

Postspinel Transformations in the System $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ and Some Geophysical Implications

EIJI ITO AND EIICHI TAKAHASHI¹

Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan

The high-pressure transformation in MgSiO_3 and those in the spinel phases of compositions from Mg_2SiO_4 to $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$ in the $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ system were investigated using a uniaxial split-sphere apparatus. The phase boundaries between ilmenite-perovskite in MgSiO_3 and between Mg_2SiO_4 spinel and the assemblage of MgSiO_3 perovskite and MgO periclase were determined to be $P(\text{GPa}) = 26.8 - 0.0025T(^{\circ}\text{C})$ and $P(\text{GPa}) = 27.6 - 0.0028T(^{\circ}\text{C})$, respectively, in the temperature range 1000–1600°C. The pseudobinary diagrams for the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ were determined at temperatures of 1100°C and 1600°C. It was demonstrated that the magnesian spinel (with $\text{Fe}/\text{Mg} + \text{Fe} < 0.22$ at 1100°C and < 0.26 at 1600°C) dissociates into perovskite and magnesio-wüstite within an extremely narrow pressure interval (< 0.15 GPa at 1600°C). The dissociation pressure was found to be almost independent of iron content and to coincide to that at 670 km depth within experimental uncertainties. These experimental results indicate that the sharpness of the 670-km discontinuity may indeed be due to this dissociation in a peridotitic or pyrolitic mantle. The current status of our understanding of deep mantle mineralogy and chemistry is discussed based on recent high-pressure and high-temperature experiments.

INTRODUCTION

Extensive early effort has been made to locate and characterize the olivine-modified spinel-spinel transformations in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ [Akimoto and Fujisawa, 1968; Ringwood and Major, 1970; Kawai *et al.*, 1970; Suito, 1972; Kawada, 1977; Katsura and Ito, 1989]. The results have indicated that assuming a peridotitic mantle composition such as pyrolite, the olivine-modified spinel transformation would be the major cause of the seismic discontinuity found at around 400 km depth and modified spinel, and spinel at greater depths, would be the dominant constituents of the transition zone [Ringwood, 1975; Akimoto *et al.*, 1976]. Following this work, Liu [1976] and Ito [1977] found that Mg_2SiO_4 spinel dissociates into an assemblage of MgSiO_3 perovskite and MgO periclase at pressures higher than 20 GPa. The implication is that the next steep increase in seismic velocities at around 670 km depth (the 670-km discontinuity) might be due to the dissociation of spinel and that perovskite and a rock salt monoxide are considered to be the major constituents in the Earth's lower mantle [Jackson, 1983; Ito *et al.*, 1984].

On the other hand, the interpretation of the 670-km discontinuity as a chemical boundary rather than a phase boundary has been discussed vigorously in many recent papers, for example, Anderson [1976, 1979], Kumazawa [1982], Liu [1979], and Lees *et al.* [1983]. These authors argued that the Si and/or Fe contents increase abruptly at the discontinuity. Bass and Anderson [1984] and Anderson and Bass [1986] proposed a model in which the mantle is chemically stratified in the order of a peridotitic composition in the upper mantle (above 400 km depth), a picritic eclogite composition ("piclogite") in the transition zone, and pyroxene composition in the perovskite structure in the lower

mantle. One of the major bases for these arguments is that any multivariant phase transformations expected to occur in the mantle might spread over a depth interval of 20 km or more and thereby conflict with the prominent characteristic of the 670-km discontinuity as a remarkable reflector of seismic waves [Lees *et al.*, 1983; Anderson and Bass, 1986].

In these contexts, information on the dissociation of the spinel phase in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ is urgently needed for discussion of the nature of the 670-km discontinuity. Yagi *et al.* [1979] first reported a model of the postspinel transformation in the system at pressures of 17–70 GPa using a diamond anvil cell coupled with a laser heating system. Their results, however, are of reconnaissance nature because the chemical compositions of the run products were not determined and the experimental temperature might contain a large uncertainty.

Our previous study [Ito *et al.*, 1984] revealed the detailed stability relation in the system MgO-FeO-SiO_2 at 26 GPa and 1600°C and discussed possible mineralogy and chemistry of the lower mantle, based on the phase relations and the estimated physical properties of the lower mantle. In this study, we have tried to get detailed information on the stability of MgSiO_3 perovskite at the MgSiO_3 and Mg_2SiO_4 compositions and on the postspinel transformations in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$. Recent advances in experimental methodology, particularly calibration of pressure and minimization of the effect of temperature gradients, are crucial to this study. We report the results with their special implications for the nature of the 670-km discontinuity.

EXPERIMENTAL PROCEDURE

High-pressure and high-temperature experiments were performed using a uniaxial split-sphere apparatus installed in our laboratory (USSA-5000), in which an inner cubic anvil assembly of tungsten carbide is compressed with the aid of a 5000-ton hydraulic press. A cross section of the specimen assembly is shown in Figure 1. The pressure medium was semisintered magnesia containing 5% Cr_2O_3 to reduce thermal conductivity. A CaO-doped zirconia sleeve served as a

¹Now at Earth and Planetary Sciences, Tokyo Institute of Technology, Japan.

