

THE SYSTEM FORSTERITE-DIOPSIDE-SILICA WITH AND WITHOUT WATER AT HIGH PRESSURES

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ABSTRACT. The phase equilibrium relations in the system forsterite–diopside–silica have been studied at 20 kilobars (kb) under both anhydrous and hydrous conditions by the piston-cylinder, solid-media pressure apparatus. Under anhydrous conditions, the forsterite–pyroxene liquidus boundary shifts toward forsterite with an increase of pressure from 1 atm to at least 20 kb. At 20 kb the join diopside–enstatite is a thermal barrier between silica-saturated and silica-undersaturated parts of the system forsterite–diopside–silica. In the subsolidus region of the join diopside–enstatite there is a narrow field of pigeonitic clinopyroxene at about diopside 20 enstatite 80 wt percent at temperatures above 1450°C. The first synthesis of “iron-free pigeonite” has been made in this and adjoining fields. The join forsterite–diopside is not binary, forsterite and diopside crystallized from this join being solid solutions containing small amounts of the components CaMgSiO_6 and MgSiO_3 , respectively.

Under hydrous conditions, the forsterite–enstatite solid solution liquidus boundary does not shift toward forsterite but shifts toward silica with increasing pressure. At 20 kb water pressure, forsterite is on the liquidus over a wide compositional range in the join diopside–enstatite and is not a thermal barrier.

If partial melting of olivine-rich lherzolite, which is believed to be the upper mantle material, takes place at pressures higher than at least 10 kb under anhydrous conditions, liquids undersaturated with respect to silica are formed. The residual materials after partial melting are more magnesian lherzolite, saxonite, or dunite. Wehrlite and pyroxenites cannot be the residual products of the partial melting of an olivine-rich lherzolite. Under hydrous conditions, where the water pressure is equal or nearly equal to total pressure, the liquids formed by the partial melting of lherzolite at pressures at least near 20 kb are silica saturated. Even if the water pressure is lower than the total pressure, silica-saturated magmas can be formed at considerably higher pressures under water-present conditions than under anhydrous conditions.

INTRODUCTION

The system forsterite (Mg_2SiO_4)–diopside ($\text{CaMgSi}_2\text{O}_6$)–silica is one of the most fundamental systems for the understanding of the crystallization of basaltic magmas. Bowen (1914) studied this system in detail at 1 atm and showed crystallization courses of liquids as well as the similarity in the crystallization behavior between the liquids in this synthetic system and natural basaltic magmas. Although part of the equilibrium relations given by Bowen has been revised lately (Schairer and Yoder, 1962; Kushiro and Schairer, 1963), his studies have contributed greatly to the understanding of crystallization of natural basaltic magmas.

The system forsterite–diopside–silica includes forsterite, diopside, and enstatite which are principal minerals of peridotites, and, therefore, the liquidus relations of this system are also fundamental for the understanding of the melting and crystallization of peridotites. The process of melting of peridotites would be closely related to that of the generation of basaltic magmas, because the upper mantle, where basaltic magmas are generated, most likely consists of olivine-rich lherzolite. As basaltic magmas are generated at considerable depths, it would be de-

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sirable to determine the liquidus relations of this ternary system at high pressures. The liquidus relations in this ternary system at high pressures would also be important for understanding the crystallization of basaltic magmas at relatively deep levels.

For these reasons, the liquidus relations in the system forsterite–diopside–silica, particularly in the subsystem forsterite–diopside–enstatite, have been studied at 20 kb corresponding to the depth of about 60 km. Experiments were also made at 20 kb water pressure in order to discover the effect of water pressure on the liquidus relations in this system. Although the experiments under hydrous conditions have not been completed, the results obtained are sufficiently important to include for comparison.

THE SYSTEM FORSTERITE–DIOPSIDE–ENSTATITE AS
A “SIMPLE PERIDOTITE AND PYROXENITE SYSTEM”

The system forsterite–diopside–enstatite, which is the silica-undersaturated portion of the system forsterite–diopside–silica, includes the principal components of the minerals of peridotites and pyroxenites. In general, peridotites consist essentially of forsteritic olivine and lesser amounts of clinopyroxene (diopsidic pyroxene) and orthopyroxene (enstatitic pyroxene). Although they contain some spinel, garnet, amphibole, and mica depending on the load and water pressures and the chemical composition, the amounts of these phases are relatively small in most peridotites. The principal rock types of peridotites and pyroxenites can be shown in the system forsterite–diopside–enstatite (fig. 1). However, this system may be described as “simple peridotite and pyroxenite system” because the peridotites and pyroxenites shown in the figure consist only of MgO, CaO, and SiO₂. Nevertheless, the system forsterite–diopside–enstatite represents more than 80 wt percent oxide components of most peridotites. Other major oxide components are FeO, Al₂O₃, and Fe₂O₃. “Clinopyroxenite” used here includes diopsidite and diallagite, and “orthopyroxenite” includes enstatolite¹ and bronzitite (if a small amount of iron is present).

EXPERIMENTAL PROCEDURE

All the experiments were carried out in the piston-cylinder, solid-media pressure apparatus similar to that designed by Boyd and England (1960). The furnace assemblies are the same as those described by Boyd and England (1961). Platinum capsules with 2.0 and 1.8 mm in outside diameter were used as sample containers for the anhydrous runs and the hydrous runs, respectively. The vacant space between the smaller capsule and ceramic sleeve was filled with crushable alumina powder. The capsules were sealed for the hydrous runs. The content of water in most of

¹ The name “enstatolite” was used by Pratt and Lewis (1905) for a rock consisting entirely of enstatite. “Harzburgite” is often used instead of saxonite. The distinction between saxonite and harzburgite is not clear. Johannsen (1938) used “saxonite” for rocks composed essentially of olivine and orthopyroxene and “harzburgite” for olivine-orthopyroxene rocks with considerable amounts of iron ores. According to this definition, “saxonite” is preferred over “harzburgite” for the “simple peridotite and pyroxenite system”.

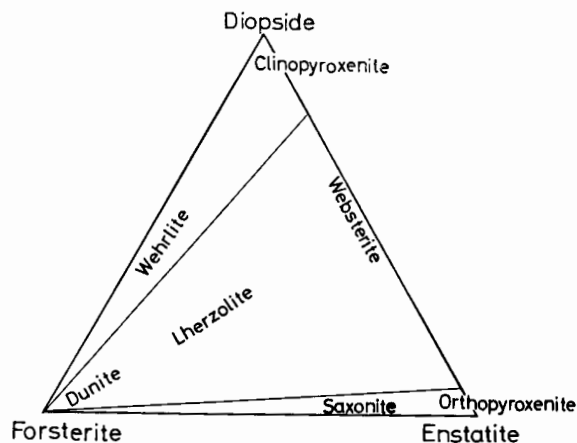


Fig. 1. "Simple peridotite and pyroxenite system" showing representative, simplified peridotites and pyroxenites.

the hydrous runs was 25 to 50 wt percent, and the charges were wet after the runs. The present experiments have been carried out with about -3 percent pressure correction according to Clark, Schairer, and de Neufville (1962). Recently Richardson, Bell, and Gilbert (1968) have shown that the piston-out runs without correction give satisfactory results as compared with those obtained by the gas-media apparatus, and that the discrepancy between the piston-in runs and the piston-out runs is about 2 kb in the pressure range 12 to 28 kb and in the temperature range 800° to 1500°C. In the present experiments pressure was raised to the desired value first, then the temperature was brought to the desired value. The friction of this method is smaller than that of the piston-in method but is larger than that of the piston-out runs. The error of the pressure measurements in the present experiments is, therefore, within ± 1.5 kb near 20 kb. Temperature was measured with a Pt/Pt90Rh10 thermocouple, and the error of the temperature measurements is believed to be within $\pm 20^\circ$. No correction was made for the effect of pressure on the *emf* of the thermocouple. In most of the anhydrous experiments requisite temperatures were above 1600°C, and 5 to 30 minutes were considered to be adequate. In the hydrous experiments requisite temperatures were between 950° and 1275°C, and 30 to 150 minutes were considered to be necessary for equilibrium even if liquid and vapor existed. In the presence of water vapor, crystals grow rapidly, and euhedral or subhedral crystals were usually obtained in 30 minute runs even below the solidus.

The starting materials were glass crystallized at 1 atm and glass prepared in the systems forsterite-diopside-silica by Schairer and Yoder (1962) and Kushiro and Schairer (1963) and in the system diopside-enstatite by Boyd and Schairer (1964) and Kushiro and Schairer (1963).

The phases after the runs were identified by petrographic microscope or X-ray powder diffractometer, or both. In the present experi-

TABLE 1

Results of experiments in the system forsterite-diopside
at 20 kb under anhydrous conditions

| Composition of starting material, weight percent | | Temp., °C | Time, min. | Results |
|--|-----|-----------|------------|---|
| Fo | Di | | | |
| 0 | 100 | 1630 | 5 | Di ($\Delta 2\theta = 0.614^\circ \pm 0.006$) |
| | | 1640 | 5 | Di + q-Cryst |
| | | 1650 | 5 | q-Cryst |
| 5 | 95 | 1500 | 60 | Di _{SS} + Fo _{SS} ? |
| | | 1625 | 6 | Di _{SS} |
| | | 1645 | 5 | q-Cryst + Gl(s) |
| 5 (Mechanical mixture) | 95 | 1600 | 10 | Di _{SS} |
| 8 | 92 | 1600 | 10 | Fo _{SS} (s) + Di _{SS} ($\Delta 2\theta = 0.590^\circ \pm 0.013$, 4 wt % En) |
| | | 1635 | 6 | Di _{SS} + q-Cryst(s) |
| 10 | 90 | 1630 | 5 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.542^\circ \pm 0.013$, 10 wt % En) |
| | | 1650 | 5 | q-Cryst + Gl(s) |
| 15 | 85 | 1635 | 5 | Di _{SS} + q-Cryst(s) + Gl(s) |
| | | 1645 | 5 | q-Cryst + Gl(s) |
| 20 | 80 | 1610 | 5 | Fo _{SS} + Di _{SS} |
| | | 1625 | 5 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.543^\circ \pm 0.005$, 10 wt % En) |
| | | 1630 | 5 | Fo _{SS} + Di _{SS} |
| | | 1645 | 5 | q-Cryst + Gl(s) |
| 30 | 70 | 1630 | 7 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.519^\circ \pm 0.006$, 13 wt % En) |
| | | 1650 | 6 | Fo _{SS} (s) + q-Cryst + Gl(s) |
| | | 1670 | 5 | Fo _{SS} (s) + q-Cryst + Gl(s) |
| | | 1690 | 5 | Fo _{SS} (s) + q-Cryst + Gl(s) |
| | | 1705 | 5 | Fo _{SS} (very rare) + q-Cryst + Gl(s) |
| 50 | 50 | 1625 | 6 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.505^\circ \pm 0.015$, 15 wt % En) |
| | | 1645 | 5 | Fo _{SS} + q-Cryst |
| | | 1670 | 5 | Fo _{SS} + q-Cryst |
| 65 | 35 | 1630 | 5 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.485^\circ \pm 0.013$, 17 wt % En) |
| | | 1650 | 5 | Fo _{SS} + q-Cryst(s) |
| 80 | 20 | 1630 | 10 | Fo _{SS} + Di _{SS} ($\Delta 2\theta = 0.27^\circ \pm 0.03$, 34 wt % En) |
| | | 1650 | 8 | Fo _{SS} + q-Cryst(s) |

Starting materials are glass, crystallized at 1 atm if not mentioned.

