MELTING AND PHASE RELATIONS IN A NATURAL PERIDOTITE TO 40 KILOBARS*

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ABSTRACT. The melting interval and phase equilibria of a garnet peridotite nodule from a kimberlite pipe were investigated at pressures up to 40 kilobars. The runs were made both in graphite and iron capsules. All iron was retained as FeO throughout the history of the run. The low pressure-high temperature stable assemblage is olivine + orthopyroxene + clinopyroxene + chrome-spinel. The high pressure-low temperature stable assemblage is olivine + orthopyroxene + clino-pyroxene + garnet. A transition zone where spinel coexists with garnet appears between the two assemblages. Garnet appears at 23 kilobars on the solidus. This pressure agrees with that determined by MacGregor for the reaction forsterite + aluminous enstatite + aluminous diopside + spinel equals forsterite + aluminous diopside + garnet + spinel. Thus a transition from spinel peridotite to garnet peridotite may occur at a shallow depth in the mantle under the ocean, but spinel peridotite probably is unstable under the continental shield.

Our peridotite begins to melt at 1100°C at 1 atm. At 20 kilobars the first detectable liquid forms at 1320°, and at 40 kilobars the first detectable liquid is at 1570°C. Thus in spite of the vast compositional difference, the solidus of our perido-tite is almost identical with recent determinations of the solidus of basalt and eclogite. Olivine is the first phase to crystallize from a peridotite liquid. It is joined by ortho-pyroxene which appears at 1375°C at 1 atm and at 1750°C at 20 kilobars. At all pres-sures the garnet and clinopyroxene in this peridotite melt within a temperature in-terval of approximately 50°. The partial melt at 20 and 40 kilobars when clinopyroxene and garnet have melted is estimated to be close to picrite in composition.

INTRODUCTION

The chemical composition of the upper mantle of the Earth and the origin of basalt magma as well have been the subject of much controversy. One common view is that the upper mantle is peridotite and that basalt magma is produced by partial melting of peridotite. An opposing view is that the upper mantle is eclogite and basalt magma is produced by either partial or complete melting of eclogite. To test these hypotheses, it is of primary importance to know the mineral equilibria and melting relations in peridotite as well as basalt and eclogite as functions of pressure and temperature. These melting rela-tions also give an upper limit to the temperature in the mantle.

The melting and phase relations of natural basalt and eclogite have been reported by several authors (Yoder and Tilley, 1962; Green and Ringwood, 1964; Tilley and Yoder, 1964; Cohen, Ito, and Kennedy, 1967). Within the last few years high-pressure work on melting and phase relations among such minerals as forsterite, enstatite, diopside, pyrope, and spinel, which compose peridotite, have been reported from the Geophysical Laboratory of Carnegie Institution. However, no experi-mental study has been made at high pressure on a system with the com-position of natural peridotite, except for a study by O'Hara (1963) and unpublished work by Green and Ringwood. The present paper is

the result of high-pressure experiments on a natural garnet peridotite and is one of a series of studies on the melting and phase relations in anhydrous basalt-peridotite systems using natural rocks as starting materials and controlling the oxidation state of iron.

STARTING MATERIAL

Peridotite used in the present work is a garnet peridotite nodule in kimberlite from Dutoitspan mine, South Africa, our specimen KA64-16. The rock is granular and is composed dominantly of dark gray altered olivine and pale yellow-green orthopyroxene, with small amounts of bright green chrome-diopside and wine-red garnet, and occasional flecks of brown phlogopite. The olivine is veined with serpentine and has small amounts of an opaque mineral. The orthopyroxene is little altered with some exsolution lamellae of clinopyroxene. The chrome-diopside is unaltered. The garnet is rimmed with dark alteration borders. The plogopite is everywhere accompanied by serpentime veinlets.

The analysis of the rock and the CIPW norm are given in table 1. For comparison, average compositions and norms of four lherzolite nodules in kimberlites (Holmes, 1936; Nixon, von Knorring, and Rooke, 1963; and the present paper) and eight peridotite nodules in basalts (Gagel, 1912; Hess, 1960; Wilshire and Binns, 1961; Hamad, 1963; and Kushiro and Kuno, 1963) are given in the same table. All of these are thought to be derived from the upper mantle. The composition of a hypothetical mantle rock, pyrolite, proposed by Green and Ringwood (1963) is also given in table 1 for comparison. The rock KA64-16 has almost exactly the same chemical composition as the average lherzolite nodule in kimberlite. It contains slightly less total iron than the average peridotite nodule in basalt.

O'Hara and Mercy (1963) concluded, in a study of garnet peridotite, that periodotite nodules from kimberlite pipes may be the samples of the upper mantle. They rejected garnet peridotites such as found in Norway and Switzerland, the olivine nudules that occur in alkali basalts, and some other types of peridotite, for example, alpine-type peridotite, as samples of undifferentiated upper mantle. Therefore, the rock chosen for the present work is a most probable representative of rock constituting the upper mantle.

The material used as the starting material for present investigation was dehydrated at 1000°C for 5 hours in an iron screw-top capsule in a reducing atmosphere. After heating, the powder was reground in acetone and was checked by X-ray to assure it to be free from serpentine and phlogopite. A small quantity of garnet remained undecomposed; hence the starting material consists of the mineral assemblage: olivine, orthopyroxene, clinopyroxene, and garnet.