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Paper number 89JB00705.
0148-0227/89/89JB-00705\$05.00

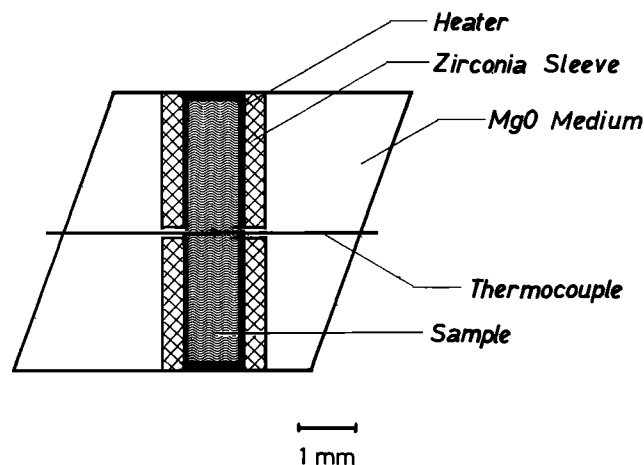


Fig. 1. Schematic drawing of a cross section of the specimen assembly.

thermal insulator. The powdered sample was packed into a cylindrical tantalum heater. The sample temperature was monitored using a 0.1-mm-diameter Pt/Pt 13% Rh thermocouple, which penetrated the center of the cylindrical heater. Powdered starting materials were also stuffed into small clearances between the thermocouple and the heater to keep electrical insulation. The terminals of the thermocouple were connected outside of the anvil assembly. No correction was made for the pressure effect on emf.

In some runs, the thermocouple was found to make contact with the tantalum heater at one side or both sides under high pressures (cf. Figure 1). The runs of one-sided contact were discarded because the leak of alternative power from heater made it impossible to measure the temperature. In the runs of two-sided contact the temperature was measured stably, registering the temperature at the thermocouple-heater junction. The temperature variation along the thermocouple should be quite small because the upper and lower halves of the cylindrical heater are symmetrical with respect to the thermocouple and thereby such runs were adopted.

The generated pressure was calibrated against the oil pressure of the press. The calibrations at room temperature were made by detecting abrupt changes in electrical resistance associated with phase transitions; Bi III-V (7.7 GPa), metallic transitions in ZnS (15.4 GPa), GaAs (18.2 GPa), and GaP (23 GPa). Pressure calibrations were also carried out at 1000°C and 1600°C based on the pressure values for transformations and dissociations in several silicates determined so far; coesite to stishovite in SiO_2 [Yagi and Akimoto, 1976], olivine-modified spinel-spinel in Mg_2SiO_4 [Suito, 1977; Akaogi *et al.*, 1984], garnet to MnO + stishovite in MnSiO_3 [Akaogi *et al.*, 1984], spinel to NiO + stishovite in Ni_2SiO_4 [Navrotsky *et al.*, 1979], and spinel + stishovite to ilmenite in MgSiO_3 [Ito and Navrotsky, 1985].

The calibration curves thus constructed are shown in Figure 2. The curve at 1000°C is located about 1 GPa below that at room temperature. However, the curve at 1600°C virtually coincides with that at room temperature. The β - γ transformation in Mg_2SiO_4 at 800°C and 15.2 GPa [Akaogi *et al.*, 1984] is plotted below the curve at 1000°C. The onset of the transformation of zirconia to a dense polymorph with the PbCl_2 structure first reduces the pressure during heating,

because the transformation proceeds even at 600°C and is accompanied by a large volume contraction of some 14% [Ohtaka *et al.*, 1988]. However, the pressure increase due to the thermal expansion of the assembly becomes more pronounced with increasing temperature, and the pressure for a constant oil pressure is assumed to increase monotonically at temperatures higher than 1000°C.

Experimental pressures at 1000°C and 1600°C were determined by extrapolating the curves up to 25.5 GPa. Pressure values at intermediate temperatures were determined by interpolation between two curves. The generated pressure was reproduced within a precision of 1.0% in oil pressure, and the absolute accuracy of the pressure determination might be within 5%.

Synthetic MgSiO_3 enstatite and olivine solid solutions were used as the starting materials. The olivine solid solutions of $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6) were synthesized from Fe-sponge, Mg-metal, and SiO_2 -gel using the technique described by Ito *et al.* [1984]. Each starting material was confirmed to be homogeneous olivine and to possess the nominal $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio within ± 1 mol % by powder X ray diffractometry and electron microprobe analysis.

The run durations were less than 60 min at 1100°C and 40 min at 1600°C for the Fe-bearing samples to minimize

