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Effect of Pressure on the Melting of Olivine and Spinel Polymorph of Fe_2SiO_4

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The effect of pressure on the melting relations and polymorphism of Fe_2SiO_4 has been studied at pressures up to 76 kb, using the tetrahedral anvil type of high-pressure apparatus. Fayalite, Fe_2SiO_4 olivine, melts congruently to 62 kb, and the data can be fitted by Simon's equation, $P(\text{kb}) = 41\ \{[T(°\text{K})/1478]^{4.8}-1\}$. The initial slope is 7.5°/kb, but it flattens to about 3.5°/kb in the pressure range 50 to 60 kb. A significant inflection was found in the melting curve of Fe_2SiO_4 at 62 kb; above that pressure the melting of Fe_2SiO_4 spinel was observed. The initial slope of the spinel melting curve is determined to be 14°/kb. The melting curve is intersected by the polymorphic olivine-spinel transition. The transition curve cannot be fitted by a simple straight line, the deviation of the curve from the straight line being large with increasing temperatures above 1150°C. The transition curve at temperatures below 1150°C is approximately expressed by a linear relation, $P(\text{kb}) = 19 + 0.033T(°\text{C})$. The triple point, fayalite–Fe_2SiO_4 spinel–liquid, was determined to be at 1520°C and 62 kb. These data suggest that a considerable inflection will be found in the melting curve of the earth's mantle at a depth of 400 to 1000 km.

INTRODUCTION

Quantitative knowledge of the effects of high pressure on the melting relations of silicate minerals provides upper temperature limits for the geothermal gradients, as well as estimates of the temperatures of basaltic magmas in the region of their origin. Seismic, geochemical, and petrological evidence all point to an ultrabasic mantle in which olivines $(Mg,Fe)_2SiO_4$ or high-pressure polymorphs of olivines are important phases. The melting curve of forsterite (Mg_2SiO_4) has already been determined at pressures up to 50 kb [*Davis and England,* 1964], and in this paper we present an analogous study of fayalite (Fe_2SiO_4). *Bowen and Schairer* [1935] have calculated the melting curve of fayalite from thermochemical data and quoted in their paper Goranson's result on the direct measurement of the initial slope without specifying experimental conditions. The data reported in this paper are the first direct determination of the melting curve of fayalite over a wide range of pressure.

It is now accepted with high probability that the solid-solid phase transformation of olivine to a spinel polymorph takes place in the high-gradient zone of seismic wave velocities at a depth of 400 to 1000 km in the earth's mantle. Hence estimates of the fusion curve of the spinel polymorph are essential to our understanding of melting in the lower mantle. Although iron-rich olivines are unlikely to occur in the earth's mantle, data on the melting of both olivine and spinel polymorphs of Fe_2SiO_4 reported in this paper may offer useful information about the melting relations that may occur in magnesium-rich $(Mg,Fe)_2SiO_4$ at pressures beyond the range of currently available experimental techniques.

As for the olivine-spinel transition in Fe_2SiO_4, a preliminary stability relation has been published over the temperature range 700 to 1200°C in the pressure range 40 to 70 kb [*Akimoto et al.,* 1965]. However, some ambiguity still remains in the high-temperature runs above 1000°C on account of the decomposition of a part of the Fe_2SiO_4, which resulted from a sample assembly described in a previous paper. Refinements in technique de-

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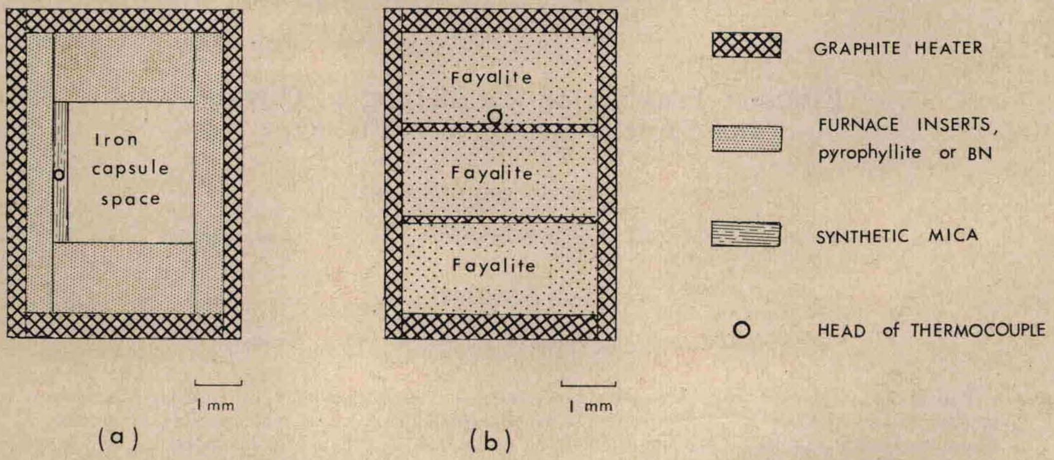

