphacites containing less than 15 percent acmite may be nearly the same as those on the join diopside-jadeite. If this is the case, the present experimental results would be applicable to many other omphacites in various quartz-bearing rocks. Further, if the effect of Fe^{2+} on the stability of omphacites and aluminous clinopyroxenes with Ca-Tschermak's component is disclosed, applications of the present results would be much broader.

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