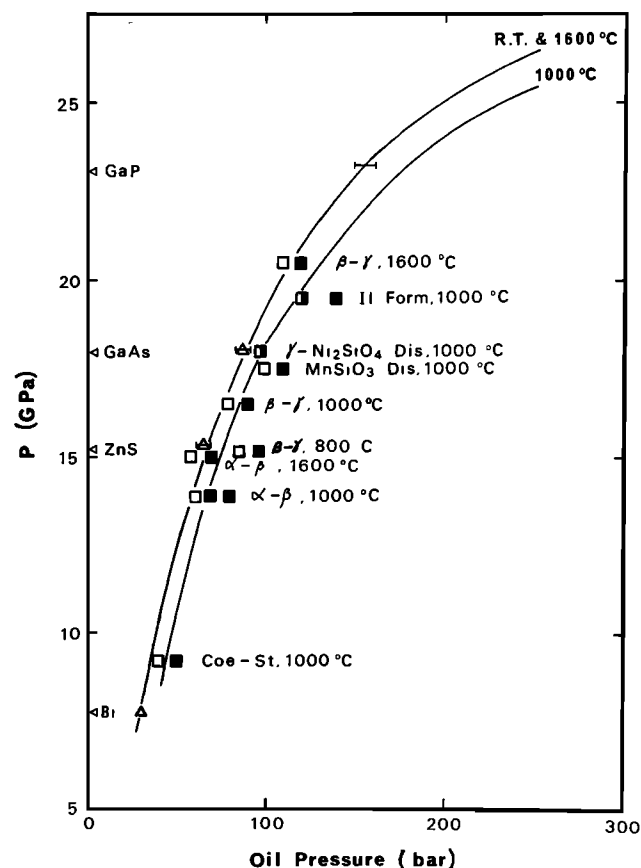


Fig. 2. Pressure calibration curves at room temperature (RT) and high temperatures (1000°C and 1600°C). The curves at high temperatures are based on transition pressures in several silicates (see text). Coe-St, coesite to stishovite in SiO_2 ; α - β , olivine to modified spinel in Mg_2SiO_4 ; β - γ , modified spinel to spinel in Mg_2SiO_4 ; MnSiO_3 Dis, garnet to MnO + stishovite in MnSiO_3 ; γ - Ni_2SiO_4 Dis, spinel to NiO + stishovite in Ni_2SiO_4 ; Il Form, spinel + stishovite to ilmenite in MgSiO_3 .

TABLE 1. Results of MgSiO_3 Runs

Run	Temperature, [†] °C	Pressure, GPa	Time, min	Phases Present [‡]
E0523	1000	24.5	74	Pv
E0605	1000	24	61	Il
E0521	1000	23.5	61	Il
E0517	1000	22.2	64	Il
EF1004*	1000	24.8	61	Pv
EF0830*	1300	24.8	62	Pv
EF1007*	1300	24.5	38	Pv
EF1017*	1300	24	13	Pv
EF0826*	1300	23.5	64	Il
E1121§	1400	23.1	60	Il
E0525	1600	24.5	20	Pv
E0621	1600	24	20	Pv
E0531	1600	23.1	22	Pv
E0603	1600	22.8	20	Il
EF0903*	1600	23.1	35	Pv
EF0904*	1600	22.8	40	Il

[†]Experimental temperature was kept constant within $\pm 5^\circ\text{C}$.[‡]Pv, MgSiO_3 perovskite, Il, MgSiO_3 ilmenite.*Both MgSiO_3 and Mg_2SiO_4 samples were charged (see text).§Starting material was MgSiO_3 perovskite.TABLE 2. Results of Mg_2SiO_4 Runs

Run	Temperature, [†] °C	Pressure, GPa	Time, min	Phase Present [‡]
F0617	1000	25	60	Pv+Pv
F0607	1000	24.5	61	Sp
EF1004*	1000	24.8	61	Sp Pv+Per
F0625	1100	25	60	Pv+Per
F0623	1100	24.8	60	Pv+Per
F0630	1100	24.5	60	Sp Pv+Per
F0701	1100	24.2	60	Sp
EF0830*	1300	24.8	62	Pv+Per
EF0007*	1300	24.5	38	Pv+Per
EF1017*	1300	24	13	Sp>Pv+Per
E0826	1300	23.5	64	Sp
F0719	1600	24.5	8	Pv+Per
F0721	1600	24.1	20	Pv+Per
F0702	1600	22.8	27	Sp
EF0903*	1600	23.1	35	Sp<Pv+Per
EF0904*	1600	22.8	40	Sp

[†]Experimental temperature was kept constant within $\pm 5^\circ\text{C}$.[‡]Sp, spinel, Pv, MgSiO_3 perovskite; Per, MgO periclase.*Both MgSiO_3 and Mg_2SiO_4 samples were charged (see text).

possible contamination of the thermocouple by Fe from the sample. After being kept at a desired condition for a certain duration, samples were quenched by shutting off the electric power supply. The thermocouple reading dropped to below 50°C in a few seconds and to ambient in 2 min. The pressure was released at a rate of 1 GPa/h, and the product was recovered at ambient conditions.

In most previous high-pressure phase equilibrium studies, the identification of phases was carried out by ordinary powder diffractometry. In this method, several milligrams of sample were needed, and the coexistence of high- and low-temperature phases was inevitably observed for products quenched at conditions near the phase boundary because of the steep temperature gradient in a small heater. In order to minimize such ambiguity in phase stability determinations, identification of phases in most of the run products was performed only on the area within $100\ \mu\text{m}$ from the thermocouple junction by a microfocused X ray diffractometer (RIGAKU Cat No. 2193D5) in which $\text{CrK}\alpha$ radiation of $100\text{-}\mu\text{m}$ diameter was used. Chemical compositions of phases were determined by electron microprobe analysis or from the unit cell dimensions determined by the ordinary X ray diffraction method.

RESULTS AND DISCUSSION

MgSiO_3 and Mg_2SiO_4

Stability relations in MgSiO_3 and Mg_2SiO_4 were examined at temperatures from 1000°C to 1600°C and pressures from 22 to 25 GPa. No phases other than the ilmenite and perovskite were observed in MgSiO_3 runs and the spinel and the assemblage of perovskite plus periclase were observed in the run products of Mg_2SiO_4 . In order to compare the stability of perovskite phase in MgSiO_3 and Mg_2SiO_4 , several runs (asterisked in Tables 1 and 2) were carried out, in which the upper and the lower halves of the sample, divided by the thermocouple (cf. Figure 1), were charged with MgSiO_3 and Mg_2SiO_4 , respectively. The phases present in both portions adjoining the thermocouple junction were examined. These runs gave evidence that spinel is stable at