Abbreviations: Di, diopside; Di_{SS}, diopside solid solution; Fo, forsterite; Fo_{SS}, forsterite solid solution; Gl, glass; q-Cryst, quench crystals; (s), small amount; En, enstatite.

$\Delta 2\theta$ is angle difference between 311 and 310 reflections in the X-ray powder diffraction pattern (by CuK α radiation) of diopside solid solution. The contents of enstatite in the diopside solid solutions are estimated approximately by the values of $\Delta 2\theta$ on the basis of the $\Delta 2\theta$ -composition curve given by Kushiro and Schairer (1963).

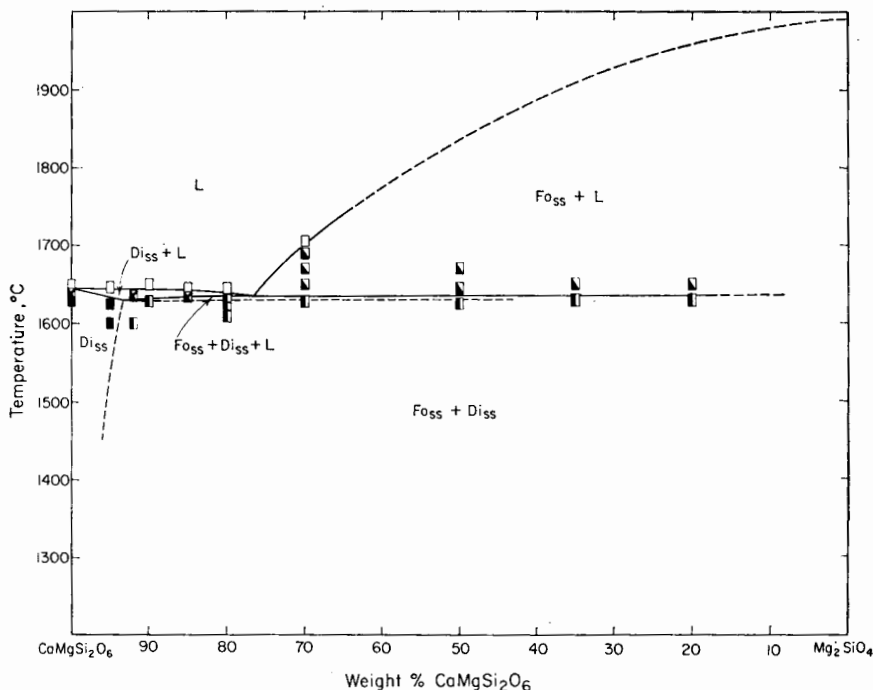


Fig. 2. Equilibrium diagram of the system forsterite (Mg_2SiO_4)-diopside ($\text{CaMgSi}_2\text{O}_6$) at 20 kb under anhydrous conditions. Abbreviations as in table 1.

ments, quench crystals, which were mostly quench pyroxene, were often encountered as fibrous or feathery-like crystals and often showed radial or fan-shaped growth. They were easily distinguished from the primary pyroxene and olivine crystals which are short prismatic or rounded.

EXPERIMENTAL RESULTS

1. *The system forsterite-diopside at 20 kb.*—The results of the runs made on nine mixtures on the Fo-Di² join at 20 kb under anhydrous conditions are shown in table 1. On the basis of these results, the equilibrium diagram of this join at 20 kb is drawn (fig. 2).

The maximum temperature of coprecipitation of forsterite and diopside solid solutions, which is a piercing point, exists at $1635 \pm 10^\circ\text{C}$ and at about Fo₂₄Di₇₆ (by weight). The melting point of pure diopside at 20 kb was determined to be $1645 \pm 10^\circ\text{C}$ (compare, $\sim 1635^\circ\text{C}$ by Boyd and England, 1963).

Diopside crystallizing from the mixtures on this join is not pure $\text{CaMgSi}_2\text{O}_6$. The angular differences between the $\bar{3}11$ and 310 reflections ($\Delta 2\theta$) in X-ray powder diffraction patterns are considerably smaller than

²Abbreviations used in the following pages: Cpx, pigeonitic clinopyroxene; Di, diopside; En, enstatite; Fo, forsterite; L, liquid; Merw, merwinite; Pr, protoenstatite; Q, silica; ss, solid solution; V, vapor.

that of pure diopside as shown in table 1. The smaller $\Delta 2\theta$ values are most probably attributed to the solid solution involving enstatite molecule as at 1 atm (Kushiro and Schairer, 1963). At constant temperature the content of MgSiO_3 in diopside solid solution increases with increase of Mg_2SiO_4 content in the mixture from which it crystallizes, as shown in table 1. The maximum content of MgSiO_3 is about 35 wt percent.

Forsterite crystallizing from mixtures on this join at temperatures higher than at least 1550°C is also not pure Mg_2SiO_4 . The X-ray powder diffraction patterns of the forsterite show that the d -spacings of 021, 130, and 112 planes are larger than those of pure forsterite, indicating that the forsterite is a solid solution containing small amounts of the component CaMgSiO_4 .

The Fo–Di join is, therefore, not binary, and this join is not a thermal barrier between the silica-undersaturated and the critically silica-undersaturated liquids in the system CaO–MgO–SiO_2 at 20 kb as well as at 1 atm. The liquids in the Fo–Di–En system probably change their compositions toward the Fo–Merw join across the Fo–Di join. On theoretical grounds, a three-phase region $\text{Fo}_{\text{ss}} + \text{Di}_{\text{ss}} + \text{L}$ should exist just above the solidus and below the $\text{Di}_{\text{ss}} + \text{L}$ and $\text{Fo}_{\text{ss}} + \text{L}$ regions as shown in figure 2.

Diopside may contain forsterite in solid solution in addition to enstatite at temperatures at least near the beginning of melting as at 1 atm. The content of forsterite in diopside does not exceed 5 wt percent. Such a diopside solid solution would have structural defects because it has excess Mg or deficient oxygen relative to the pyroxene formula.

2. *The system diopside–enstatite at 20 kb.*—The results of the runs made on nineteen mixtures on the Di–En join at 20 kb under anhydrous conditions are shown in table 2. Most of the runs have been made near solidus and liquidus temperatures on this join. On the basis of these results and the interpretation stated below, the equilibrium diagram near solidus and liquidus temperatures at 20 kb is constructed (fig. 3).

At 20 kb under anhydrous conditions neither forsterite nor a silica mineral appear on the Di–En join, and all the phases appear to have compositions on this join.

The liquidus between diopside and $\text{Di}_{62}\text{En}_{38}$ (in wt percent) is very flat, and diopside solid solution crystallizes as a primary phase in this compositional range. The solidus of diopside solid solution is close to the liquidus, and the melting interval is not wider than 30° . Quench crystals of feathery clinopyroxene are usually obtained when the liquid is quenched from temperatures above the liquidus. Glass was sometimes observed with quench crystals.

In the composition $\text{Di}_{40}\text{En}_{60}$, enstatite solid solution appears as a primary phase. Some of the crystals show overgrowth of clinopyroxene along their margins. The marginal clinopyroxene may be formed during the quench, that is, it is a quench product.

In the compositions between $\text{Di}_{50}\text{En}_{50}$ and $\text{Di}_{60}\text{En}_{40}$ and at temperatures between 1650° and 1670°C , clinopyroxene is observed with quench

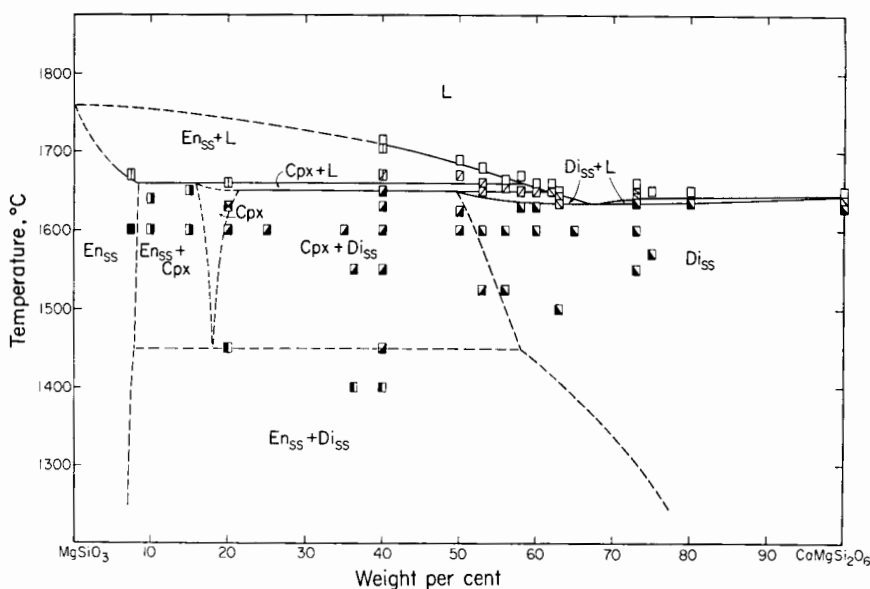


Fig. 3. Equilibrium diagram of the system diopside ($\text{CaMgSi}_2\text{O}_6$)-enstatite (MgSiO_3) at 20 kb under anhydrous conditions. Abbreviations: Cpx, pigeonitic clinopyroxene; others as in tables 1 and 2.

crystals and glass. In the X-ray powder diffraction pattern this clinopyroxene shows the 231 reflection which is characteristic of clinoenstatite or pigeonite. Some crystals show zonal structure from clinopyroxene with a smaller extinction angle in the center to that with a larger extinction angle in the margins. The marginal clinopyroxene may be more calcic than that of the core. Although the marginal clinopyroxene may be a quench product, it is probable that there is a small temperature interval over which pigeonitic clinopyroxene is stable in the liquid just above the solidus and below the enstatite + liquid field.