Fig. 1. Furnace assembly for phase equilibrium experiments at high pressures and temperatures. (*a*) Furnace assembly with iron capsule. (*b*) Simple furnace assembly particularly useful for high-temperature runs above 1500°C.

scribed in this paper have permitted the earlier result to be extended and improved.

Experimental Procedure

High-pressure and high-temperature technique. The tetrahedral-anvil high-pressure apparatus used for this study was described in a previous publication [*Akimoto et al.,* 1965]. Two different sizes of anvils made of Mitsubishi GO3-grade tungsten carbide containing about 3% cobalt were used, depending upon maximum pressures desired. An anvil having 25-mm edges was used with a pyrophyllite tetrahedron having 30-mm edges for most experiments in the range 20 to 60 kb. A combination of an anvil and a pyrophyllite tetrahedron having 20- and 25-mm edges was adopted chiefly for runs above 58 kb. The surface of the pyrophyllite tetrahedron was painted with αFe_2O_3 (thick suspension in ethanol). Pressure values in the tetrahedral press were calibrated at room temperature in the usual manner by using resistance transitions in Bi, Tl, and Ba as fixed points. Following the present trend among workers on high pressures, we used the values of 25.4 kb for the bismuth I–II transition, 36.7 kb for the thallium II–III transition, and 59 kb for the barium II–III transition. The pressure of transition was reproducible within an accuracy of ±3%.

The basic design of the furnace assembly used for this study is illustrated in Figure 1*a*. A tubular graphite furnace was placed nearly at the center of the pyrophyllite tetrahedron and used for heating the samples. Fayalite or Fe_2SiO_4 spinel powder samples encased in an iron capsule were set in the center of the graphite furnace. Fired or unfired pyrophyllite and/or boron nitride were used as furnace inserts. Unfired pyrophyllite inserts were used only for the runs of solid-solid transition of Fe_2SiO_4. Pyrophyllite inserts for the use of solid-liquid transition were fired at 1000°C for 6 hours in air.

It has proved impossible to use iron capsules with the cell design shown in Figure 1*a* above about 1500°C for runs of the order of 5 min. When the temperature condition was exceeded, the iron capsule usually began to react with the silicate samples or the furnace inserts. The simple furnace assembly shown in Figure 1*b* was successfully used for high-temperature runs from 1500°C to about 1700°C. In this assembly silicate powder samples, inserted in the graphite furnace without being encased in capsules, were separated into three parts by thin graphite disks. Only the central parts of the samples were used for the phase-equilibrium experiments.

Temperatures were measured with Pt|Pt-13Rh thermocouples. These were placed in contact with the graphite disk when no capsule was used. In runs in which iron capsules were used, the thermocouples were separated from the iron capsules by a thin plate of synthetic mica. Thermocouple leads were brought out to the faces of the pair of anvils not used for the graphite furnace contacts. The run temperatures were corrected for the increase of surface temperature of the tungsten carbide anvils. In each run no correction was made for the effect of pressure on the emf of the thermocouple. No significant change in the emf of the thermocouple with time was detected when the run time was held to 5 min in the runs at a temperature below 1500°C. This may indicate that a fatal contamination of the thermocouple by the various furnace inserts or the capsule material did not occur. However, the rate of thermocouple contamination undoubtedly increases with temperature. For this reason, run time in the range 1500 to 1700°C was reduced to 4 or 3 min.