Mg_2SiO_4 composition even in the stability field of MgSiO_3 perovskite at MgSiO_3 composition. The results are summarized in Tables 1 and 2 and shown Figures 3 and 4. The phase boundary curves for the reactions ilmenite-perovskite in MgSiO_3 and spinel-perovskite plus periclase in Mg_2SiO_4 have definitely negative Clapeyron slopes, as previously reported by Ito and Yamada [1982]. In this study, however, the result of each run is much clearer than that of Ito and Yamada [1982], because of the use of microdiffractometry. One reversal run which started from the perovskite phase was performed (run E1121; see Table 1). The starting material was synthesized at 1600°C and 25 GPa from enstatite and confirmed to be single phase of perovskite by ordinary powder X ray diffractometry. The powdered perovskite was charged in the central portion of about $0.5\ \text{mm}$ thickness including thermocouple with enstatite powder in the remainder spaces. Analysis of the quenched product by X ray microdiffractometry showed that the central portion was the

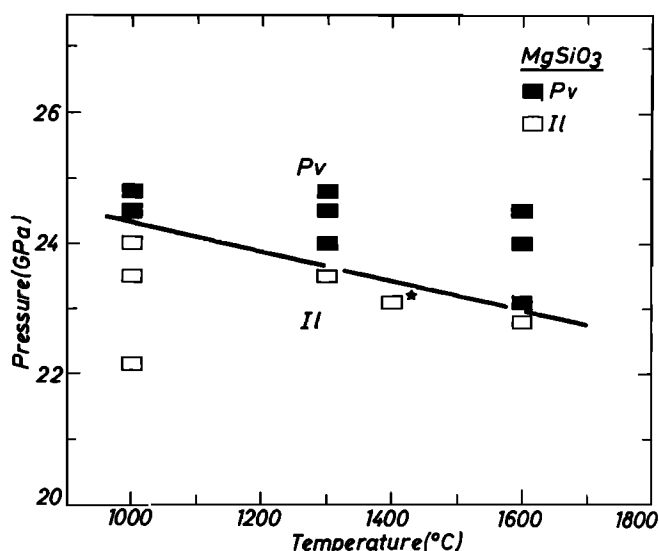


Fig. 3. Stability diagram for the ilmenite-perovskite transformation in MgSiO_3 . In the run designated by asterisk, perovskite phase was used as the starting material.

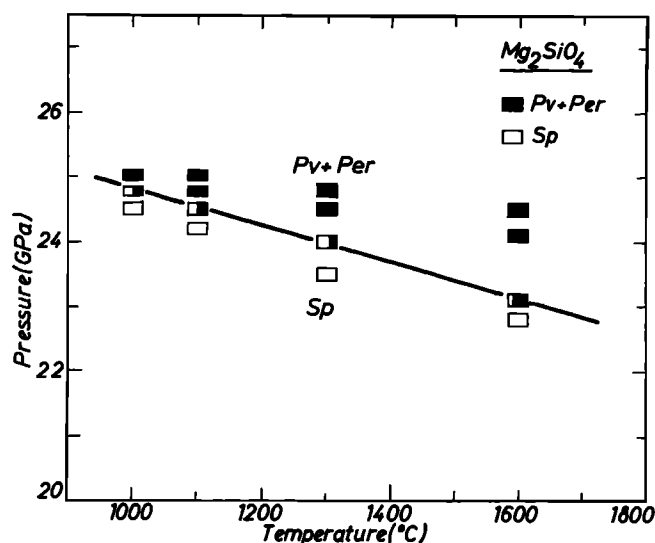


Fig. 4. Stability diagram for the dissociation of spinel into perovskite + periclase in Mg_2SiO_4 .

ilmenite phase and no perovskite phase was detected in the area along the thermocouple. Therefore the experimental condition is truly in the ilmenite stability field and the boundary between ilmenite and perovskite phases should be located at higher pressures than the condition. The phase boundary curves are expressed by the equations $P(\text{GPa}) = 26.8 - 0.00257T(^{\circ}\text{C})$ for the ilmenite-perovskite transformation in MgSiO_3 and $P(\text{GPa}) = 27.6 - 0.00287T(^{\circ}\text{C})$ for the dissociation of spinel into perovskite plus periclase in Mg_2SiO_4 . While the latter is located at slightly higher pressures than the former, both curves are close to each other, as suggested by Ito and Yamada [1982].

Phase Relations in the System Mg_2SiO_4 - Fe_2SiO_4

The experiments were performed at 1100°C and 1600°C, with pressures varying from 22 to 26 GPa. The run duration was limited to be less than 60 min at 1100°C and 40 min at

1600°C in order to minimize the possible contamination of the thermocouple by Fe from the sample. No starting material (olivine) was observed in any of the run products. The identified phase assemblages were spinel, spinel + magnesio-wüstite + stishovite, perovskite + magnesio-wüstite + stishovite, or magnesio-wüstite + stishovite depending on the pressure and temperature conditions and iron content of the starting material. The two- or three-phase assemblages were fine-grained aggregates (0.1–3 μm) with mutual intergrowth textures and the determination of compositions for individual phases by EPMA was performed only for the binary mixture of perovskite and magnesio-wüstite [see Ito *et al.*, 1984]. Iron contents of phases in the other assemblages were estimated from the cell dimensions determined by ordinary powder X ray diffraction, using the relationships for the $\text{Fe}/(\text{Mg} + \text{Fe})$ ratio versus cell dimensions for perovskite [Ito and Yamada, 1982], spinel (H. Yamada and E. Ito, unpublished data, 1980), and magnesio-wüstite [Rosenhauer *et al.*, 1976] solid solutions.

We could not specify the exact oxidation state of the sample under the high-pressure and high-temperature conditions. However, the oxidation state did not make any serious effect on the phase relations, because neither free iron nor tantalum oxide was observed in any run products.