In the subsolidus region, diopside solid solution is stable in the compositions between diopside and $\text{Di}_{53}\text{En}_{47}$ at 1600°C. In the compositions between $\text{Di}_{50}\text{En}_{50}$ and $\text{Di}_{20}\text{En}_{80}$, however, two different clinopyroxenes appear to coexist at 1600°C as inferred from the evidence that the 311 and 220 reflections in their X-ray powder diffraction patterns split into two separate reflections. The split of the 311 reflection, shown in figure 4, is more distinct than that of the 220 reflection. Possible reflections that can be derived from the diopside solid solution are not in accord with one of the split peaks. In addition, their X-ray powder patterns show the 231 plane reflection which does not occur in diopside solid solution, $\text{C}2/c$, but occurs in clinoenstatite or pigeonite, $\text{P}2_1/c$. When a mechanical mixture of pure diopside (40 wt percent) and pure orthoenstatite (60 wt percent) was held at 20 kb and 1600°C for 1 hour, orthopyroxene reflections disappeared in the X-ray diffraction pattern, and the clinopyroxene(s) showing the 231 reflection and the split 311 reflec-

TABLE 2

Results of experiments in the system diopside-enstatite
at 20 kb under anhydrous conditions

| Composition of starting material, weight percent | | Temperature, °C | Time, minutes | Results |
|--|------|-----------------|---------------|--|
| Di | En | | | |
| 7.5 | 92.5 | 1600 | 20 | En _{SS} + Cpx? |
| | | 1670 | 5 | En _{SS} + Cpx + q-Cryst? |
| 10 | 90 | 1600 | 60 | En _{SS} + Cpx |
| | | 1640 | 30 | En _{SS} + Cpx |
| 15 | 85 | 1600 | 60 | En _{SS} + Cpx |
| | | 1650 | 30 | En _{SS} + Cpx + q-Cryst? |
| 20 | 80 | 1450 | 150 | En _{SS} + Cpx? + Di _{SS} ? |
| | | 1500 | 40 | Cpx + En _{SS} ? |
| | | 1600 | 35 | Cpx + Di _{SS} |
| | | 1630 | 30 | Cpx |
| | | 1660 | 15 | En _{SS} + q-Cryst |
| 25 | 75 | 1600 | 45 | Cpx + Di _{SS} |
| 35 | 65 | 1600 | 60 | Cpx + Di _{SS} |
| 36.3 (Mechanical mixture) | 63.7 | 1400 | 80 | En _{SS} + Di _{SS} (≅ Di ₆₂ En ₃₈) |
| | | 1550 | 40 | Cpx + Di _{SS} |
| 40 | 60 | 1600 | 20 | Cpx + Di _{SS} |
| | | 1630 | 20 | Cpx + Di _{SS} |
| | | 1650 | 6 | Cpx + Di _{SS} |
| | | 1670 | 5 | En _{SS} ? + Cpx + q-Cryst |
| | | 1705 | 5 | En _{SS} (s) + q-Cryst |
| | | 1715 | 5 | q-Cryst + Gl(s) |
| 40 (Glass) | 60 | 1400 | 180 | Di _{SS} + En _{SS} |
| | | 1450 | 140 | Cpx + Di _{SS} |
| | | 1550 | 40 | Cpx + Di _{SS} |
| 40 (Mechanical mixture) | 60 | 1600 | 60 | Cpx + Di _{SS} |
| 50 (Glass) | 50 | 1690 | 6 | q-Cryst + Gl(s) |
| | | 1600 | 15 | Cpx + Di _{SS} |
| | | 1625 | 40 | Cpx + Di _{SS} |
| 53 | 47 | 1670 | 10 | Cpx + q-Cryst |
| | | 1525 | 90 | Cpx + Di _{SS} |
| | | 1600 | 20 | Di _{SS} |
| | | 1650 | 7 | Cpx + q-Cryst |
| | | 1660 | 5 | Cpx + q-Cryst + Gl(s) |
| 56 | 44 | 1680 | 5 | q-Cryst + Gl(s) |
| | | 1525 | 90 | Di _{SS} |
| | | 1600 | 20 | Di _{SS} |
| | | 1655 | 5 | Cpx + q-Cryst |
| 58 | 42 | 1665 | 5 | q-Cryst + Gl(s) |
| | | 1630 | 5 | Di _{SS} |
| | | 1650 | 5 | Cpx + q-Cryst(s) |
| 60 | 40 | 1670 | 5 | q-Cryst + Gl(s) |
| | | 1600 | 18 | Di _{SS} |
| | | 1630 | 5 | Di _{SS} |
| | | 1650 | 5 | Cpx + q-Cryst + Gl |
| | | 1660 | 5 | q-Cryst |

TABLE 2 (continued)

| Composition of starting material, weight percent | | Temperature, °C | Time, minutes | Results |
|--|----|-----------------|---------------|---|
| Di | En | | | |
| 62 | 38 | 1650 | 4 | $Di_{ss} + q\text{-Cryst} + Gl(s)$ $q\text{-Cryst} + Gl$ |
| | | 1660 | 5 | |
| 63 | 37 | 1500 | 40 | Di_{ss} |
| | | 1635 | 5 | $Di_{ss} + q\text{-Cryst}(s)$ |
| | | 1645 | 5 | $Di_{ss} + q\text{-Cryst}$ |
| | | 1650 | 5 | $q\text{-Cryst}$ |
| 65 | 35 | 1600 | 20 | Di_{ss} |
| 73 | 27 | 1550 | 30 | Di_{ss} |
| | | 1600 | 20 | Di_{ss} |
| | | 1635 | 6 | Di_{ss} |
| | | 1645 | 5 | $Di_{ss} + q\text{-Cryst}$ |
| | | 1650 | 5 | $Di_{ss} + q\text{-Cryst}$ |
| | | 1660 | 5 | $q\text{-Cryst} + Gl(s)$ |
| 75 | 25 | 1570 | 30 | Di_{ss} |
| | | 1650 | 5 | $q\text{-Cryst}$ |
| 80 | 20 | 1635 | 6 | Di_{ss} |
| | | 1650 | 5 | $q\text{-Cryst} + Gl(s)$ |

Starting materials are glass, crystallized at 1 atm if not mentioned.

Abbreviations: Cpx, clinopyroxene solid solution showing 231 plane reflection in the X-ray powder diffraction pattern; En_{ss} , enstatite solid solution. Others as in table 1.

tion was also obtained. The clinopyroxene formed from a glass of composition $Di_{40}En_{60}$ at 1600°C showed no split in both the 311 and the 220 reflections. However, when this clinopyroxene was held at 20 kb and 1620°C for 30 minutes, both the reflections were clearly split. The same phenomena was observed for the clinopyroxene formed from the composition $Di_{35}En_{65}$ at 1600°C; that is, the 220 reflection was observed to split after this clinopyroxene was held at 1620°C for 40 minutes. The reheated specimen ($Di_{40}En_{60}$) was examined by the electron probe micro-analyzer and was shown to have two phases, a Ca-rich phase and a Ca-poor phase, which are interlocking one another in a single grain. From these observations it is suggested that diopside solid solution and pigeonitic clinopyroxene coexist in the compositional area between $Di_{50}En_{50}$ and $Di_{20}En_{80}$ at about 1600°C as shown in figure 3. At 1525°C, clinopyroxene(s) crystallized from the composition $Di_{53}En_{47}$ shows the 231 reflection, but that crystallized from the composition $Di_{56}En_{44}$ does not show the 231 reflection. This evidence indicates that the Cpx + Di_{ss} region may be between $Di_{53}En_{47}$ and about $Di_{20}En_{80}$ at 1525°C. Because of the difficulty of detecting a small amount of pigeonitic clinopyroxene by the X-ray method, the actual boundary between the Di_{ss} and the $Di_{ss} + Cpx$ regions could be more diopside-rich than that suggested in figure 3. In the Cpx + Di_{ss} region in figure 3, the relative intensities of the split 311 reflections appear to change with bulk composition (fig. 4).