The temperature gradient within the graphite furnace containing the iron capsule was measured by inserting two sets of thermocouples within the furnace space, one in the place shown in Figure 1*a* and the other in the upper surface of the BN spacers, 0.2 mm thick, which separate the iron capsule from the upper pyrophyllite disk. A precision of temperature measurement of ±20°C was obtained at temperatures as high as 1500°C. The temperature gradients within the furnace assembly such as shown in Figure 1*b* have already been reported [*Akimoto et al.*, 1965]. Satisfactory temperature distribution was obtained by the reduction of the sample space.

A single-stage piston cylinder type of high-pressure apparatus was used for three runs at 17 kb. The furnace and thermocouple assemblies, which are essentially similar to those described by *Boyd and England* [1963], were used for these runs.

Starting materials. Fayalite, used as the starting compound for all the phase-equilibrium experiments reported in this paper, was microcrystalline Fe_2SiO_4 prepared by Katsura and Kitayama from wüstite and silica. Details of the synthesis were given in a previous publication [*Akimoto and Fujisawa*, 1965]. The starting compound was established by means of microscopic observation and X-ray diffraction to be a single-phase material with olivine structure.

Determination of the melting curve and the olivine-spinel transition curve. The quenching method used in determining the melting curve of Fe_2SiO_4 was essentially the same as that used for forsterite [*Davis and England*, 1964]. Fayalite samples were brought to desired temperatures at constant pressure over an interval of 4 to 6 min, held at the desired temperatures for 3 to 5 min, and quenched isobarically. Most of the reaction products were examined under the microscope. The X-ray diffraction method was also used to ensure the absence of contamination.

The olivine-spinel transition curve of Fe_2SiO_4 was determined by the same method as described previously [*Akimoto et al.*, 1965]. Reactions from olivine to spinel and from spinel to olivine were examined.

EXPERIMENTAL RESULTS

Results of quenching runs upon which the melting curve and the olivine-spinel transition curve of Fe_2SiO_4 are based are summarized in Table 1.

Usually liquid of fayalite composition could not be quenched to room temperature, but melting could easily be detected by a difference in texture between runs which had crystallized from liquid during the quench and those which had recrystallized below the melting curve. Fayalite which had recrystallized without melting was granular, whereas that formed from liquid upon quenching had fibrous or lamellar textures, both of which are typical features of quench crystals. In several runs, both quench crystals and recrystallized crystals coexisted in the run products. This may be caused by a combination of thermal gradient along the sample space and temperature fluctuation during the run. Results obtained with various types of cell assembly described earlier have been cross-checked, and no significant difference has been found except for the runs above 1500°C with iron capsule and boron nitride furnace inserts. Glass and coesite crystals produced in two runs entered the liquid region of this furnace assembly. This may suggest that boron nitride inserts reacted with the fayalite sample through the iron capsule at temperatures above 1500°C. It is safely concluded from the data listed in Table 1 that fayalite melts congruently at pressures up to about 62 kb. The melting curve of fayalite shown in Figure 2