Experimental results at 1100°C are summarized in Table 3. The spinel phase with compositions from Mg_2SiO_4 to $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ dissociated into the assemblage perovskite + magnesio-wüstite at pressures higher than 24.5 GPa. For the nominal compositions $(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$ and $(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$, the observed assemblages changed from spinel to spinel + magnesio-wüstite + stishovite and finally to perovskite + magnesio-wüstite + stishovite with increasing pressure. In $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$ runs, however, no perovskite phase was observed, and the spinel phase finally decomposed into magnesio-wüstite and stishovite after passing through the region of coexistence of spinel, magnesio-wüstite, and stishovite.

The results are shown in Figure 5a as a pseudobinary diagram. The $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios of coexisting spinel and magnesio-wüstite are indicated by dots referring to the hori-

TABLE 3. Results of Experiments for the System Mg_2SiO_4 - Fe_2SiO_4 at 1100°C

Run	Composition	Pressure, GPa	Time, min	Phase Present†	100Fe/(Fe+Mg)‡
910430	$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$	24.5	60	Sp Pv+Mw	...
910427	$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$	24	60	Sp	...
821127	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	25.5	40	Pv+Mw	Pv:6, Mw:44 (X)
821203	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	25	63	Pv+Mw	Pv:7, Mw:45 (E)
820131	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	24.5	40	Pv+Mw>Sp	Pv:4, Mw:34, Sp:16 (X)
821123	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	24	60	Sp	Sp:80 (X)
730724	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	25.5	60	Pv+Mw+St	Pv:8, Mw:44 (X)
730507	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	25	42	Pv+Mw+St	...
730504	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	24.5	42	Sp+Mw+St>Pv	Sp:22, Mw:46 (X)
731209	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	24	37	Sp+Mw+St	Sp:27, Mw:60 (X)
641201	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	25	40	Pv+Mw+St	Pv:7, Mw:44 (X)
641214	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	24.5	59	Sp+Pv+Mw+St	...
641216	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	24	60	Sp+Mw+St	Sp:25, Mw:54 (X)
550701	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	25.5	60	Mw+St	Mw:50 (X)
550702	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	23.2	60	Sp+Mw+St	Sp:31, Mw:73 (X)
550630	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	22.5	60	Sp+Mw+St	Sp:46, Mw:80 (X)
550708	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	22	60	Sp	... (X)

†Pv, perovskite; Mw, magnesio-wüstite; St, stishovite; Sp, spinel.

‡(E) and (X) denote the iron content determined with EPMA and powder X ray diffraction, respectively.