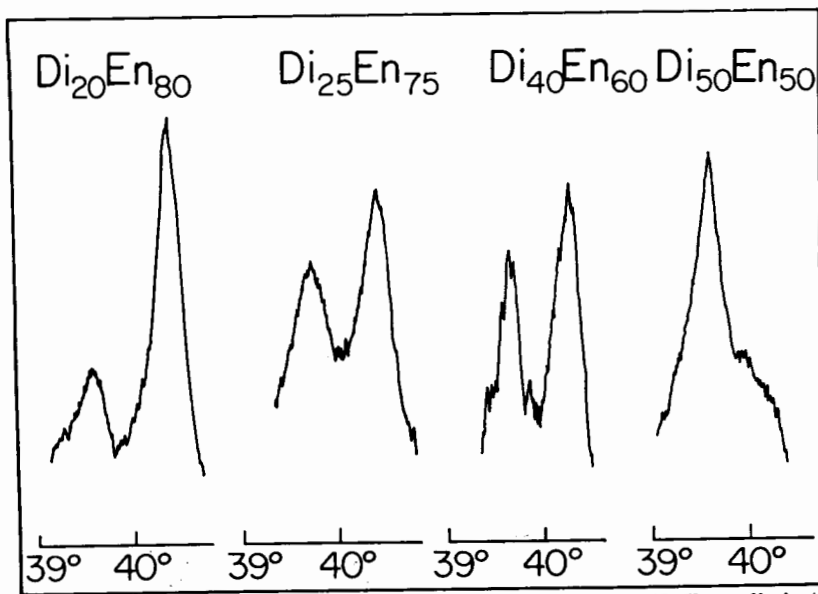


Fig. 4. X-ray powder diffraction patterns of 311 reflections ($\text{CuK}\alpha$ radiation) of clinopyroxenes crystallized from the mixtures of compositions $\text{Di}_{20}\text{En}_{80}$, $\text{Di}_{25}\text{En}_{75}$, $\text{Di}_{40}\text{En}_{60}$, and $\text{Di}_{50}\text{En}_{50}$ (wt percent) at 1600° , 1600° , 1650° , and 1600°C , respectively, at 20 kb.

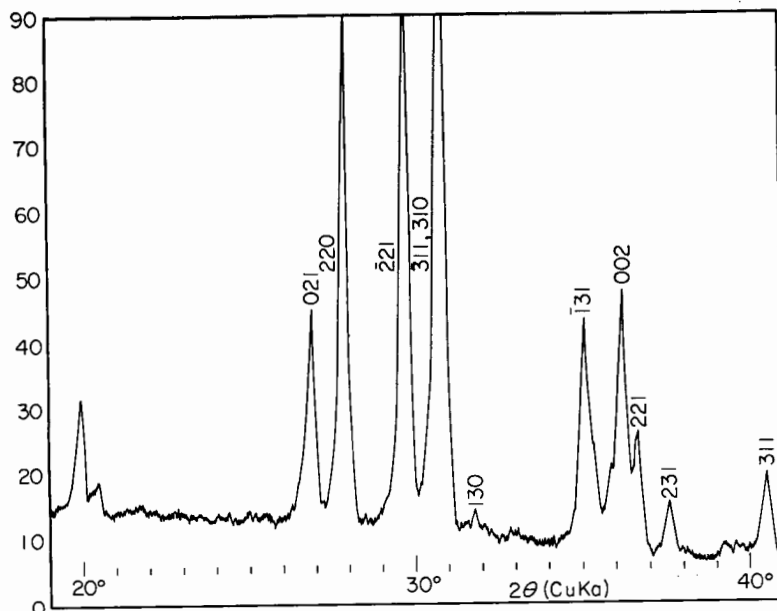


Fig. 5. X-ray powder diffraction pattern ($\text{CuK}\alpha$ radiation) of a single pigeonitic clinopyroxene synthesized from the mixture of composition $\text{Di}_{20}\text{En}_{80}$ at 1630°C at 20 kb.

The clinopyroxene crystallized from the composition $\text{Di}_{20}\text{En}_{80}$ at 1600°C shows the split 311 reflection, but that crystallized at 1630°C is a single pigeonitic clinopyroxene showing a sharp 231 plane reflection (fig. 5). The pattern is very similar to those of natural pigeonites. In the compositions $\text{Di}_{15}\text{En}_{85}$ and $\text{Di}_{10}\text{En}_{90}$, both orthoenstatite and pigeonitic clinopyroxene coexist at temperatures at least between 1600° and 1650°C . The field of pigeonitic clinopyroxene is, therefore, limited in a narrow compositional range between $\text{Di}_{20}\text{En}_{80}$ and $\text{Di}_{15}\text{En}_{85}$. It is significant that the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio of this compositional range (0.08 – 0.10) is very close to the $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe}^{2+})$ ratio of natural pigeonites, although they usually contain considerable amounts of iron. The pigeonitic clinopyroxene synthesized in its own field may be called "iron-free pigeonite" from the similarity to natural pigeonite in $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe}^{2+})$ ratio and in X-ray diffraction pattern. To the best of the writer's knowledge this is the first synthesis of pigeonite. Lindsley and Munoz (1969) appear to have also synthesized a clinopyroxene similar to pigeonite in $\text{Ca}/(\text{Ca}+\text{Fe}^{2+})$ ratio and structure on the join hedenbergite-ferrosilite join at 20 kb.

At 1400°C , a glass of composition $\text{Di}_{40}\text{En}_{60}$ crystallized to diopside and enstatite solid solutions without pigeonitic clinopyroxene, and a mechanical mixture of pure diopside (36.3 wt percent) and pure enstatite (63.7 wt percent) also reacted to form enstatite solid solution and diopside solid solution of composition about $\text{Di}_{62}\text{En}_{38}$, estimated by the 2θ of the 311 reflection on the basis of Boyd and Schairer (1964). At 1450°C , a glass of composition $\text{Di}_{40}\text{En}_{60}$ crystallized to diopside solid solution and pigeonitic clinopyroxene without orthoenstatite. The pigeonitic clinopyroxene is stable, therefore, at temperatures at least above 1450°C at 20 kb.

The temperature of the stability field of pigeonite may change with both pressure and iron content. It may be expected that the temperature of the pigeonite stability field, bounded by the solidus and the lower temperature limit, is lowered with decreasing pressure or with increasing iron content or with both. In the pressure-temperature condition of the crystallization of natural basaltic magmas and for their iron contents, pigeonites with considerable amounts of iron ($\text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+})$ ratio ≥ 0.3) crystallize. At 1 atm, it is suggested that there is a field of pigeonite near the $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe}^{2+})$ ratio of 0.10 and in the $\text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+})$ ratio greater than 0.30.

On the basis of the present experimental results, it is suggested that pigeonite has more Ca than clinoenstatite, protoenstatite, orthoenstatite (orthopyroxene), and that pigeonite inverts to orthoenstatite (orthopyroxene) with exsolution of diopside solid solution (augite) at lower temperatures. These suggestions are consistent with natural evidence as well as that on the Ca content.

The present results are not inconsistent with some of the results obtained by Davis and Boyd (1966) at 30 kb. The diopside-rich limb of the solvus given by them may correspond to the limit of the pigeonitic

clinopyroxene solid solution where it is stable ($>$ about 1450°C) and to that of the diopside solid solution where pigeonitic clinopyroxene is not stable ($<$ about 1450°C). Of course, the solvus by Davis and Boyd was determined at 30 kb, and the position is not necessarily in accord exactly with that of the present experiments which were made at 20 kb.

On the basis of the solidus relations described above, there should be a peritectic point where enstatite solid solution reacts with liquid to form pigeonitic clinopyroxene. From the results obtained at liquidus temperatures, this point would exist at about $\text{Di}_{58}\text{En}_{42}$. In addition, there may be another peritectic point where pigeonitic clinopyroxene reacts with liquid to form diopside solid solution. This position is located probably at about $\text{Di}_{61}\text{En}_{39}$ from the evidence that the pigeonitic clinopyroxene appears on the liquidus on the enstatite side of the composition $\text{Di}_{60}\text{En}_{40}$, whereas diopside solid solution appears on the diopside side of the composition $\text{Di}_{62}\text{En}_{38}$. The temperatures of the two peritectic points are estimated to be about 1660° and 1650°C , respectively, as shown in figure 3.

3. *The system forsterite–diopside–enstatite at 20 kb.*—The results of the runs made on eight mixtures at 20 kb under anhydrous conditions are shown in table 3. On the basis of these results and those obtained in the Fo–Di system and the Di–En system, a portion of the liquidus diagram in the Fo–Di–En system at 20 kb under anhydrous conditions is constructed (fig. 6). Forsterite crystallizing within the Fo–Di–En system at 20 kb may be a solid solution containing a small amount of the component CaMgSiO_4 as at 1 atm, although it was not confirmed in the present experiments.

The liquidus surface of diopside solid solution is very flat, the temperature of liquidus being within $1640 \pm 10^{\circ}\text{C}$. As shown in table 1 the melting point of pure diopside at 20 kb determined in the present experiments is $1645 \pm 10^{\circ}\text{C}$. The solidus in this area is $1630 \pm 10^{\circ}\text{C}$ which is close to the liquidus temperature. Enstatite liquidus surface is steeper, the liquidus temperature increasing toward enstatite. As shown in the Di–En join, enstatite is a primary phase in the compositions between enstatite and about $\text{Di}_{58}\text{En}_{42}$, and pigeonitic clinopyroxene is a primary phase from about $\text{Di}_{58}\text{En}_{42}$ to $\text{Di}_{61}\text{En}_{39}$. The composition $\text{Fo}_{30}\text{Di}_{60}\text{Q}_{10}$ (DFS-7) yields a pigeonitic clinopyroxene with quench crystals and glass, indicating that the liquidus field (primary phase field) of pigeonitic clinopyroxene exists in the Fo–Di–En system. The boundary between the primary phase fields of enstatite solid solution and pigeonitic clinopyroxene may be located at about $\text{Di}_{58}(\text{En}+\text{Fo})_{42}$ as shown by a dashed line in figure 6, although its position could not be determined precisely because of insufficient data. The boundary between pigeonitic clinopyroxene and diopside solid solution located at about $\text{Di}_{61}(\text{En}+\text{Fo})_{39}$ as shown in figure 6.