TABLE 1. Melting and Olivine-Spinel Transition of Fe_2SiO_4

Starting* Material	Pressure,† kb	Temperature, °C	Time, min	Furnace Assembly‡	Results
A	17.0	1225 ± 5§	5	Fe(I)	Fayalite crystals
A	17.0	1275 ± 5	5	Fe(I)	Fayalite crystals
A	17.0	1315 ± 5	5	Fe(I)	50% fayalite crystals + 50% fayalite quench crystals
A	28.0	1340 ± 5	5	Fe(I)	Fayalite crystals
A	28.0	1400 ± 5	5	Fe(I)	Fayalite quench crystals
A	30.0	1390 ± 5	5	Fe(II)	Fayalite crystals
A	30.0	1415 ± 10	5	Fe(II)	60% fayalite crystals + 40% fayalite quench crystals
A	31.0	1345 ± 10	5	Fe(II)	Fayalite crystals
A	36.5	755 ± 10	120	Fe(III)	Fayalite crystals
A	40.5	755 ± 5	120	Fe(III)	Fayalite crystals
A	42.5	875 ± 5	45	Fe(III)	Fayalite crystals
A	44.0	755 ± 10	120	Fe(III)	Fayalite crystals + spinel crystals (small amount)
A	45.0	1415 ± 5	5	Fe(II)	Fayalite crystals
A	45.0	1455 ± 5	5	Fe(II)	70% fayalite crystals + 30% fayalite quench crystals
A	45.0	1475 ± 10	5	Fe(II)	10% fayalite crystals + 90% fayalite quench crystals
A	45.5	880 ± 10	45	Fe(III)	Fayalite crystals
A	45.5	1020 ± 10	20	Fe(III)	Fayalite crystals
A	46.0 ± 1.0	755 ± 10	120	Fe(III)	Spinel crystals
A	48.5	1020 ± 10	20	Fe(III)	Fayalite crystals
A	49.5	870 ± 10	45	Fe(III)	80% spinel crystals + 20% fayalite crystals
A	52.0	1025 ± 15	30	Fe(III)	Spinel crystals
B	52.0	1145 ± 10	15	Fe(III)	Fayalite crystals
A	54.5	1025 ± 10	20	Fe(III)	Spinel crystals
A	55.0	1180 ± 10	10	Fe(III)	Fayalite crystals
A	55.0	1480 ± 5	5	Fe(I)	Fayalite crystals
A	55.0	1515 ± 5	5	Fe(I)	Glass + coesite
A	56.0	1205 ± 5	12	C	Fayalite crystals
A	56.0	1400 ± 5	5	C	Fayalite crystals
B	57.0	1110 ± 10	15	Fe(III)	Spinel crystals
A	57.0	1165 ± 15	10	Fe(III)	Fayalite crystals
A	57.0	1380 ± 5	5	Fe(III)	Fayalite crystals
A	58.0	1170 ± 10	10	Fe(III)	60% spinel crystals + 40% fayalite crystals
B	58.0	1355 ± 5	10	Fe(III)	Fayalite crystals
A	58.0	1505 ± 10	5	C	20% fayalite crystals + 80% fayalite quench crystals
A	58.0	1555 ± 10	4	C	Fayalite quench crystals
A	58.5	1375 ± 5	5	Fe(III)	Fayalite crystals
B	60.0	1320 ± 5	10	Fe(III)	Fayalite crystals
A	60.0	1480 ± 5	5	Fe(I)	Fayalite crystals
A	60.0	1530 ± 5	5	Fe(I)	Glass + coesite
A	60.0	1555 ± 5	5	Fe(IV)	Fayalite quench crystals + garnet ?
A	61.0 ± 1.0	1300 ± 5	10	C	70% fayalite crystals + 30% spinel crystals
A	61.5	1205 ± 5	12	C	Spinel crystals + fayalite crystals (small amount)
A	61.5	1400 ± 10	5	C	Fayalite crystals
A	62.0	1485 ± 5	5	C	80% spinel crystals + 20% fayalite crystals
A	62.0	1535 ± 5	4	Fe(IV)	Fayalite quench crystals + garnet ?
A	63.0	1340 ± 5	10	C	80% spinel crystals + 20% fayalite crystals

TABLE 1. (Continued)

Starting* Material	Pressure,† kb	Temperature, °C	Time, min	Furnace Assembly‡	Results
A	63.0	1495 ± 5	5	Fe(IV)	Spinel crystals
A	66.5	1475 ± 5	4	C	Spinel crystals
A	66.5	1575 ± 5	4	C	Spinel quench crystals + spinel crystals (small amount)
A	68.5	1515 ± 5	4	C	Spinel crystals
A	70.0	1350 ± 5	10	Fe(IV)	Spinel crystals
A	70.0	1615 ± 10	4	C	Spinel crystals + spinel quench crystals (rare)
A	70.0	1650 ± 10	4	C	Spinel quench crystals + spinel crystals (small amount)
A	71.0	1560 ± 10	4	C	Spinel crystals
A	76.0	1640 ± 10	4	C	Spinel crystals
A	76.0	1710 ± 10	3	C	Spinel crystals + spinel quench crystals

* A, fayalite; B, Fe_2SiO_4 spinel.

† Unless otherwise stated, precision of pressure control is about ±0.5 kb.