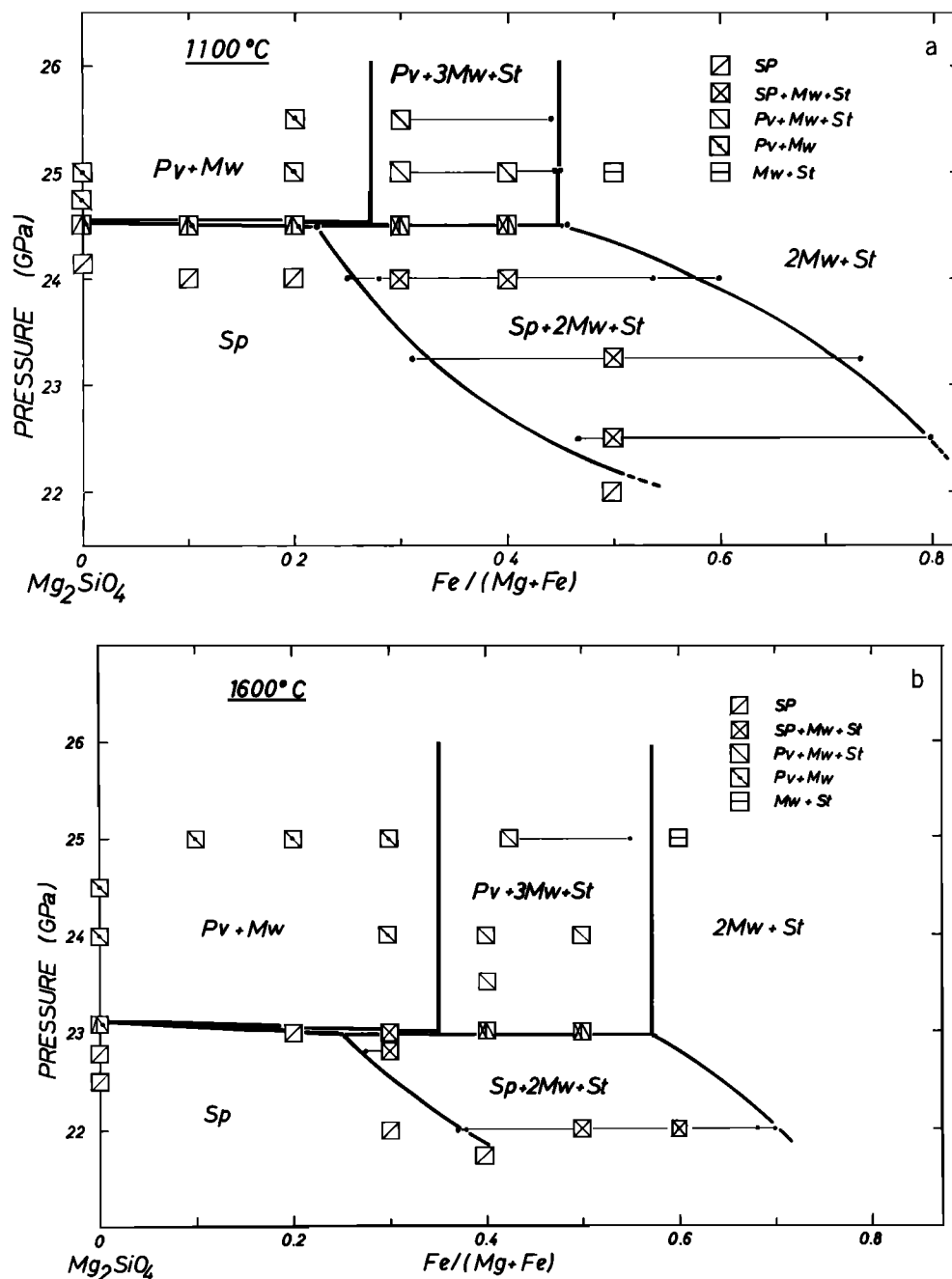


Fig. 5. Pseudobinary diagrams in the system Mg_2SiO_4 - Fe_2SiO_4 at (a) 1100°C and (b) 1600°C. Sp, spinel; Mw, magnesiowüstite; St, stishovite; Pv, perovskite. The iron contents $\text{Fe}/(\text{Fe} + \text{Mg})$ of determined phases which are present are indicated by dots referring to the horizontal axis and those of coexisting phases are connected to each other with light lines.

zonal axis and connected to each other with light lines. This procedure facilitates the determination of the three-phase loop of spinel, magnesiowüstite, and stishovite. The loop terminates at about 24.5 GPa, and $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios of 0.22 for spinel and 0.46 for magnesiowüstite (see runs 730504 and 641201), constraining the location of the univariant boundary along which spinel, magnesiowüstite, and perovskite coexist. Therefore the compositional range in which the spinel phase directly dissociates into perovskite + magnesiowüstite is inferred to be from $\text{Fe}/(\text{Mg} + \text{Fe}) = 0$ to 0.22, and the topological relations indicate that the dissociation pressure decreases slightly with increasing iron content. However, no appreciable difference in pressure values was

observed between the dissociation of Mg_2SiO_4 and the univariant reaction within the uncertainty of the pressure measurements (less than 0.5 GPa), and the three-phase assemblage spinel + perovskite + magnesiowüstite was found only in the run product which was quenched at 24.5 GPa in the series of experiments on $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ composition.

The iron contents of perovskite and magnesiowüstite in the three-phase assemblage perovskite + magnesiowüstite + stishovite indicate that the maximum solubility of iron in perovskite is about 8 mol % and that for coexisting magnesiowüstite is about 46 mol %. The inferred phase relations at 25 GPa and 1100°C are shown as a ternary diagram of

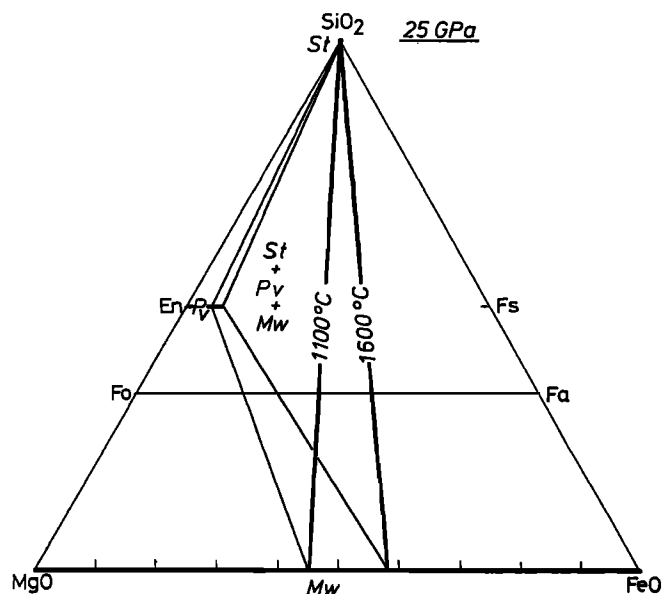


Fig. 6. Phase relations in the system MgO-FeO-SiO_2 at 25 GPa. Pv, perovskite; Mw, magnesiowüstite; St, stishovite.

MgO-FeO-SiO_2 in Figure 6, together with those at 25 GPa and 1600°C [cf. Ito *et al.*, 1984]. The almost vertical phase boundaries located at $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.27$ (between Pv + Mw and Pv + 3Mw + St) and 0.45 (between Pv + 3Mw + St and 2Mw + St) in Figure 5a are located at the intersection of the Mg_2SiO_4 - Fe_2SiO_4 join and the stability boundaries of Pv + Mw + St in Figure 6.

The experimental results at 1600°C are summarized in Table 4 and shown in Figure 5b. The results already reported

by us [Ito *et al.*, 1984] are included with a revised pressure value of 25 GPa using the present pressure calibration. The overall topology is similar to that at 1100°C. However, all phase boundaries of the perovskite-forming reactions shift both to lower pressures and to higher $\text{Fe}/(\text{Mg} + \text{Fe})$ ratios with increasing temperature. This further supports the negative dP/dT for perovskite-forming reactions in these systems. The three-phase assemblage Pv + 3Mw + St was not observed in runs with compositions from Mg_2SiO_4 to $(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$ but was evident in $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$ runs at pressures higher than 23 GPa. The compositional relations in the three-phase field Pv + 3Mw + St are consistent with those of Ito *et al.* [1984]: The $\text{Fe}/(\text{Mg} + \text{Fe})$ ratios are 0.11 for perovskite and 0.58 for magnesiowüstite, respectively (Figure 6). The univariant boundary is located at about 23 GPa and has a compositional range from $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.26$ to 0.58. The boundary between Pv + Mw and Pv + 3Mw + St is located near $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.34$.