EXPERIMENTAL TECHNIQUE

The apparatus and experimental method used in this investigation were the same as those used for the work on basalt in our laboratory

TABLE 1

Chemical compositions and norms of rocks

	1	2	3	4	5
SiO_2	43.86	45.85	45.62	44.14	43.15
TiO_2	0.39	0.41	0.20	0.15	0.58
Al_2O_3	1.96	2.05	2.55	2.56	4.00
Cr_2O_3	0.46	0.48	0.34	0.32	0.42
Fe_2O_3	0.69	—	1.38	1.93	1.66
FeO	6.21	7.14	5.89	7.16	6.67
MnO	0.14	0.15	0.13	0.13	0.13
NiO	0.25	0.26	0.25	0.26	0.39
MgO	39.82	41.63	41.41	40.71	39.40
CaO	1.68	1.76	1.90	2.24	2.66
Na_2O	0.14	0.15	0.19	0.28	0.61
K_2O	0.08	0.08	0.12	0.07	0.22
P_2O_5	0.03	0.03	0.03	0.03	0.08
H_2O+	4.06	—	—	—	—
H_2O-	0.06	—	—	—	—
Total	99.83	99.99	100.01	99.98	99.99
Total Fe as FeO	—	7.14	7.14	8.90	8.16
Or	0.44	0.45	0.72	0.39	1.28
Ab	1.21	1.26	1.52	2.36	5.15
An	4.48	4.70	5.74	5.53	7.52
Di	2.89	3.02	2.76	4.23	4.01
Hy	25.82	25.87	25.26	17.67	7.35
Ol	58.40	63.14	61.14	66.17	70.31
Il	0.74	0.77	0.38	0.29	1.17
Mt	1.00	—	1.99	2.81	2.41
Cm	0.67	0.71	0.49	0.47	0.62
Ap	0.07	0.07	0.07	0.07	0.20
Rem	4.12	—	—	—	—
Total	99.87	99.99	100.07	99.99	100.02
$\dfrac{Mg}{Mg + Fe + Ni + Mn}$	92.5	91.5	93.3	91.4	92.5

1. Garnet lherzolite nodule in kimberlite, KA 64-16, Dutoitspan mine, South Africa (analyst, H. Onuki).
2. The same rock, recalculated from (1) with total Fe as FeO and water free.
3. Average lherzolite nodule in kimberlite.*
4. Average peridotite nodule in basalt.*
5. Pyrolite (Green and Ringwood, 1963).*
* Recalculated water free.

(Cohen, Ito, Kennedy, 1967). Solid-media high-pressure apparatus of the piston-cylinder type was used for all runs. A sleeve of 1 millimeter wall pyrex glass tubing was placed between the carbon tube and the talc in most runs to prevent the talc from dehydrating and yielding a hydrous atmosphere. Carbon capsules, machined from graphite of spectrographic quality, or iron capsules, from Armco magnetic ingot iron, were used. Temperatures were measured with Pt/Pt-10 Rh thermo-

couples, which were separated from the capsules by an alumina disk 0.4 millimeter thick. A 0.025 millimeter disk of platinum was placed between the capsule and the alumina disk when an iron capsule was used. Linear extrapolation of the emf-temperature curve for Pt/Pt-10 Rh thermocouples was made to determine temperature in the range 1760° to 1850°C.

Boyd, England, and Davis (1964) found, in determining the melting curve of enstatite, that the emf of Pt/Pt-10 Rh thermocouple decreased with time at temperatures above 1500°C, probably due to the contamination of the thermocouple. Boyd and England (1963a) also found, in determining the melting curve of diopside, that there is no significant error in determining the melting curve if the run time is held to 5 to 10 minutes. No attempt was made to check the effect of length of run in the present study. The runs in the temperature range 1550° to 1700°C were held for 10 minutes, and runs in the range 1700° to 1800°C were held for 3 or 5 minutes. At temperatures above 1820°C significant drop of thermocouple emf was observed over short time intervals while the furnace input power was kept constant, therefore runs above 1820°C lasted less than one minute.

Cohen, Ito, and Kennedy (1967) found in the work on melting of basalt, with the same apparatus and a similar furnace assembly, that the probable friction correction for runs in the temperature range 1200° to 1650° is half a kilobar with a sign of the correction depending on the direction of piston motion. No friction correction was made on the reported pressure in the present paper, but the sign of friction correction is reported in the table of runs.

Cohen, Ito, and Kennedy used iron capsules in the work on basalt to control the oxidation state of the iron. They cited evidences that the Fe_2O_3/FeO ratio in basaltic silicate melt in equilibrium with metallic iron is very low. Further, they found the enrichment of iron in basalt melt from the iron capsule was limited to the very edge of the sample during runs in similar pressure-temperature-time conditions as the present experiments. In the present experiments runs in graphite capsules and runs in iron capsules are consistent with each other, and no significant differences in Fe_2SiO_4 content in olivine was found between runs in graphite and in iron.

All runs at temperatures above the melting point of iron were made in graphite capsules. All the present runs were checked with a strong magnet to see if metallic iron was precipitated as a result of reduction of ferrous iron, but none of them were found to be magnetic. In the present experiments the reduction of ferrous iron was either prevented or minimized because of low total iron and the low FeO/MgO ratio in olivine in our peridotite. Thus, all iron was presumed to be retained as FeO throughout the history of the runs, both in iron and graphite capsules.

IDENTIFICATION OF PHASES

All the runs were examined both under the microscope and by X-ray diffraction. Thin sections were made of some runs. Crystal settling was pronounced in many instances. Melting was detected by observation of glass under the microscope. Quench pyroxene, with feather shape, predominates in the glass when the glass exceeds 10 percent of the sample. Quench olivine with lamella shape appears in runs quenched from the very highest temperatures.

Complete melting was not observed in the temperature range of the present study. Limits of the fields of orthopyroxene stability were determined by examination of the quenched runs under both X-ray and microscope. Clinopyroxene was detected by the presence of its (220) peak on the X-ray chart. Spinel, when present, is in such small quantity that it can only be detected under the microscope. Garnet was identified both under the microscope and by X-ray. Relative proportions of crystalline phases were roughly estimated from X-ray peak intensities, and the percentage of glass was estimated from examination of powder under the microscope.

The composition of the olivine was estimated using Yoder and Sahama's (1957) correlation data for the (130) spacing as a function of composition of natural olivine. Unit cell dimension of garnet was measured from the d-spacings of the (420) reflection. All measurements were made on Norelco unit using CuKα radiation with goniometer speed half a degree per minute. Quartz was used as an internal standard with 2θ of (101) reflection of quartz taken at 26.663°. Six or eight oscillation scans were made on individual samples.