‡ Fe(I): Iron capsule, BN disk and BN sleeve.
Fe(II): Iron capsule, fired pyrophyllite disk and BN sleeve.
Fe(III): Iron capsule, unfired pyrophyllite disk and unfired pyrophyllite sleeve.
Fe(IV): Iron capsule, fired pyrophyllite disk and fired pyrophyllite sleeve.
C: Graphite capsule, fayalite disk.

§ Precision of temperature control.

reveals an evident curvature, and the initial slope of 7.5°/kb flattens to about 3.5°/kb in the pressure range 50 to 60 kb. In drawing this curve, we used as a reference point the melting point of the used fayalite at atmospheric pressure, which was determined to be 1205 ± 5°C by K. Kitayama (private communication). Considering the precision of experiments, the data can be fitted satisfactorily by Simon's equation, $P(\text{kb}) = 41\{[T(°\text{K})/1478]^{4.8}-1\}$, which was obtained by the trial and error method of computation.

A significant inflection was found in the melting curve of Fe_2SiO_4 at about 62 kb, the melting point increasing abruptly with pressure in the range above that pressure. Both microscopic observation and X-ray analysis of the run products indicate that this inflection is attributable to the beginning of the melting of Fe_2SiO_4 spinel. Melting in Fe_2SiO_4 spinel was also detected by examining the difference in texture under the microscope. Fe_2SiO_4 spinel which had been transformed from fayalite without melting was characterized by the aggregate of the fine-grained crystals, whereas that formed upon quenching from the liquid state was composed of the aggregate of coarse-grained crystals, prismatic or fibrous in texture. The melting curve of Fe_2SiO_4 spinel thus determined to 76 kb is also shown in Figure 2, initial slope being estimated experimentally to be about 14°/kb. It seems likely that the melting curve of Fe_2SiO_4 spinel is slightly curved above pressures of 70 kb. We did not try to fit the curves to Simon's equation, however, because the experimental data hitherto obtained were too few for such a treatment.

A stability diagram representing the olivine-spinel transition of Fe_2SiO_4 is also given in Figure 2. The transition was easily detected by microscopic observation and X-ray analysis of the run products. Since, in the earlier study [*Akimoto et al.*, 1965], the fast decomposition of Fe_2SiO_4 made it difficult to determine the olivine-spinel transition boundary at temperatures above 1200°C, particular effort was made to extend the earlier result to the higher-temperature range. We succeeded by using the techniques described in the section on the experimental procedure. Phases other than fayalite and spinel were not observed in the run products at temperatures ranging from 1200 to 1500°C if an iron capsule or a simple graphite capsule was used. Ferrosilites, which were