The phase relations obtained in the present study are topologically consistent with those of Yagi *et al.* [1979]. However, Yagi *et al.*'s Pv + 3Mw + St field is much richer in Fe than that of the present results, extending from $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.47$ to 0.76. This discrepancy was discussed in detail by Ito *et al.* [1984], and it was suggested that either the experimental temperature of Yagi *et al.* was much higher than the nominal value or their run products were not in equilibrium. In Yagi *et al.*'s diagram, the pressure value of the univariant reaction is about 5 GPa lower than that of the dissociation of Mg_2SiO_4 . This pressure difference probably does not exist, as described above (see also a later section). It is possible that in Yagi *et al.*'s work, the actual temperature of the $(\text{Mg}_{0.49}\text{Fe}_{0.51})_2\text{SiO}_4$ runs from which the univariant boundary was determined was much higher than that of

TABLE 4. Results of Experiments for the System Mg_2SiO_4 - Fe_2SiO_4 at 1600°C

Run	Composition	Pressure, GPa	Time, min	Phase Present†	100Fe/(Fe+Mg)‡
910525	$(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$	25	40	Pv+Mw	Pv:3, Mw:17 (X)
820317	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	25	40	Pv+Mw	Pv:6.5, Mw:34 (E)
820915	$(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$	23.1	33	Sp	Sp:20 (E)
730510	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	25	40	Pv+Mw	Pv:8, Mw:55 (E)
730707	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	24	21	Pv+Mw	Pv:7, Mw:56 (X)
730619*	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	23.2	25	Sp>>Mw+St	Sp:76 (X)
	Mg_2SiO_4			Sp	...
731618*	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	23	18	Sp>>Mw+St	Sp:73 (X)
	Mg_2SiO_4				...
730504	$(\text{Mg}_{0.7}\text{Fe}_{0.3})_2\text{SiO}_4$	22	20	Sp	...
640529	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	25	40	Pv+Mw	Pv:9.5, Mw:55 (X)
640610*	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	24	20	Pv+Mw+St	...
	Mg_2SiO_4			Pv+Per	...
640607	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	23.5	20	Pv+Mw+St	...
	Mg_2SiO_4			Pv+Per	...
641008	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	23.1	20	Pv+Mw+St+Sp	...
	Mg_2SiO_4			Pv+Per+Sp	...
640515	$(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$	21.7	21	Sp	...
551005*	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	24	18	Pv+Mw+St	Pv:11.5, Mw:56 (E)
	Mg_2SiO_4			Pv+Per	...
550929*	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	23.1	20	Pv+Mw+St+Sp	...
	Mg_2SiO_4			Pv+Per+Sp	...
551007	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	22	23	Sp+Mw+St	Sp:38, Mw:70 (X)
551111	$(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$	21.5	22	Sp+Mw+St	...
460901	$(\text{Mg}_{0.4}\text{Fe}_{0.6})_2\text{SiO}_4$	25	40	Mw+St	MW:61 (X)
461121	$(\text{Mg}_{0.4}\text{Fe}_{0.6})_2\text{SiO}_4$	22	25	Sp+Mw+St	Sp:37, Mw:68 (X)

†Pv, Perovskite; Mw, magnesiowüstite; St, stishovite; Per, periclase; Sp, spinel.

‡(E) and (X) denote the iron content determined with EPMA and powder X ray diffraction, respectively.

*Both Mg_2SiO_4 and $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ solid solution were charged (see text).

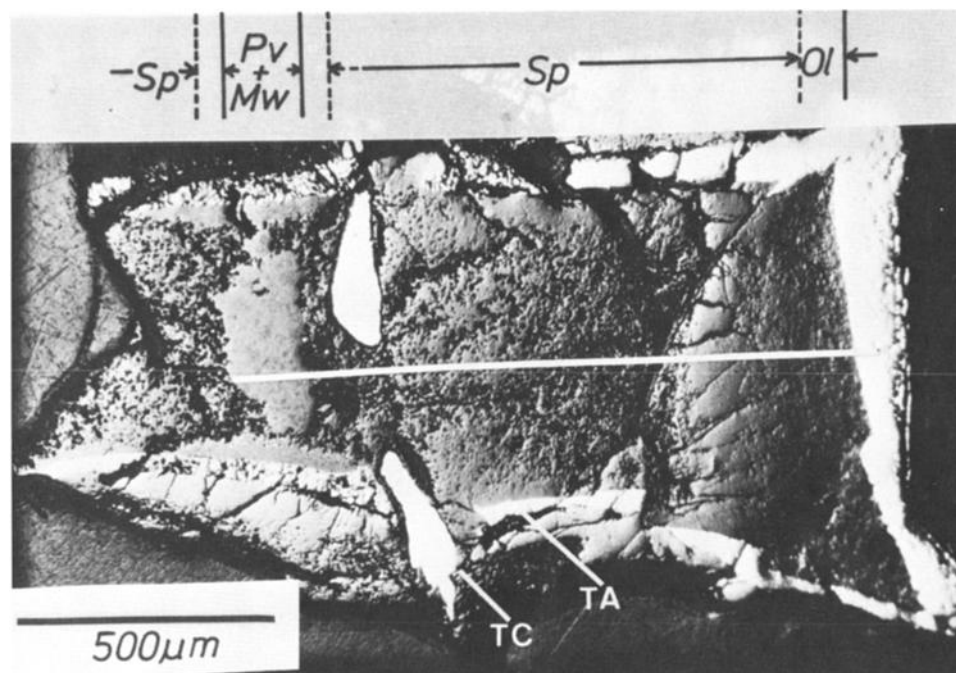


Fig. 7a. Microphotograph of a cross section of the run product of $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ quenched at 23.1 GPa and 1600°C (run 820915 in Table 4). The phases present along the central line are shown in the upper margin. Sp, spinel; Pv, perovskite; Mw, magnesiowüstite; Ol, olivine. TA and TC denote the tantalum heater and thermocouple, respectively.

the Mg_2SiO_4 runs, because the former compound absorbs the laser beam more effectively than the latter. A higher temperature in the $(\text{Mg}_{0.49}\text{Fe}_{0.51})_2\text{SiO}_4$ runs would explain the apparent lowering of pressure for the univariant boundary (cf. Figures 5a and 5b).