RESULTS OF EXPERIMENTS

The results of quenching runs along the melting interval of the peridotite are given in table 2 and plotted in figure 1. Compositions of olivine are shown as a function of temperature and pressure in figure 2.

At low pressures, the stable mineral assemblage is olivine + orthopyroxene + clinopyroxene + chrome spinel. At high pressures, the stable assemblage is olivine + orthopyroxene + garnet + clinopyroxene. Garnet appears at 23 kilobars on the solidus. A transition zone where both garnet and spinel coexist with other phases is present between the two assemblages. The liquidus was not determined but is higher in temperature than the melting curve of platinum. Olivine is stable throughout the temperature and pressure range of the present investigation, and it is the first phase to crystallize from the liquid. Olivine is joined by orthopyroxene at 1375°C at 1 atm and at 1750°C at 20 kilobars. At high pressures all the garnet and clinopyroxene melt within a temperature interval of approximately 50° above the solidus.

The compositional data of olivine in the sub-solidus runs indicate that there was no significant iron contamination from the capsule when

TABLE 2

Results of quenching runs on a natural garnet peridotite (KA 64-16)

No.	P* (Kb)	Temp (°C)	Time (min)	Liquid	Crystal proportion					Composition		Remarks**
					Ol	Opx	Cpx	ChSp	Ga	Ol (Fo%)	Ga (a)	
1	0	1150	90	tr	1	m	—	tr	—	89	—	Fe, P
2	"	1200	45	tr	1	m	—	tr	—	89	—	Fe
3	"	1300	21	10	1	m	—	tr	—	90	—	Fe
4	"	1350	20	10	1	s	—	tr	—	nd	—	Fe
5	"	1400	20	10	1	—	—	tr	—	89	—	Fe
6	"	1774†	1	50	1	—	—	—	—	95	—	C, P, Q
7	16.3+	1680	10	50	1	—	—	—	—	90	—	C, P, Q
8	20.4−	1300	42	0	1	m	tr	tr	—	89	—	C, P
9	"	1350	10	tr	1	m	—	tr	—	nd	—	Fe
10	"	1480	20	10	1	m	—	tr	—	88	—	C, P, Q
11	20.4+	1560	10	10	1	m	—	—	—	90	—	Fe, Q
12	"	1720	5	40	1	s	—	—	—	93	—	C, P, Q
13	"	1750	5	40	1	tr	—	—	—	nd	—	C, P, Q
14	"	1800	3	40	1	—	—	—	—	92	—	C, P, Q
15	"	1820	1	50	1	—	—	—	—	nd	—	C, P, Q
		1830	1									
16	"	1850	1	80	1	—	—	—	—	nd	—	C, P, Q
17	21.8−	1200	120	0	1	m	—	tr	tr	90	nd	C, P, rem-Ga

TABLE 2 (Continued)

No.	P* (Kb)	Temp (°C)	Time (min)	Liquid	Crystal proportion					Composition		Remarks**
					Ol	Opx	Cpx	ChSp	Ga	Ol (Fo%)	Ga (a)	
18	23.1—	1320	60	0	1	m	tr	tr	tr	88	nd	C, P, rem-Ga, rex'l Ga
19	25.8—	1350	40	0	1	m	—	tr	tr	91	nd	C, P, rem-rex'l Ga
20††	25.8—	1350	90	0	1	m	tr	—	tr	89	nd	Fe, P
21	29.9—	1400	30	0	1	m	tr	—	s	89	11.54	C, P
22	29.9	1500	20	5	1	m	—	—	—	89	—	C, P
23	29.9+	1850	1	50	1	s	—	—	—	93	—	C, P, Q
24	40.8—	1500	21	0	1	m	tr	—	s	88	11.54	C, P
25	"	1550	10	0	1	m	tr	—	s	91	11.54	C, P
26	"	1600	10	tr	1	m	—	—	s	89	nd	C, P
27	"	1660	10	20	1	m	—	—	—	90	—	C, P, Q

* + friction correction positive.
— friction correction negative.

** C, graphite capsule used; Fe, iron capsule used; P, pyrex glass tubing used; Q, quench crystal present.

† Platinum thermocouple melted.

†† The result of #13 (Ol + Opx + quench Px + Gl) added with 10 percent dehydrated garnet peridotite powder was used as the starting material.

Abbreviations: Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; ChSp, chrome spinel; Ga, garnet; Fo, forsterite; l, large; m, medium; s, small; tr, trace; rem, remnant; rex-l, recrystallized.
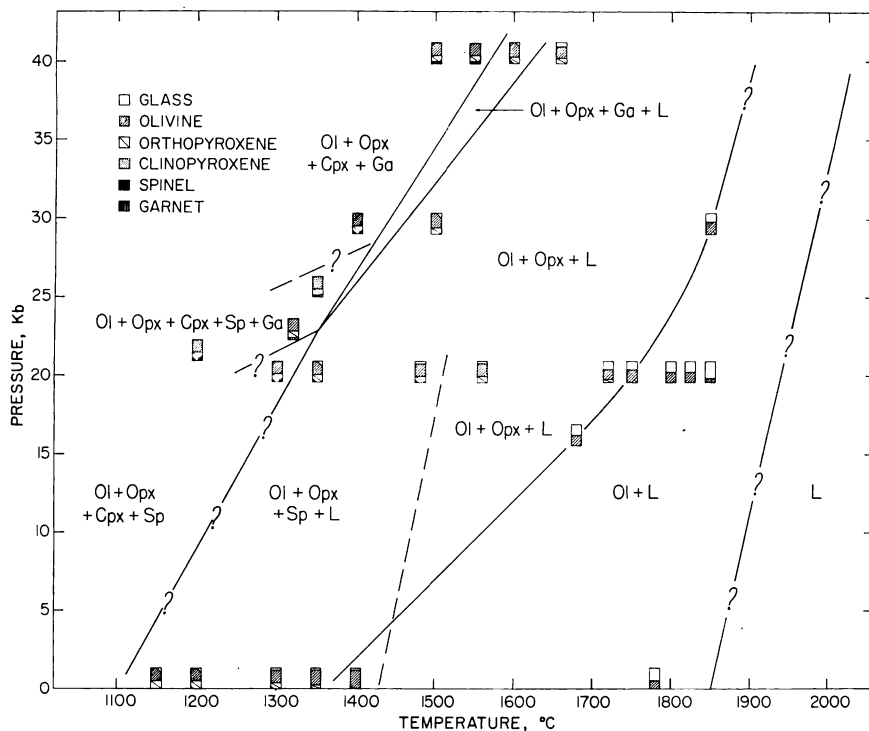
Fig. 1. P-T diagram for a natural peridotite, KA64-16.