On the Fo–pyroxene liquidus boundary, there should be two different isobaric invariant points. One is shown by point P, and the other is shown by point P', although the position of P' is not determined di-

TABLE 3

Results of experiments in the system forsterite-diopside-
silica at 20 kb under anhydrous conditions

| No. | Composition of starting material, weight percent | | | Temp., °C | Time, min. | Results |
|--------|--|----|------------------|--------------|---------------|--|
| | Fo | Di | SiO ₂ | | | |
| DFS-4 | 20 | 75 | 5 | 1630 | 8 | Di _{ss} + Fo*(s) |
| | | | | 1635 | 5 | Di _{ss} + Fo(s) |
| | | | | 1635 | 7 | Di _{ss} + q-Cryst(s) |
| | | | | 1640 | 7 | Di _{ss} (s) + q-Cryst |
| DFS-5 | 23 | 70 | 7 | 1625 | 10 | Di _{ss} + Fo(s) |
| | | | | 1635 | 10 | Di _{ss} + q-Cryst(s) (Di _{ss} : $\Delta 2\theta = 0.355^\circ \pm 0.007$, ≈ 29 wt % En) |
| | | | | 1640 | 7 | Di _{ss} + q-Cryst + Gl(s) |
| | | | | 1650 | 5 | q-Cryst + Gl |
| DFS-6 | 25 | 65 | 10 | 1550 | 20 | Di _{ss} (Di _{ss} : $\Delta 2\theta = 0.294^\circ \pm 0.007$, ≈ 33 wt % En) |
| | | | | 1630 | 5 | Di _{ss} |
| | | | | 1650 | 5 | q-Cryst |
| DFS-7 | 30 | 60 | 10 | 1625 | 5 | Di _{ss} + Fo? |
| | | | | 1630 | 5 | Di _{ss} + Fo? + q-Cryst |
| | | | | 1635 | 5 | Di _{ss} + Fo? + q-Cryst(s) |
| | | | | 1640 | 5 | Cpx + q-Cryst(s) + Gl(s) |
| | | | | 1645 | 5 | Cpx + q-Cryst |
| | | | | 1655 | 5 | Cpx(s) + q-Cryst + Gl(s) |
| | | | | 1660 | 5 | q-Cryst + Gl(s) |
| DFS-17 | 33 | 60 | 7 | 1630 | 7 | Di _{ss} + Fo |
| | | | | 1650 | 7 | Fo + q-Cryst |
| | | | | 1670 | 5 | q-Cryst |
| | | | | 1690 | 5 | q-Cryst |
| DFS-8 | 37 | 50 | 13 | 1630 | 5 | Cpx + Fo(s) |
| | | | | 1635 | 30 | Cpx + Fo(s) |
| | | | | 1650 | 6 | Cpx + Fo? |
| | | | | 1670 | 5 | Cpx + q-Cryst |
| | | | | 1680 | 5 | q-Cryst + Gl(s) |
| DFS-9 | 50 | 30 | 20 | 1500 | 35 | Cpx + Fo(s) |
| | | | | 1635 | 21 | Cpx + En _{ss} ? + Fo |
| | | | | 1650 | 5 | Cpx + Fo + q-Cryst(s) |
| | | | | 1670 | 7 | En _{ss} + Cpx + q-Cryst(s) + Gl(s) |
| DFS-10 | 65 | 10 | 25 | 1635 | 22 | En _{ss} + Cpx + Fo |
| | | | | 1670 | 7 | En _{ss} + Cpx + q-Cryst |

Starting materials are glass, crystallized at 1 atm.

Abbreviations as in tables 1 and 2.

*Forsterite in this system may be a solid solution containing a small amount of Ca.

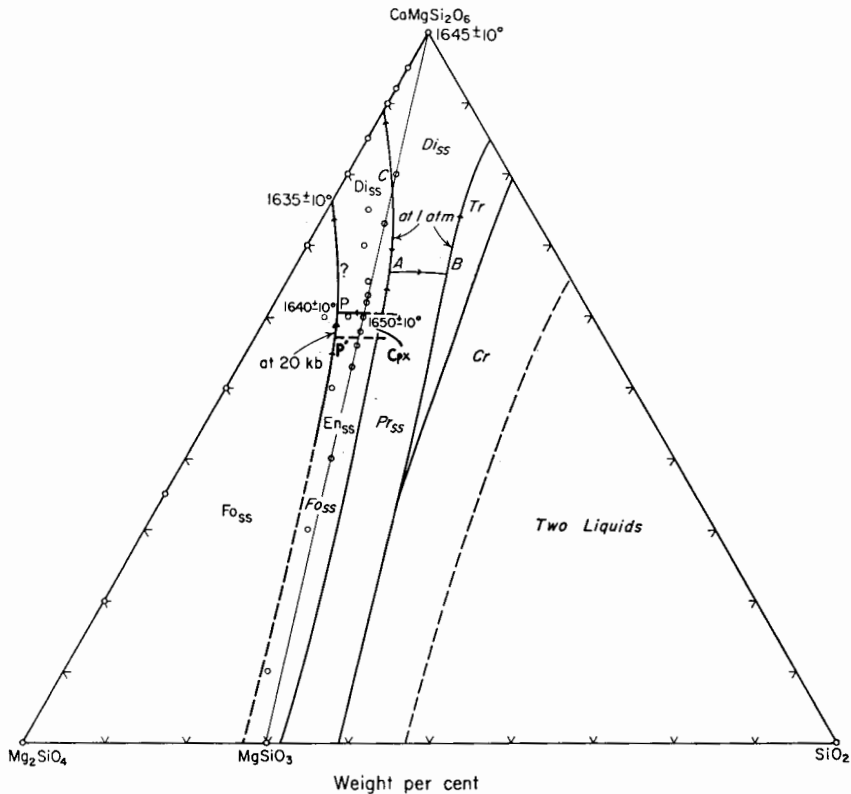


Fig. 6. Liquidus diagram of the system forsterite (Mg_2SiO_4)–diopside ($\text{CaMgSi}_2\text{O}_6$)–enstatite (MgSiO_3) at 20 kb under anhydrous conditions. Liquidus diagram of the system forsterite–diopside–silica at 1 atm is from Bowen (1914), Schairer and Yoder (1962), and Kushiro and Schairer (1963). Italic letters are for diagram at 1 atm.

rectly. It is not certain whether the point P is a reaction point or a eutectic point. The nature of this point depends on the composition of the diopside solid solution in equilibrium with liquid at P. If the composition of the diopside solid solution is more enstatite rich than the intersection of the Di–En join and the extension of the Fo–P join ($\sim\text{Di}_{67}\text{En}_{33}$), the point P is a reaction point. In the present experiments, however, the composition of the diopside solid solution at P could not be determined because of the presence of a large amount of quench pyroxene. If the temperature of the Fo–Di_{ss} liquidus boundary drops continuously from the point P to the minimum on the Fo–Di join, the point P is a reaction point. However, the temperature difference between P and the minimum on the Fo–Di join is too small to determine with certainty the temperature profile along the Fo–Di_{ss} liquidus boundary. The point P' is most likely a reaction point where the reaction $\text{En}_{\text{ss}} + \text{L} \rightleftharpoons \text{Fo} + \text{Cpx}$ (pigeonitic clinopyroxene) takes place, although this reaction has not been observed in nature.

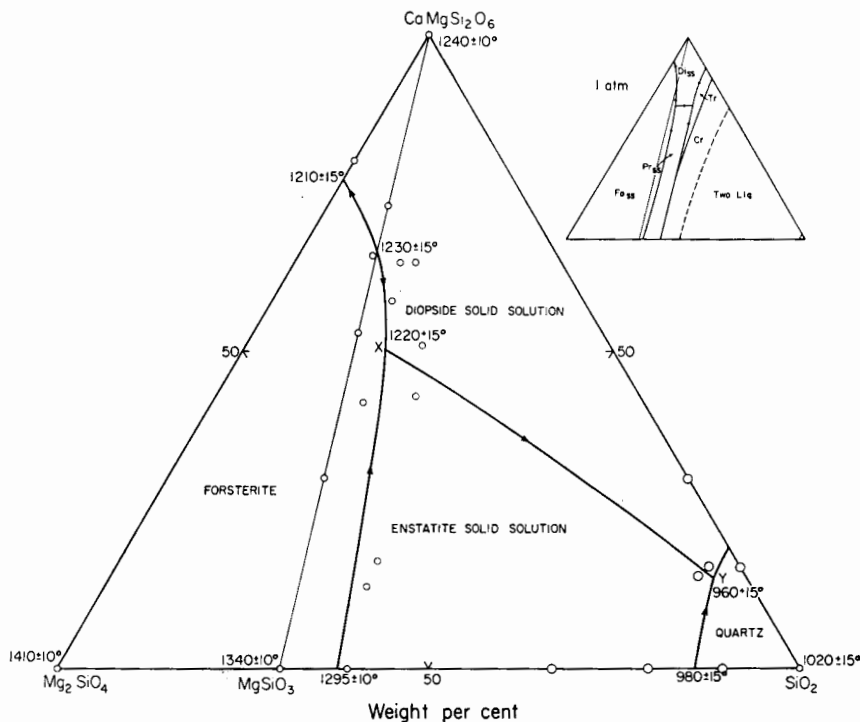


Fig. 7. The liquidus diagram of the system forsterite-diopside-silica at 20 kb P_{H_2O} . The boundaries are those projected onto this ternary system from the H_2O -apex in the quaternary system forsterite-diopside-silica- H_2O .

4. *The system forsterite-diopside-silica at 20 kb under hydrous conditions.*—In order to find out the effect of water pressure on the liquidus relations in the Fo-Di-Q system, experiments have been carried out on twenty-one selected compositions at 20 kb under hydrous conditions.³ Seven of the compositions are mechanical mixtures as recorded in table 4. Results for $MgSiO_3$ at 20 kb P_{H_2O} (water pressure) are from Kushiro, Yoder, and Nishikawa (1968). Duplicate runs were made for compositions $Fo_{51.9} Di_{13} Q_{35.1}$, $Di_{53} En_{47}$, and $Fo_{37.8} Di_{42} Q_{20.2}$ from both glass and crystallized glass. The results are the same for different starting materials for $Di_{53} En_{47}$ and $Fo_{37.8} Di_{42} Q_{20.2}$ as shown in table 4. For the composition $Fo_{51.9} Di_{13} Q_{35.1}$, however the results are different for different starting materials. In this case, crystallized glass may be more reliable because there is a possibility that some silica might have been leached preferentially from glass by the gas phase. For all other compositions, therefore, crystalline materials were used as starting materials. The charges were wet, and free water existed after all the runs, suggesting that the water pressure was equal to load pressure during all the runs. However, there is a possi-

³ "Hydrous conditions" used here means the conditions where water pressure is equal to total pressure, if not particularly mentioned.