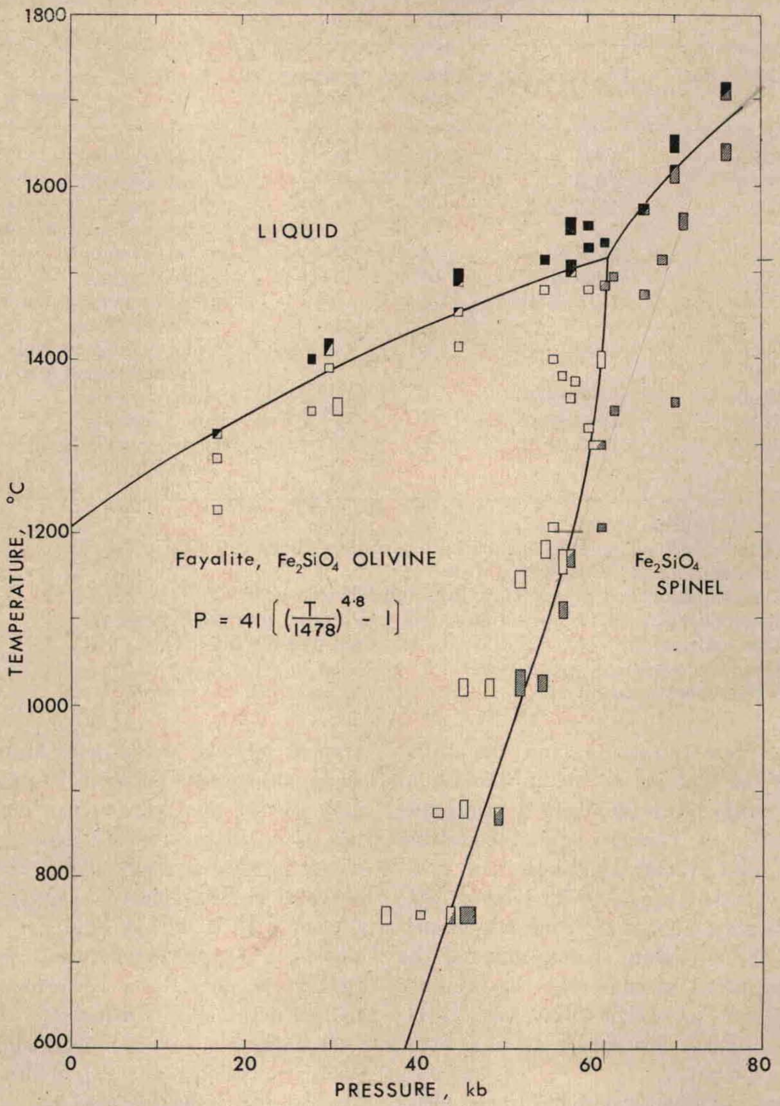

Fig. 2. Effect of pressure on the melting relations and polymorphism of Fe_2SiO_4.

produced in the high-temperature runs with the earlier cell assembly, were not identified in the present study. The inversion curve for the olivine-spinel transition of Fe_2SiO_4 shown in Figure 2 could not be approximated by a simple straight line, the deviation of the curve from the straight line being remarkably large for temperatures above 1150°C. Four runs from spinel to olivine established that, within the precision of the experiments, the transition was reversible over a wide range of pressure and temperature. The transition curve at temperatures below 1150°C is well fitted by the revised linear relation $P(\text{kb}) = 19 + 0.033T(°\text{C})$. It seems likely that a nonlinear equation such as Simon's equation would improve the fit of the curve to the experimental data over the wider range of temperature from 700°C to about 1500°C. Combining all the results on the melting curve of fayalite and Fe_2SiO_4 spinel, as well as the olivine-spinel transition of Fe_2SiO_4, the triple point in the system fayalite–Fe_2SiO_4 spinel–liquid was determined to be at 1520°C and 62 kb.

DISCUSSION

Bowen and Schairer [1935], using the Clapeyron-Clausius equation, calculated an initial slope for the melting curve of fayalite to be 3.5°/kb. The latent heat of fusion of fayalite used in their calculation was derived from the solidus and liquidus curves for the Mg_2SiO_4-Fe_2SiO_4 system. The volume change of fayalite upon melting was roughly estimated by extrapolating the refractive index data of both crystal and glass in the Mg_2SiO_4-Fe_2SiO_4 system. They also stated that direct measurement by Goranson [*Bowen and Schairer,* 1935, p. 208] showed the rise of melting point to be approximately twice as much as the calculated value. The slope of 7.5°/kb obtained in the present study essentially verified Goranson's earlier result. Inaccurate estimation of both the latent heat and the volume change of fayalite may be chiefly responsible for the disagreement between the calculated and experimental values.

Experimental results on the olivine-spinel transition in Fe_2SiO_4 obtained in this study essentially agree with those by *Boyd and England* [1960], who used a piston-cylinder type of high-pressure apparatus with similar furnace assembly. The stability field of Fe_2SiO_4 spinel shown in Figure 2 consistently involves the experimental conditions of 1400°C at 65 kb which were determined by them to be in the spinel field.