iron capsules were used. Neither was there decomposition of the fayalite component in olivine when graphite capsules were used. Since the composition of olivine in the starting material was Fo_{95} measured by X-ray determination of the (130) spacing, the olivines in the sub-solidus runs, having Fo_{89}, seem to be recrystallized olivines.
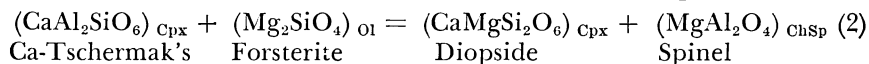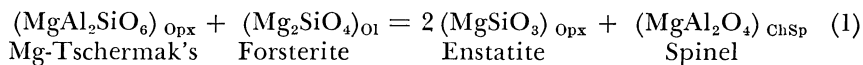
SUB-SOLIDUS PHASE RELATIONS

1. Low-pressure mineral assemblage.—The assemblage olivine + orthopyroxene + clinopyroxene + chrome-spinel is stable up to 23 kilobars on the solidus. No plagioclase was found.

The same mineral assemblage is widely found in peridotites, such as the stratiform type peridotite, the alpine-type peridotites, and the peridotite nodules in alkali basalts. The present investigation may give the maximum limit of the depth at which those spinel-bearing peridotites might have been crystallized.

The spinel crystallized at 1 atm is deep reddish brown in color. The chemical composition of chrome spinel is roughly indicated by the color in thin section: the redness of spinels increases with chromium content (Fisher, 1929). Therefore, the spinel at 1 atm is probably rich in the chromite component. The color of spinels crystallized at 20 kilobars changes to yellowish brown, indicating less chromium content.

The color change of the spinel with pressure suggests either that more chromium goes into clinopyroxene, making chromium diopside with increasing pressure, or that the following reactions

$(MgAl_2SiO_6)_{Opx}$ + $(Mg_2SiO_4)_{Ol}$ = 2 $(MgSiO_3)_{Opx}$ + $(MgAl_2O_4)_{ChSp}$ (1)
Mg-Tschermak's   Forsterite   Enstatite   Spinel

$(CaAl_2SiO_6)_{Cpx}$ + $(Mg_2SiO_4)_{Ol}$ = $(CaMgSi_2O_6)_{Cpx}$ + $(MgAl_2O_4)_{ChSp}$ (2)
Ca-Tschermak's   Forsterite   Diopside   Spinel

advance toward the right, and consequently the Al_2O_3 of both pyroxenes decrease when pressure increases and amount of spinel increases. This suggestion is supported by MacGregor's work indicating that the Al_2O_3 content of diopside coexisting with forsterite and spinel in the CaO–MgO–Al_2O_3–SiO_2 system decreases with increasing pressure at constant temperature (MacGregor, 1965b). Unfortunately there is no published data on the solubility of Al_2O_3 in enstatite coexisting with forsterite and spinel.

The volume calculations of equation (1), within the uncertainty of the calculations, give no guidance as to the effect of pressure on the stability relation of the minerals of equation (1).

The suggestion that Al_2O_3 content of pyroxenes decreases with increasing pressure is contrary to Hess' suggestion that pressure may
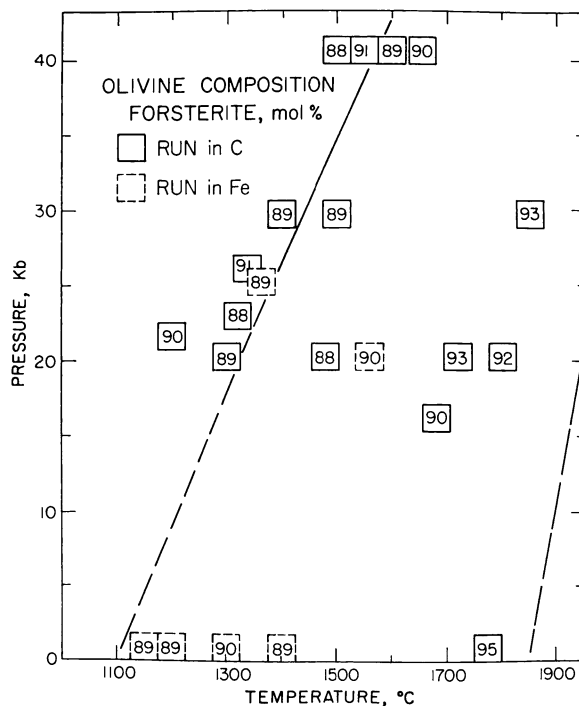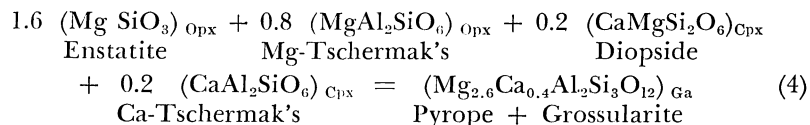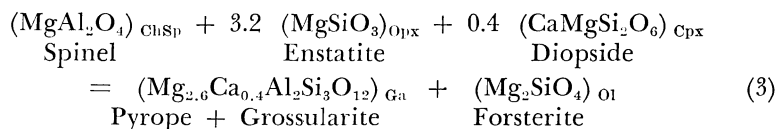

Fig. 2. Composition of olivine, estimated by X-ray method.

favor entry to Al into ortho- and clinopyroxene structure (Hess, 1952, 1960). Hess (1952) drew attention to the higher Al_2O_3 content of enstatites in nodules in alkali basalts than in intrusive peridotites. Boyd and England (1960) experimentally investigated the solubility limit of Al_2O_3 in $MgSiO_3$ in the system $MgSiO_3$–Al_2O_3 and found that the limit is small at 1 atm, increasing up to at least 14 weight percent at 18.2 kilobars at 1400°. They considered that their results supported Hess' suggestion. The distribution of Al_2O_3 in pyroxenes and other minerals depends on the solid phases present. In the assemblage enstatite + sapphirine + sillimanite studied by Boyd and England (1963b) and in the assemblage enstatite + anorthite studied by Kushiro and Yoder (1964) pressure strongly favors the formation of aluminous enstatite. However, in spinel-peridotite, pressure seems to favor the formation of spinel from aluminous pyroxenes.