TABLE 4

Results of experiments in the system forsterite-diopside-silica at 20 kb under
hydrous conditions (20 kb water pressure)

| Composition of starting material, weight percent | | | Starting material | Temp., °C | Time, min. | H ₂ O content, weight percent | Results |
|--|--------------------------------------|------------------|-------------------|-----------|------------|--|---|
| Fo | Di | SiO ₂ | | | | | |
| 20 | 80 | ... | Crystal. | 1200 | 50 | 25.0 | Di _{SS} + q-Cryst |
| | | | Crystal. | 1215 | 60 | 31.3 | q-Cryst + Gl |
| 19 | 73 | 8 | Crystal. | 1225 | 60 | 35.1 | Di _{SS} + Gl + q-Cryst? |
| | (Di ₇₃ En ₂₇) | | | | | | |
| 25 | 65 | 10 | Glass | 1175 | 40 | 42.2 | Di _{SS} |
| | | | Glass | 1225 | 30 | 39.0 | Fo + Di _{SS} + q-Cryst(s) |
| | | | Crystal. | 1235 | 40 | 53.7 | Fo + Di _{SS} + q-Cryst |
| | | | Glass | 1250 | 30 | 35.7 | q-Cryst. |
| 21.7 | 64 | 14.3 | Crystal. | 1220 | 60 | 26.8 | Di _{SS} (s) + q-Cryst + Gl |
| 19.6 | 64 | 16.4 | Crystal. | 1200 | 40 | 28.0 | Di _{SS} + En _{SS} (s) + q-Cryst(s) + Gl(s) |
| | | | Crystal. | 1225 | 60 | 41.0 | q-Cryst + Gl(s) |
| 25.9 | 58 | 16.1 | Crystal. | 1225 | 60 | 41.6 | Di _{SS} (s) + q-Cryst + Gl(s) |
| | | | Crystal. | 1235 | 60 | 30.6 | q-Cryst + Gl(s) |
| 33 | 53 | 14 | Glass | 1200 | 30 | 29.3 | Fo + En _{SS} + Di _{SS} ? + Gl(s) + q-Cryst(s) |
| | (Di ₅₃ En ₄₇) | | Crystal. | 1225 | 40 | 29.7 | Fo(s) + q-Cryst |
| | | | Glass | 1250 | 30 | 34.6 | Fo(s) + q-Cryst |
| | | | Crystal. | 1250 | 40 | 38.4 | Fo(s) + q-Cryst + Gl(s) |
| 25.2 | 51 | 23.8 | Crystal. | 1215 | 60 | 29.8 | Di _{SS} (s) + q-Cryst + Gl(s) |
| 30.1 | 43 | 26.9 | Crystal. | 1215 | 60 | 31.8 | En _{SS} (s) + q-Cryst + Gl(s) |
| 37.8 | 42 | 20.2 | Glass | 1250 | 40 | 49.2 | Fo + q-Cryst + Gl(s) |
| | | | Crystal. | 1250 | 45 | 44.4 | Fo + q-Cryst + Gl(s) |
| 49 | 30 | 21 | Glass | 1150 | 60 | 24.3 | En _{SS} + Di _{SS} + Fo(s) + Gl(s) |
| | (Di ₃₀ En ₇₀) | | Glass | 1275 | 30 | 43.8 | Fo + q-Cryst + Gl(s) |
| 48.4 | 17 | 34.6 | Glass | 1200 | 40 | 31.9 | En _{SS} + Di _{SS} + Gl? |
| | | | Crystal. | 1250 | 40 | 36.1 | En _{SS} + q-Cryst + Gl |
| 51.9 | 13 | 35.1 | Glass | 1250 | 40 | 41.0 | En _{SS} + Fo(s) + q-Cryst + Gl(s) |
| | | | Crystal. | 1250 | 40 | 21.5 | En _{SS} + q-Cryst + Gl(s) |
| 61.2 | ... | 38.8 | Crystal. | 1250 | 40 | 28.4 | En + q-Cryst(s) + Gl |
| | | | Crystal. | 1290 | 60 | 36.0 | En + q-Cryst + Gl + Fo? |
| 33.2 | ... | 66.8 | Crystal. | 1100 | 80 | 28.2 | En + q-Cryst + Gl |
| | (Mech. mix.*) | | Crystal. | 1240 | 60 | 28.7 | En(s) + q-Cryst + Gl |
| 20.4 | ... | 79.6 | Crystal. | 1100 | 70 | 26.9 | En(s) + q-Cryst + Gl |
| | (Mech. mix.*) | | Crystal. | 1125 | 60 | 26.1 | En(s) + q-Cryst + Gl |
| | | | Crystal. | 1150 | 90 | 37.7 | q-Cryst + Gl |
| | | | Crystal. | 1250 | 45 | 62.4 | En(s) + q-Cryst + Gl |
| | | | | 1100 | 90 | | |
| 10.2 | ... | 89.8 | Crystal. | 1000 | 90 | 27.4 | Q + Gl + En? |
| | (Mech. mix.*) | | Crystal. | 1050 | 90 | 32.4 | Gl |
| ... | 30 | 70 | Crystal. | 1100 | 100 | 30.2 | Di(s) + Gl |
| | (Mech. mix.**) | | Crystal. | 1150 | 100 | 35.0 | Gl |
| ... | 16 | 84 | Crystal. | 975 | 120 | 41.8 | Q(s) + Gl |
| | (Mech. mix.**) | | | | | | |

TABLE 4 (continued)

| Composition of starting material, weight percent | | | Starting material | Temp., °C | Time, min. | H ₂ O content, weight percent | Results |
|--|------|------------------|-------------------|-----------|------------|--|--|
| Fo | Di | SiO ₂ | | | | | |
| 6.3 (Mech. mix.***) | 14.7 | 79 | Crystal. | 1000 | 120 | 45.5 | Di _{ss} (s) + En(s) + Gl |
| | | | Crystal. | 1025 | 120 | 42.9 | Di _{ss} (s) + En(s) + Gl |
| | | | Crystal. | 1050 | 130 | 36.4 | En _{ss} (s) + Gl + Di _{ss} ? |
| 4.1 (Mech. mix.***) | 16 | 79.9 | Crystal. | 1035 | 172 | 42.5 | Di _{ss} (s) + Gl + En _{ss} ? |
| ... | ... | 100 | Cristo- balite | 1005 | 150 | 24.4 | Q + Gl |
| | | | | 1020 | 140 | 33.3 | Q + Gl |
| | | | | 1050 | 120 | 40.3 | Gl |

Abbreviations: Crystal., glass crystallized at 1 atm; Q, quartz; others as in tables 1 and 2.

*Mechanical mixture of clinoenstatite and cristobalite.

**Mechanical mixture of diopside and cristobalite.

***Mechanical mixture of clinoenstatite and diopside solid solutions and cristobalite.

bility that free water observed after the run was completely dissolved in liquid at the conditions of the run and released during the quench. In this case water pressure could be lower than the load pressure during the runs even if free water existed after the run. However, the water content in the present experiments is higher than the maximum content of water that can dissolve in forsterite melt at 20 kb (about 20 wt percent) determined by Kushiro and Yoder (unpub. data), and the water pressure was probably equal to load pressure. Therefore, the water pressure of the experiments is considered to be 20 kb. Figure 7 shows the liquidus boundaries under water-saturated conditions. That is, these boundaries are between primary-phase volumes projected from the H₂O apex onto the Fo-Di-Q plane in the system Fo-Di-Q-H₂O. As shown in the figure, the Fo-En_{ss} liquidus boundary at 20 kb P_{H₂O} is located on the silica-rich side of that at 1 atm. The Fo-Di_{ss} liquidus boundary is located, however, on the forsterite side of that at 1 atm in the Fo-Di-En area. The most remarkable change is that the primary phase fields of diopside and enstatite solid solutions expand greatly toward silica, as shown in figure 7. This occurs because of large drop of melting temperature of quartz at high water pressures (Stewart, 1967) as compared with those of diopside, (Yoder, 1964) and enstatite (Kushiro, Yoder and Nishikawa, 1968). It may be possible, however, that metastable pyroxene persists even in the presence of liquid and vapor. To check this possibility, a run was made in which the mixture of composition Fo₂₀Q₈₀ was heated to a temperature well above the liquidus and then held at a temperature just below the liquidus. In this run a small amount of large euhedral enstatite was obtained with glass, indicating that enstatite is not metastable at least for composition En₂₀Q₈₀ at 20 kb P_{H₂O}.

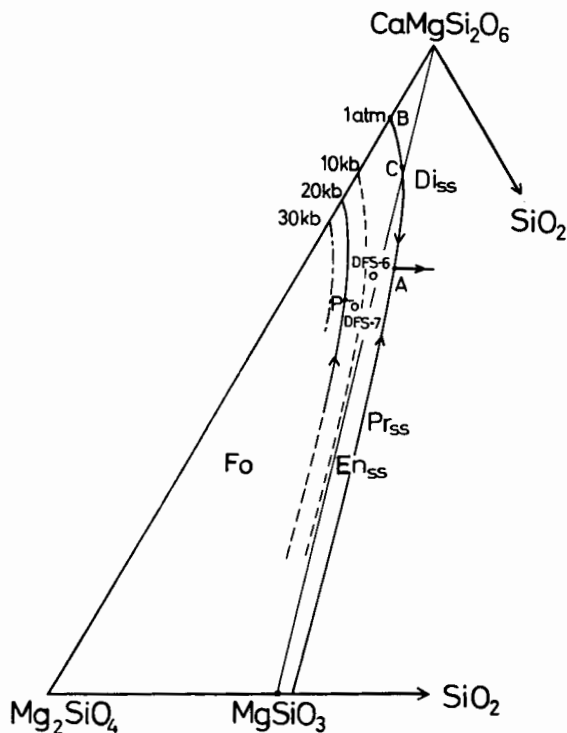


Fig. 8. Shift of the forsterite–pyroxene liquidus boundary with pressure under anhydrous conditions. The boundary at 30 kb is based on the liquidus relations on the join forsterite–diopside at 30 kb determined by Davis (1964). The boundary at 10 kb is very close to that predicted by Yoder and Tilley (1962, p. 412).