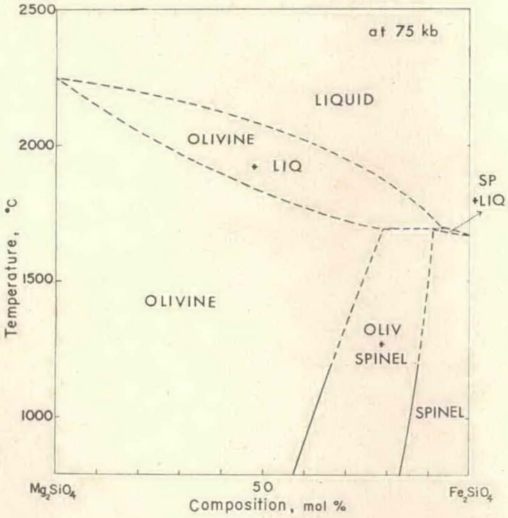

Fig. 3. Equilibrium diagram of the system Mg_2SiO_4-Fe_2SiO_4 at pressures near 75 kb. Melting point of forsterite is obtained by extrapolating the curve given by *Davis and England* [1964]. The liquidus and solidus are assumed. The solvus is based on the olivine-spinel transition in the system Mg_2SiO_4-Fe_2SiO_4 at 800, 1000, and 1200°C (Akimoto and Fujisawa, unpublished data).

The average slope of the melting curve for fayalite is 5.1°/kb, being close to that for forsterite, 4.77°/kb, in the pressure range up to about 50 kb [*Davis and England,* 1964]. It is expected, therefore, that the melting relations in the system Mg_2SiO_4-Fe_2SiO_4 at pressures up to 62 kb would be essentially the same as those at atmospheric pressure. At pressures higher than 62 kb, however, $(Mg,Fe)_2SiO_4$ spinel appears to be on the liquidus, and the solidus of olivine solid solution is intersected by the solvus between olivine and spinel solid solutions. Figure 3, the estimated equilibrium diagram of the system Mg_2SiO_4-Fe_2SiO_4 at about 75 kb, shows such relations. With increasing pressure the solvus shifts toward Mg_2SiO_4, and the liquidus and solidus of spinel solid solution become wider.

The remarkable inflection in the melting curve of Fe_2SiO_4, which coincides with the melting of Fe_2SiO_4 spinel, is of considerable geophysical importance. This suggests that a similar inflection should be anticipated in the melting-point gradient of the earth's mantle, provided that the olivine-spinel transformation takes place in the transition zone of the mantle. Positive support of the above inference is found in calculations on the melting curve of the mantle. *Uffen* [1952] estimated quite independently the change in melting temperature of the mantle with depth using seismic data on the basis of the Einstein-Debye theory of solids and Lindemann's theory of fusion. *Clark* [1963], considering thermodynamics and the effect of the transition zone, derived a melting curve for the mantle. We can find a considerable inflection in both melting curves around the transition zone. Since the chemical composition of the olivine in the mantle is generally supposed to be in the Mg_2SiO_4-rich side of the Mg_2SiO_4-Fe_2SiO_4 system, it is highly desirable to extend this work to a comprehensive study of the fusion of the Mg_2SiO_4-Fe_2SiO_4 system at high pressures.

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REFERENCES

Akimoto, S., and H. Fujisawa, Demonstration of the electrical conductivity jump produced by the olivine-spinel transition, *J. Geophys. Res., 70,* 443–449, 1965.

Akimoto, S., H. Fujisawa, and T. Katsura, The olivine-spinel transition in Fe_2SiO_4 and Ni_2SiO_4, *J. Geophys. Res., 70,* 1969–1977, 1965.

Bowen, N. L., and J. F. Schairer, The system, MgO-FeO-SiO_2, *Am. J. Sci., 29,* 151–217, 1935.

Boyd, F. R., and J. L. England, The fayalite-Fe_2SiO_4 spinel transition, *Carnegie Inst. Wash. Year Book 59,* pp. 48–49, 1960.

Boyd, F. R., and J. L. England, Effect of pressure on the melting of diopside, $CaMgSi_2O_6$, and albite, $NaAlSi_3O_8$, in the range up to 50 kilobars, *J. Geophys. Res., 68,* 311–323, 1963.

Clark, S. P., Jr., Variation of density in the earth and the melting curve in the mantle, in *The Earth Sciences,* edited by T. W. Donnelly, pp. 5–42, University of Chicago Press, 1963.

Davis, B. T. C., and J. L. England, The melting of forsterite up to 50 kilobars, *J. Geophys. Res., 69,* 1113–1116, 1964.

Uffen, R. J., A method of estimating the melting-point gradient in the earth's mantle, *Trans. Am. Geophys. Union, 33,* 893–896, 1952.

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