  2. Transition from spinel peridotite to garnet peridotite.—The assemblage olivine + orthopyroxene + clinopyroxene + garnet is stable at high pressures. Garnet appears at approximately 23 kilobars on the solidus. Between 23 kilobars and about 27 kilobars chrome spinel coexists with garnet. The transition reaction was reversed. In runs (8 and 9) at 20.4 kilobars garnets in the starting material were completely decomposed. In a run (20) at 25.8 kilobars the material of run 13, olivine + orthopyroxene + glass (with quench crystals), was used as the starting material to which was added about 10 percent by volume of the garnet periodotite powder. No garnet peak was detectable in the X-ray diffraction of the starting material, but the (420) reflection of garnet appeared in the product. In a run (18) at 23.1 kilobars both globular recrystallized garnets and angular remnant garnets were observed under the microscope. At a temperature 140° below the solidus, no recrystallized garnet was found under the microscope, but the angular garnet in the starting material remained unreacted; no further attempt was made to extend the transition curve to lower temperature. We can write the following reactions to explain the appearance of garnet in a peridotite:

$$(MgAl_2O_4)_{ChSp} + 3.2\ (MgSiO_3)_{Opx} + 0.4\ (CaMgSi_2O_6)_{Cpx}$$
$$\text{Spinel} \qquad\qquad \text{Enstatite} \qquad\qquad \text{Diopside}$$
$$= (Mg_{2.6}Ca_{0.4}Al_2Si_3O_{12})_{Ga} + (Mg_2SiO_4)_{Ol} \qquad\qquad (3)$$
$$\text{Pyrope + Grossularite} \qquad \text{Forsterite}$$

$$1.6\ (Mg\ SiO_3)_{Opx} + 0.8\ (MgAl_2SiO_6)_{Opx} + 0.2\ (CaMgSi_2O_6)_{Cpx}$$
$$\text{Enstatite} \qquad\qquad \text{Mg-Tschermak's} \qquad\qquad \text{Diopside}$$
$$+\ 0.2\ (CaAl_2SiO_6)_{Cpx} = (Mg_{2.6}Ca_{0.4}Al_2Si_3O_{12})_{Ga} \qquad\qquad (4)$$
$$\text{Ca-Tschermak's} \qquad\qquad \text{Pyrope + Grossularite}$$

where the composition of garnet is taken close to the composition of natural garnet in garnet peridotite (O'Hara and Mercy, 1963). The reactions (3) and (4) are coupled with each other because reactions (1) and (2) are simultaneously taking place.

Kushiro and Yoder (1965) demonstrated that the assemblage clino-
pyroxene solid solution + orthopyroxene solid solution + spinel +
forsterite, in the system anorthite 1 + forsterite 2, transformed at high
pressure to the assemblage garnet + forsterite + clinopyroxene solid
solution. The reaction occurred at about 16.5 kilobars at 1200°, at about
21 kilobars at 1400°, and at about 19 kilobars at the solidus tempera-
ture of our peridotite. MacGregor (1965b) also reported that the as-
semblage forsterite + orthopyroxene solid solution + clinopyroxene solid
solution + spinel, in the system $CaO-MgO-Al_2O_3-SiO_2$, transformed at
high pressure to the assemblage forsterite + garnet + clinopyroxene
solid solution + spinel. The reaction took place at about 16 kilobars at
1100° and at about 26 kilobars at 1500°, occurring at 22.5 kilobars at
the solidus temperature of our peridotite.

The pressure of appearance of garnet found in this investigation,
23 kilobars, is about 4 kilobars higher than Kushiro and Yoder's pres-
sure and agrees with MacGregor's within the uncertainty of experiment.
The agreement with MacGregor's pressure may be fortuitous. In the
natural peridotite the olivine contains about 10 mole percent fayalite
component, and the spinel is chrome spinel. The proposed reactions
(3) and (4) indicate that the transition pressure and temperature is
dependent on the Al_2O_3 content of the pyroxenes and consequently on
the composition of the spinel.

To test the effects of added Al_2O_3, FeO, and CaO on the pressure
of transition from spinel peridotite to garnet peridotite, several runs
were made with our peridotite and synthetic spinel, natural fayalite
from Rockport, Massachusetts, and synthetic diopside added. The results
of runs are given in table 3. In run 28, the added 3 weight percent
$MgAl_2O_4$ caused the appearance of garnet at lower pressure, as expected
from the equations (3) and (4). In run 29 10 weight percent fayalite
was added in the peridotite, KA64-16. Since olivine does not dissolve
Al_2O_3 and Cr_2O_3, the addition of fayalite causes an increase in the
amount of olivine and increase in the FeO/MgO ratio in each crystalline
phase. Therefore, run 29 in which added fayalite caused the appear-
ance of garnet at lower pressure, suggests that in a peridotite with

TABLE 3

Results of quenching runs on a peridotite, KA64-16,
with other components added

| No. | P (Kb) | Temp (°C) | Time (min) | \multicolumn{5}{c}{Crystal proportion*} | Remarks |
				Ol	Opx	Cpx	ChSp	Ga	
28	20.4—	1300	40	1	m	tr	tr	s	3% $MgAl_2O_4$ added
29	"	"	"	1	m	tr	—	tr	10% fayalite added
30	"	"	"	1	m	s	—	—	5% diopside added

* l, large; m, medium; s, small; tr, trace.

higher FeO/MgO ratio garnet appears at lower pressure. In run 30 5 weight percent $CaMgSi_2O_6$ added did not cause the formation of garnet at lower pressure.