On the Fo–pyroxene liquidus boundary, there is a projection of the isobaric invariant point $\text{Fo} + \text{En}_{\text{ss}} + \text{Di}_{\text{ss}} + \text{L} + \text{V}$, which is located at about $\text{Fo}_{30}\text{Di}_{50}\text{Q}_{20}$ (X in fig. 7). This point is a reaction point where forsterite reacts with liquid to form diopside and enstatite solid solutions in the presence of vapor phase. The projection of another isobaric invariant point $\text{Di}_{\text{ss}} + \text{En}_{\text{ss}} + \text{Q} + \text{L} + \text{V}$ appears at about $\text{Fo}_5\text{Di}_{14}\text{Q}_{81}$ (Y in fig. 7). It is not certain whether this is a reaction point or a eutectic point.

On the liquidus of quartz (on the Di–Q and En–Q joins), rounded or square quartz crystals crystallize as a primary phase. They are probably high quartz, although double terminated pyramids are rarely seen. In the runs quenched from the temperatures above the liquidus, irregular-shaped glass including many bubbles and glass in the form of globules were obtained. However, it is not certain whether both vapor and liquid coexisted or only a super critical fluid existed during the runs made above the liquidus.

TABLE 5

Results of experiments on the compositions $\text{Fo}_{25}\text{Di}_{65}\text{Silica}_{10}$ (by weight)
(DFS-6) and $\text{Fo}_{30}\text{Di}_{60}\text{Silica}_{10}$ (DFS-7) under anhydrous conditions

| Pressure, kb | Temperature, °C | Time, minutes | Results |
|-----------------|--------------------|------------------|---|
| DFS-6 | | | |
| 7 | 1475 | 30 | Di_{ss} |
| 7 | 1490 | 20 | q-Cryst |
| 8 | 1495 | 20 | Gl |
| 9 | 1500 | 12 | $\text{Di}_{\text{ss}} + \text{q-Cryst}(s)$ |
| 9 | 1520 | 15 | q-Cryst |
| 11 | 1550 | 15 | q-Cryst |
| 13 | 1550 | 20 | $\text{Di}_{\text{ss}} + \text{Fo}?$ |
| 13 | 1570 | 20 | q-Cryst + Gl |
| 15 | 1520 | 20 | $\text{Di}_{\text{ss}} + \text{q-Cryst}$ |
| DFS-7 | | | |
| 12 | 1540 | 7 | $\text{Di}_{\text{ss}} + \text{Fo}(s)$ |
| 12 | 1550 | 15 | $\text{Fo}(s) + \text{q-Cryst}$ |
| 12 | 1560 | 15 | q-Cryst + Gl |

Starting materials are glass, crystallized at 1 atm.

Abbreviations as in tables 1 and 2.

CHANGE OF LIQUIDUS RELATIONS WITH PRESSURE UNDER ANHYDROUS CONDITIONS

The liquidus relations in the Fo-Di-En system change considerably with pressure. Figure 8 shows the Fo-pyroxene liquidus boundaries at 1 atm (Bowen, 1914; Schairer and Yoder, 1962; Kushiro and Schairer, 1963) and those at 20 kb under anhydrous conditions. As shown in the figure, the primary phase field of forsterite is much reduced at 20 kb as compared with that at 1 atm. The most significant difference between the liquidus relations at 1 atm and those at 20 kb is that at 1 atm there exists a reaction point (A) where forsterite reacts with liquid to form diopside and protoenstatite solid solutions, whereas at 20 kb forsterite does not react with liquid, but pigeonitic clinopyroxene may react with liquid to form forsterite and diopside solid solution at the invariant point (P).

In order to determine the pressure at which such a changeover takes place, additional runs have been made on two mixtures DFS-6 ($\text{Fo}_{25}\text{Di}_{65}\text{Q}_{10}$) and DFS-7 ($\text{Fo}_{30}\text{Di}_{60}\text{Q}_{10}$) at pressures between 7 and 15 kb (table 5). The composition DFS-6 does not lie in the primary phase field of forsterite at pressures at least higher than 7 kb, indicating that the primary phase field of forsterite is already on the forsterite-side of the composition DFS-6 at 7 kb. The composition DFS-7 lies in the primary phase field of forsterite at 12 kb. The pressure at which the changeover from a

forsterite liquidus to a pyroxene liquidus takes place for this composition is estimated to be about 15 kb by comparing the results in table 5 with those at 1 atm and 20 kb. The Fo–pyroxene liquidus boundary at 10 kb, therefore, passes between the compositions DFS-6 and DFS-7 and is shown by a dashed line in figure 8. Although the data are insufficient, it is suggested that the reaction $\text{Fo} + \text{L} \rightleftharpoons \text{Di}_{\text{ss}} + \text{Pr}_{\text{ss}}$ or $\text{Fo} + \text{L} \rightleftharpoons \text{Di}_{\text{ss}} + \text{En}_{\text{ss}}$ takes place at pressures less than 6 or 7 kb under anhydrous conditions.

Because of the significant change of the liquidus relations in the Fo–Di–Q system with pressure under anhydrous conditions the trends of liquids by crystallization at 1 atm and at high pressures are significantly different from one another. As shown by Bowen (1914), Schairer and Yoder (1962), and Kushiro and Schairer (1963), the liquids from which forsterite crystallizes as a primary phase, except those in the area Fo–B–C in figure 8, change their compositions toward silica-saturated compositions across the Di–En join by fractional crystallization at 1 atm. On the other hand, at 20 kb all the liquids in the forsterite field never cross the Di–En join, and they change probably toward critically silica-undersaturated compositions across the Fo–Di join by fractional crystallization. Of course, if there is a maximum on the Fo–Di_{ss} liquidus boundary, only liquids close to the Fo–Di join in the forsterite field can change their compositions across the Fo–Di join.

It should be noted that the primary phase field of forsterite is reduced continuously with increase of pressure under anhydrous conditions. In the Fo–NaAlSiO₄–Q, Fo–CaAl₂SiO₆–Q, and Fo–MgAl₂O₄–Q systems, the primary phase field of forsterite is also reduced with increase of pressure (Kushiro, 1968). Therefore, if a magma is formed by the partial melting of olivine-rich lherzolite, which is probably an upper mantle material, at high pressures under anhydrous conditions, and crystallization of the magma takes place at low pressures, the first phase to crystallize from the magma is forsteritic olivine. The primary phase field of forsterite expands, and the composition of the magma enters into the forsterite field with decreasing pressure. In other words, crystallization of forsteritic olivine from a basaltic magma as a primary phase indicates that the magma has been formed at higher pressures than the pressure where crystallization takes place. This argument is based on the assumption that the partial melting of peridotite takes place at the invariant point where forsteritic olivine and orthopyroxene (or Ca-poor clinopyroxene) are involved or along the univariant or divariant surface, et cetera where forsteritic olivine and orthopyroxene (or pigeonite) are involved.⁴ In some basalts, however, orthopyroxene is the primary phase to have crystallized. One example is a bronzite-bearing alkali basalt in Taka-sima (Kuno, 1964), although the bronzite is aluminous.

⁴ This assumption is justified by the recent experiments on the melting of a natural lherzolite (Ito and Kennedy, 1967) and the “pyrolite” composition (Green and Ringwood, 1967b), in which forsteritic olivine and orthopyroxene persist through a large range of partial melting.

In experiments on some natural basalts, aluminous orthopyroxene also begins to crystallize as a primary phase (Green and Ringwood, 1967a). These results may be explained by the presence of water when the magma is formed, as discussed later.

EFFECT OF WATER PRESSURE ON THE LIQUIDUS RELATIONS IN
THE SYSTEM FORSTERITE-DIOPSIDE-SILICA

As shown in the experimental results at 20 kb under anhydrous and hydrous conditions, the presence of water significantly changes the equilibrium relations. Under anhydrous conditions, the primary phase field of forsterite becomes smaller with increase of pressure, and at 20 kb the Fo-En_{ss} liquidus boundary is on the forsterite side of the Di-En join. Under hydrous conditions, however, the Fo-En_{ss} liquidus boundary (and a part of the Fo-Di_{ss} liquidus boundary) shifts toward silica with increase of water pressure, although the shift from that at 1 atm is not large. It is significant that the primary phase field of forsterite covers the Di-En join at high water pressures. This would suggest that the silica-saturated liquids can be formed from silica-undersaturated liquids (for example, olivine tholeiite magma) by fractional crystallization or from peridotites by partial melting at pressures at least up to 20 kb P_{H_2O} . Above 20 kb P_{H_2O} and up to at least 30 kb P_{H_2O} enstatite still melts incongruently to forsterite and liquid (Kushiro, Yoder, and Nishikawa, 1968), indicating that there is still a possibility of producing silica-saturated liquids from silica-undersaturated liquids or peridotites at 30 kb P_{H_2O} . This conclusion is important for the origin of silica-saturated magmas, such as quartz tholeiite magma, in the upper mantle. That is, if free water exists in some parts of the upper mantle (depths to at least 100 km) and if partial melting takes place in those parts, silica-saturated magmas can be generated. If the fractional crystallization of olivine tholeiitic magma containing water takes place in the upper mantle, silica-saturated magmas can also be formed. By further fractional crystallization, silica-rich magmas such as andesitic and dacitic magmas may be produced, as predicated from figure 7. It is noted that a considerable amount of water (more than 10 wt percent) would be necessary for the water pressure in the magma to become equal to total pressure at pressures higher than 20 kb because of the large solubility of water in the silicate melt at such high pressures. Even if water pressure is considerably less than the total pressure, however, the effect of the water pressure cannot be disregarded. That is, silica-saturated magmas can be formed at higher water pressures than under anhydrous conditions either by the fractional crystallization of olivine tholeiitic magma or by the partial melting of the upper mantle peridotite.