Ringwood, MacGregor, and Boyd (1964), Boyd and MacGregor (1964), and MacGregor (1964) show extensive data and discuss the transition from spinel peridotite and pyroxene peridotite to garnet peridotite both for natural and synthetic systems. Ringwood, MacGregor, and Boyd (1964) show a hypothetical phase diagram for Ringwood's pyrolite that is not unlike our figure 1 for our natural garnet lherzolite. However their phase diagrams suggest that a pyroxene with a composition of ours, 6.4 weight percent Al_2O_3, undergoes a transition to garnet peridotite at a pressure of approximately 45 kilobars and 1600°C, whereas we find the transition to garnet peridotite appearing on the solidus at approximately 23 kilobars and 1350°C. Ringwood, Mac-Gregor, and Boyd (1964) suggest that the very high pressure transition of aluminous pyroxene to garnet peridotite explains the 14° seismic discontinuity found by some workers in the sub-oceanic mantle. It is clear that our results do not bear out this suggestion of Ringwood and others. In our natural rock, garnet forms at much too low a pressure to account for the break in the travel time curves for P body waves in the vicinity of 14° corresponding to a depth between 150 and 200 kilometers in the Earth. Neither do our results confirm the statement by Ringwood, McGregor, and Boyd (1964) that " for rocks approaching the pyrolite composition it does not appear likely that equilibrium involving garnet will play an important role in the geneses of magmas by direct fractional melting at depths less than 150 kilometers". We find garnets stable at the liquidus at all depths below approximately 75 kilometers. We strongly suspect that garnet is a stable phase in equilibrium with basalt magma at all depths in the Earth where basalt magmas presumably form by fractional melting.

The general petrological model presented by Ringwood, McGregor, and Boyd (1964) contrasts remarkably with the experimental results presented by Boyd and McGregor (1964) who studied the reaction 4 enstatite + spinel = forsterite + pyrope. In this simplified system they find the reaction to pyrope running at approximately 27 kilobars at 1350° which agrees well with our results on the natural system.

The difference between our results and those summarized in Ringwood, MacGregor, and Boyd (1964) may well be because calcium is present in a natural system. MacGregor (1965a) subsequently investigated the effect of CaO on the appearance of garnet and experimentally demonstrated that garnet appears at considerably lower pressure in the reaction forsterite + enstatite solid solution + diopside solid solution + spinel = forsterite + garnet + diopside solid solution than in a reaction 4 enstatite + spinel = forsterite + garnet. Therefore, garnet would appear at relatively lower pressure in a two-pyroxene bearing peridotite than in a peridotite bearing only orthopyroxene.

3. High pressure mineral assemblage.—Spinel in our rock is not stable above 27 kilobars. Chromium is presumed to be present mainly in the garnet phase. Olivine, orthopyroxene, clinopyroxene, and garnet are stable up to the highest pressure investigated. The cell constant of garnet does not change throughout the pressure range of the present investigation. The unit cell, 11.54, is in close agreement with that of 11.53 of natural garnet in garnet peridotite (O'Hara and Mercy, 1963) but is substantially larger than the 11.51 of garnet in the synthetic systems investigated by MacGregor (1965a).

The proportion of garnet in the crystalline phases apparently increases with increasing pressure. The reaction may be expressed by equation (4), and consequently pyroxenes must become poorer in Al_2O_3 at increased pressure. This observation agrees with the experimental investigations on the system enstatite-pyrope by Boyd and England (1964) and by MacGregor and Ringwood (1964). The Al_2O_3 content of enstatite solid solution coexisting with pyrope is reported to decrease remarkably with increasing pressure.

MELTING OF PERIDOTITE

The first liquid in detectable amount, at 1 atm pressure, appears at 1150°C. At this temperature olivine, orthopyroxene, and spinel coexists with liquid. Clinopyroxene was not detected. Orthopyroxene disappears at 1375°C, and olivine + spinel coexist with the liquid. Olivine is the last phase to disappear. The liquidus of this rock lies at temperatures substantially greater than the melting temperature of platinum, 1774°C, and must, of necessity, be lower than the melting temperature of forsterite (1890°C).

Reay and Harris (1964) experimentally investigated the partial fusion of peridotite. However, they used a mixture of oxides, carbonates, and ferrous oxalates to give the composition of Nockold's (1954) average peridotite. They observed approximately 4 percent glass at 1250°C. Thus, their solidus temperature is approximately 100° higher than our solidus. The detection of a solidus point in a natural rock is very difficult as minute amounts of glass in quench products may be readily overlooked. In our rock, the beginning of melting at 1 atm was detected not only by the presence of glass but also by the disappearance of clinopyroxene. It is unlikely that minute amounts of water have seriously lowered our solidus point. Our starting material was dehydrated at 1000°C before the run, and the furnace assemblage in our experimental apparatus was fired before the run to eliminate all traces of water. Nonetheless the uncertainty in determining our solidus may be as much as 50°. We believe we err on the high side and probably did not detect minute amounts of glass appearing at lower temperatures. Reay and Harris found only olivine and magnetite as crystalline phases. These results testify to the highly oxidized state of their starting materials and also suggest that they failed to nucleate enstatite at 1 atm pressure.

Since basalts are widely believed to be produced by partial melting of peridotite in the mantle, it is of primary importance to know the liquid composition of partial melts from peridotite at different pressures. At 1 atm, because enstatite melts incongruently to olivine and liquid, the first liquid from peridotite is expected to be oversaturated with SiO_2. Reay and Harris chemically analyzed the quenched glass produced by varying degrees of partial fusion of their synthetic peridotite. They found that the liquids are oversaturated with silica up to 1310° and 15 percent fusion, correspondingly close to tholeiitic basalts.

It must be abundantly clear that we do not propose these 1 atm melting relations to have any bearing on the origin of andesites in nature. Certainly garnet lherzolite must be at a pressure of at least 30 kilobars in even an area of abnormally steep geothermal gradients before its solidus is reached. At these pressures the melting relations are grossly different.

In our rock the amount of liquid does not seem to increase very much with increasing temperature below 1400°. However, above this temperature the amount of liquid increases rapidly. At 1400° the liquid proportion of our peridotite is estimated to be no more than 10 percent. Wyllie (1960) has suggested a plateau on the liquidus of the basalt-peridotite system on the basis of experimental data in the system CaO–MgO–FeO–SiO_2. He considered that the partial fusion of peridotite would produce only basaltic magma over a wide temperature range and that a high proportion of a picritic magma would crystallize in a small temperature interval with the precipitation of forsterite olivine. Our observations support Wyllie's suggestion. However, there is a large uncertainty in the estimation of amount of liquid owing to the presence of quench crystals.

The melting interval of the peridotite is more than 700° at 1 atm and about 700° at 10 kilobars. The liquidus temperature is above 1800°; thus, it is quite unlikely that anhydrous peridotite magma is present in the crust or in the uppermost part of the mantle.

At 20 kilobars our peridotite begins to melt at approximately 1320°C. Clinopyroxene was not found in a run at 1350°C. Spinel has disappeared by 1500°C and orthopyroxene by 1750°C. Above these temperatures only olivine coexists with the liquid. The melting interval of orthopyroxene is remarkably larger at 20 kilobars than at 1 atm.

At 40 kilobars, the first detectable liquid forms at approximately 1570°C, the clinopyroxene melts immediately above the solidus, and garnet melts within a temperature interval of 50° above the solidus. This points up one of the more important results of these investigations. In spite of the vast compositional difference, the solidus temperature of our peridotite is almost identical with that shown from recent determinations of the solidus of basalt and eclogite (Cohen, Ito, and Kennedy, 1967). Furthermore at 40 kilobars the temperature interval over which clinopyroxene and garnet melt is almost exactly the same as the tem-

perature interval over which a natural basalt freezes to an eclogite made of garnet and clinopyroxene.

In spite of the identity of the freezing interval of a natural tholeiitic basalt at these pressures with the melting interval of clino-pyroxene and garnet in our rock, we cannot assume that the liquid which forms in the 30 to 40 kilobar melting region is tholeiitic in composition. It is certain that this liquid must be saturated with olivine as it is in equilibrium and coexists with olivine, therefore, the liquid is much more likely to be chemically equivalent to a picritic basalt with substantially higher magnesia content than normal tholeiitic basalt. Olivine never crystallizes from rocks of tholeiitic basalt composition at these very high pressures. Yoder and Tilley (1962) investigated the melting of two eclogites at different pressures. One eclogite, 35090, did not crystallize olivine at any pressures. Another eclogite, 35083, crystallized olivine at 1 atm but did not crystallize olivine above 10 kilobars. Green and Ringwood (1964) investigated the melting of an olivine-rich tholeiite and a picrite at between 10 and 25 kilobars. They found that in both rocks olivine is the primary phase crystallizing first from the melts below 15 kilobars, but orthopyroxene is the primary phase at 20 kilobars. Tilley and Yoder (1964) reported experiments on the crystallization of an olivine tholeiite and a picrite at 20 kilobars. The olivine tholeiite did not crystallize olivine, but the picrite crystal-lized olivine on the liquidus at that pressure. Further Cohen, Ito, and Kennedy (1967) investigated the phase relations of an olivine tholeiite along the melting interval to 40 kilobars, and they confirmed that olivine does not crystallize above 10 kilobars in the melting interval of their basalt. All these data indicate that basaltic liquid is under-saturated with olivine at high pressures.

Experiments were made on the olivine-tholeiite, NM5, which was used in the investigation by Cohen, Ito, and Kennedy, to test the degree of undersaturation of olivine in basaltic liquid at high pressure. A melt made from 75 percent basalt and 25 percent of our peridotite crystallized olivine as the primary phase below 20 kilobars; however, olivine never crystallized above 25 kilobars. A melt was made from 50 percent basalt and 50 percent peridotite. Olivine crystallized as the primary phase both at 20 kilobars and at 40 kilobars. Therefore, the composition of liquid which is in equilibrium with an olivine-bearing rock at a depth below 70 kilometers must be more mafic than 75 percent basalt and 25 percent peridotite. The detailed data will be reported in another paper.

These results cast a serious doubt on the widely-believed view that basalt magmas are primary magmas and they are produced by partial melting of peridotite in the mantle. The results favor the alternative view proposed by O'Hara (1965) that basalt magmas are not primary but are the residual liquids of well advanced crystal fractionation process at relatively shallow depth.

These results may be taken by some to indicate that a tholeiitic basalt cannot be generated by partial fusion of a garnet peridotite in the deep mantle. We do not believe this to be true nor do we intend to imply this. At the very high temperatures involved in melting at around 40 kilobars, 1600°C basalt is enormously fluid. The effect of pressure on viscosity is extremely small, and the effect of temperature on the viscosity is very great. Even tholeiitic basalt at 1200°C has relatively low viscosity. In runs of only 5 minutes duration, olivine crystals settled to the bottom of our very small experimental capsules. Picritic liquid formed by partial fusion of a garnet lherzolite will steadily precipitate olivine as it moves toward the surface of the Earth. The magnesium content of the liquid will drop continuously. Picritic basalts can be expected as surface flows only where lava travels from very great depths to the surface at very high speeds. Tholeiitic basalt will result when olivine has had time to precipitate and settle from a more slowly upward moving melt.