As has been discussed previously, under anhydrous conditions forsteritic olivine crystallizes as the earliest phase at lower pressures from the magmas formed by the partial melting of peridotite at higher pressures. If, however, a magma is formed in the upper mantle in the pres-

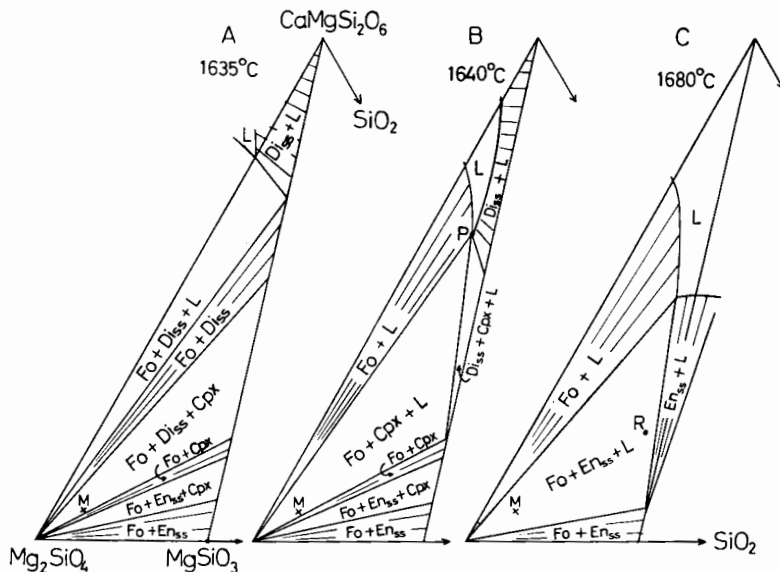


Fig. 9. Isobaric and isothermal sections in the system forsterite–diopside–enstatite at 1635°C (A), 1640°C (B), and 1680°C (C) at 20 kb under anhydrous conditions. Abbreviations as in tables 1 and 2. Ca in forsterite is not shown.

ence of water, and if water in the magma escapes during the ascent of the magma, it is possible that orthopyroxene will crystallize as a primary phase instead of forsteritic olivine. The primary phase field of forsterite relative to that of orthopyroxene is reduced with decrease of water content in the melt, and if the effect of escaping water is larger than the effect of lowering load pressure which expands the forsterite field, it is possible that the primary phase field of orthopyroxene relative to that of olivine field expands with ascending magma and orthopyroxene crystallizes as the earliest phase.

PARTIAL MELTING PROCESS IN THE SIMPLE PERIDOTITE AND PYROXENITE SYSTEM AT 20 Kb

The process of partial melting in the simple peridotite and pyroxenite system at 20 kb may contribute to an understanding of the process of partial melting of a peridotite upper mantle and also the process of generating magmas in the upper mantle. The mantle peridotite is considered to be a lherzolite which is rich in forsteritic olivine relative to enstatitic and diopsidic pyroxenes and has some normative plagioclase. Its composition (for example, average of four peridotite inclusions in basaltic rocks by Kushiro and Kuno, 1963; average lherzolite nodule in kimberlite by Ito and Kennedy, 1967) plots close to Fo in the Fo–Di–En system (M in fig. 9) after subtracting fayalite, ferrosilite, and feldspar normative components. The process of partial melting of this peridotite is considered in the isothermal sections at 20 kb (fig. 9). Fig. 9A shows the

isothermal section at about 1635°C, in which 'mantle peridotite' is not included in the liquid-present region and, therefore, "mantle peridotite" is not melted at this temperature. Some of the simple wehrlites and pyroxenites are included in the three-phase region $Fo + Di_{ss} + L$ and two-phase region $Di_{ss} + L$, and they are partially melted. At 1640°C, the reaction $Fo + Di_{ss} \rightleftharpoons Cpx$ (pigeonitic clinopyroxene) + L takes place and a new three-phase region $Fo + Cpx + L$ is formed (fig. 9B). The "mantle peridotite" is included in this new three-phase region and begins to be melted. The temperature is constant until diopside solid solution in the "mantle peridotite" disappears. At this temperature, wehrlite is included in $Fo + L$, $Di_{ss} + L$, or L region and partially or completely melted depending upon the composition. On the other hand, simple saxonite (or harzburgite) is still not melted. When diopside solid solution disappears, the temperature begins to increase, and the composition of liquid begins to move toward the Fo - En join along the Fo - Cpx liquidus boundary, and the three-phase triangle also begins to move toward the Fo - En join. At about 1650°C, when the temperature of another invariant point (P' in fig. 6) is attained, the reaction $Fo + Cpx \rightleftharpoons En_{ss} + L$ takes place, and new three-phase triangle $Fo + En_{ss} + L$ is formed. When pigeonitic clinopyroxene disappears, the temperature begins to increase, and the liquid changes its composition toward the Fo - En join along the Fo - En_{ss} liquidus boundary. Part of the saxonite is now included in the three-phase region $Fo + En_{ss} + L$ (fig. 9C). With further increase of temperature, the amount of liquid in the "mantle peridotite" increases, and composition of the enstatite solid solution coexisting with liquid becomes Ca-poor. When the liquid reaches the composition of the intersection of the Fo - En_{ss} liquidus boundary and the extension of the Fo - M join (R in fig. 9C), enstatite solid solution disappears, and with further increase of temperature the liquid moves toward M .

As shown above, the first liquid formed by the melting of the "mantle peridotite" at 20 kb has the composition P . If the liquid is removed from the system by a process such as filter pressing at the temperature of P , the material left consists of Fo , Cpx , and Di_{ss} , which may change to lherzolite by the inversion of Cpx to En_{ss} (having an exsolved Di_{ss}) with decreasing temperature. If the liquid is removed from the system at temperatures higher than that of the invariant point P but below that of P' , the material left consists of Fo and Cpx , which may change to saxonite with decreasing temperature. At temperatures higher than P' but below R , the material left is saxonite, and at temperatures higher than that of R , the material left is dunite. However, wehrlite, clinopyroxenite, websterite, and orthopyroxenite cannot be residual materials left after the partial melting of the "mantle peridotite". These conclusions would still be valid even if small amounts of iron and alumina are added to this ternary system. If iron is added, for example, the invariant points P and P' are replaced by univariant lines, and the univariant lines are replaced by divariant surfaces. In this case, the

residual materials after the partial melting would become more magnesian. Lherzolite, saxonite (or harzburgite), and dunite can both be the residual materials after partial melting or crystal accumulates from basic magmas. These conclusions would also be applicable to the partial melting of the “mantle peridotite” which takes place in a wide pressure range from 1 atm to at least up to 30 kb under anhydrous conditions and also in a wide range of water pressure, although the compositions of liquids formed by the partial melting are different from those at 20 kb.

SUMMARY

1. The Fo–Di join is not binary and is not a thermal barrier at 20 kb under anhydrous conditions, diopside and forsterite crystallized from this join being solid solutions containing small amounts of the components CaMgSiO_4 and MgSiO_3 , respectively. The maximum temperature of coprecipitation of forsterite and diopside solid solutions, which is a piercing point, is $1635 \pm 10^\circ\text{C}$ at 20 kb.

2. The Di–En join is most likely binary and is a thermal barrier at 20 kb under anhydrous conditions. On this join there exist two peritectic points at temperatures near 1650°C . At one peritectic point enstatite solid solution reacts with liquid to form pigeonitic clinopyroxene, and at another peritectic point pigeonitic clinopyroxene reacts with liquid to form diopside solid solution of composition about $\text{Di}_{50}\text{En}_{50}$.

3. In the subsolidus region of the Di–En join there is a narrow field of pigeonitic clinopyroxene near the composition $\text{Di}_{20}\text{En}_{80}$. The Ca/(Ca+Mg) ratio of this composition is very close to the Ca/(Ca+Mg+Fe²⁺) ratio of natural pigeonites. In this and adjoining fields, iron-free pigeonite has been synthesized.

4. In the Fo–Di–En system, there exist two isobaric invariant points on the Fo–pyroxene liquidus boundary. One is a reaction point where enstatite solid solution reacts with liquid to form pigeonitic clinopyroxene and forsterite, and the other may be a ternary eutectic point or a reaction point where pigeonitic clinopyroxene reacts with liquid to form diopside solid solution and forsterite. It is also not certain whether or not a temperature maximum exists on the Fo–Di_{ss} liquidus boundary.

5. The Fo–pyroxene liquidus boundary shifts toward forsterite, and consequently, the primary phase field of forsterite is reduced with an increase of pressure under anhydrous conditions. The reaction $\text{Fo} + \text{L} = \text{Di}_{ss} + \text{Pr}_{ss}$ or $\text{Fo} + \text{L} = \text{Di}_{ss} + \text{En}_{ss}$ takes place, or the reaction relation between forsterite and pyroxene holds, at pressures less than 6 or 7 kb under anhydrous conditions.

6. The Fo–pyroxene liquidus boundary shifts toward silica with an increase of pressure under hydrous conditions ($P_{\text{H}_2\text{O}} \cong P_{\text{load}}$), and at 20 kb $P_{\text{H}_2\text{O}}$ forsterite is on the liquidus over a wide compositional range in the Di–En join, and the join is not a thermal barrier.

7. The primary phase fields of diopside and enstatite solid solutions are greatly expanded toward silica at 20 kb $P_{\text{H}_2\text{O}}$ as compared with those at 1 atm.

8. If partial melting of olivine-rich lherzolite, believed to be an upper mantle material, takes place under anhydrous conditions, silica-undersaturated liquids will be produced at pressures higher than 6 or 7 kb, whereas if partial melting takes place under hydrous conditions ($P_{H_2O} \cong P_{load}$), silica-saturated liquids will be produced at pressures from near 1 atm to at least 30 kb P_{H_2O} .

9. Silica-rich magmas, such as andesite and dacite magmas, may be produced from olivine tholeiitic magmas by fractional crystallization at high pressures under hydrous conditions.

10. The residual material after partial melting of the olivine-rich lherzolite are more magnesian lherzolite, saxonite, and dunite in a wide pressure range under both anhydrous and hydrous conditions. Wehrlite and pyroxenites cannot be residual materials of the olivine-rich lherzolite. They may be products of crystal accumulation from basaltic magmas.

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