The amount of liquid at 20 kilobars does not seem to increase very much when temperature increases from 1320 to 1600°. Our observation indicates that the partial melting of peridotite at 20 kilobars produces only a liquid with a composition close to the first liquid co-existing with olivine, orthopyroxene, clinopyroxene, and spinel over a wide temperature range, as Wyllie (1960) suggested for the melting of peridotite at 1 atm. As the liquid rises toward the surface, maintaining equilibrium with surrounding peridotite, the liquid crystallizes large amounts of olivine because of both temperature and pressure decrease. We thus explain why a majority of basalts are without, or have only small amounts, of olivine while partial melts of peridotite in the mantle are much richer in magnesia than are normal basalts.

PHASE TRANSITIONS OF PERIDOTITE IN THE UPPER MANTLE

The transition pressure from spinel-bearing to garnetiferous peridotite is of both petrological and geophysical importance. The transition pressure and temperature set limits on the conditions under which the various peridotites were formed. The transition results in a change of density of the rock and also in a change in seismic velocity of the rock. Some authors attribute a discontinuity of seismic velocity at 210 kilometers depth in the mantle to this transition (Ringwood, MacGregor, and Boyd, 1964).

The chemical composition of the upper mantle has been the subject of discussion and controversy, and no conclusive evidence has yet been obtained. On the supposition that peridotite constitutes the upper mantle of the Earth, four different types of peridotite have been proposed as the mantle material. One is the typical peridotite nodule of basalt (Kushiro and Kuno, 1963), one is garnet peridotite nodule in kimberlite (O'Hara and Mercy, 1963), one is a hypothetical rock, pyrolite, composed of 1 part basalt and 3 part peridotite (Green and Ringwood, 1963), and the other is the silicate fraction of chondritic meteorite, which is feldspathic peridotite (MacDonald, 1959). Among

TABLE 4

Atomic ratios, when 0 = 6.00, of hypothetical pyroxene phases
in the rocks in table 1*

	2	3	4	5
Si	1.885	1.876	1.859	1.771
Al_z	0.115	0.124	0.141	0.229
Al_y	0.099	0.143	0.184	0.294
Ti	0.027	0.014	0.012	0.049
Fe^{+2}	0.146	0.139	0.159	0.121
Mn	0.003	0.003	0.002	0.002
Ni	0.005	0.005	0.005	0.006
Mg	1.525	1.472	1.317	1.065
Ca	0.163	0.177	0.254	0.303
Na	0.025	0.033	0.058	0.131
K	0.008	0.014	0.009	0.031

* All Fe is assumed to be FeO.

these, chondritic peridotite has a sodic feldspar and is not likely to be a material producing basaltic magma (Boyd, 1964). Therefore, this rock must be discarded as the material of the upper mantle. The compositions of these rocks, except peridotite in chondrite, are shown in table 1.

We found that the pressure at which garnet appears in the rock depends much on the Ca and Al content of the pyroxene phases. If all the Ca, Al, Ti, Na, and K in the rock are assumed to be in the pyroxene phase, the pyroxene phase in our peridotite contains the least Ca and Al of the various postulated peridotite. The atomic ratios of the pyroxene phases are compared in table 4. Therefore, garnet will appear in the other peridotites at lower pressures than in our peridotite. The determined transition pressure in our rock lies approximately upon the equilibrium curve for the reaction forsterite + enstatite solid solution + diopside solid solution + spinel = forsterite + diopside solid solution + garnet, determined by MacGregor (1965a). Essentially the same reaction is assumed for the appearance of garnet in our rock, and the same pressure-temperature slope as that of the above reaction may be assumed for the transition curve in our peridotite. On this assumption a P-T diagram of a peridotite is constructed and is given in figure 3. Possible oceanic and Precambrian shield geotherms are also in figure 3 after Clark and Ringwood (1964).

Although the temperature in the Earth is a subject of great uncertainty and also the extrapolation of the sub-solidus phase boundary to lower temperatures is uncertain, the experimental evidences indicate that in the mantle below the Precambrian shield, garnet peridotite is stable and spinel peridotite is unstable. In the mantle below the oceans and below the orogenic zones, spinel peridotite may be stable at shallow depth, but it is certainly unstable below 70 kilometers
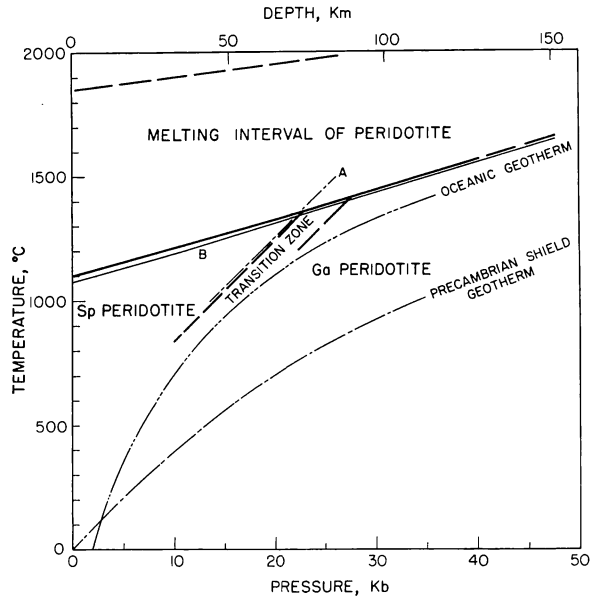
Fig. 3. P-T diagram of a peridotite and its relation to possible oceanic and Precambrian geotherms after Clark and Ringwood (1964). Also included are the curve (A) for the reaction forsterite + enstatite solid solution + diopside solid solution + spinel = forsterite + diopside solid solution + garnet (MacGregor, 1965a) and the curve (B), the solidus of a basalt and eclogite (Cohen, Ito, and Kennedy, 1967).

depth. Below this depth probably no phase transition in the silicate phases occurs until the decomposition of enstatite into olivine and stishovite (Sclar, Carrison, and Schwartz, 1964) which possibly occurs at 300 to 400 kilometers. Thus, if a chemically homogeneous peridotite mantle is presumed, any discontinuity of seismic velocity distribution in the upper mantle cannot be attributed to sub-solidus phase changes in peridotite.

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