Dissociation of Spinel Into Perovskite + Magnesiowüstite

Figures 5a and 5b indicate that the transitional three-phase region of spinel + perovskite + magnesiowüstite is quite narrow in pressure. In experiments at 1600°C, special attention was paid to the pressure interval over which the dissociation of magnesian spinel into the assemblage perovskite + magnesiowüstite proceeds.

In order to compare the pressure value of the univariant boundary directly with that of the dissociation in Mg_2SiO_4 several runs (asterisked in Table 4) were performed at pressures of 23–24 GPa, in which the upper and the lower halves of the sample, divided by the thermocouple (see Figure 1 and preceding section), were charged with Mg_2SiO_4 and $(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$ or $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$, respectively. The phases present in both portions adjoining the thermocouple junction were carefully examined using the microdiffractometer and the scanning electron microscope (SEM). No appreciable diffusion of Mg and Fe was observed through the interface between the two charges. The results on Mg_2SiO_4 are consistent to those shown in Table 2 and Figure 4 within the precision of pressure measurements. As shown in Table 4, no differences in the pressure at which the perovskite phase appears were observed between the two portions. In other words, the pressure values in question are very close and the transitional region should be quite narrow.

This conclusion is supported by the microscopic observation of the run product of $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ quenched at 23.1 GPa and 1600°C (820915 in Table 4), which is symbolized as spinel in Figure 5b. A microphotograph of a section made from the product is reproduced in Figure 7a. The phases present along the central line were identified by the microdiffractometry, as shown in the upper margin. Figure 7b shows the backscattered electron image along the border of the area of Pv + Mw. There are some patchy concentrations of perovskite in the Pv + Mw area. However, equigranular spinel and the intergrown texture of perovskite and magnesiowüstite suggest that the product was at or close to equilibrium. As the whole section is presumably almost

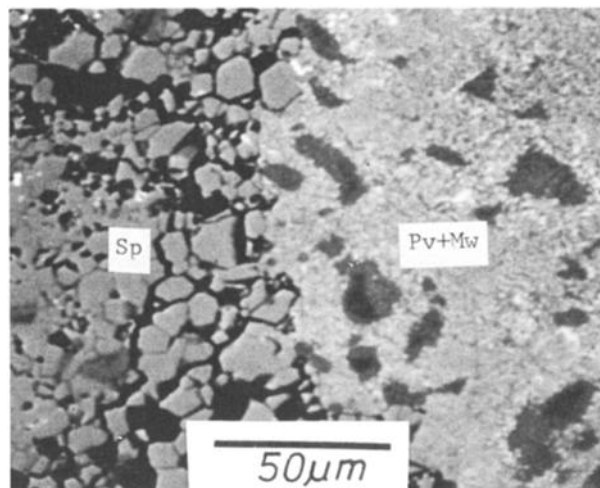


Fig. 7b. Backscattered electron image (BSEI) along the border of area of Pv + Mw. Black parts were scratched off during polishing.

isobaric, the change in phase should be due to the temperature gradient in the sample. As a point 100 μm away from the border of the Pv + Mw area was confirmed to be spinel by X ray diffraction using a 100- μm beam, the area corresponding to the transitional region should be limited to within 50 μm of the Pv + Mw area. The temperature gradient in the sample along the central line is estimated to be less than $1^\circ/\mu\text{m}$, because the temperature at the olivine-spinel interface is about 600°C , the minimum temperature at which the transformation proceeds (E. Ito, unpublished data, 1976). Therefore, considering the slope of -0.0028 GPa/deg for the boundary curve in the dissociation in Mg_2SiO_4 spinel, the pressure interval of the transitional region is estimated to be less than 0.15 GPa for the composition $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ at temperatures close to 1600°C .

GEOPHYSICAL IMPLICATIONS

As briefly mentioned in the introduction, the mineralogy and chemistry of the transition zone and the lower mantle are matters of active debate, several models having been proposed for various depth regions.

In a peridotitic mantle model such as Ringwood's [1975] pyrolite, the olivine-modified spinel transformation can be regarded as the major cause of the 400-km discontinuity, while majorite formation by dissolving of pyroxenes into garnet proceeds over depths of 350–450 km. The lower half of the transition zone (500–670 km depth) is regarded as a combination of spinel (60%) and majorite (40%) [Ito and Takahashi, 1987a; Irifune and Ringwood, 1987]. Recently, Bass and Anderson [1984] compared the elastic velocities and density along an adiabat, initiated at 1400°C and 0 GPa, for various candidate mantle phases and assemblages with seismic mantle properties. For the transition zone, they proposed "piclogite" (80% eclogite, 16% olivine, and trace orthopyroxene) as a better model composition than pyrolite. However, Weidner [1985] showed that the pyrolite model is compatible with the observed seismic velocities down to 670 km depth within the uncertainties of the available mineral physics and seismological data.

Recently, Yagi *et al.* [1987] demonstrated that bulk moduli of majorites in enstatite-pyrope and ferrosilite-almandine solid solutions are close to or slightly smaller than those of common garnets and are about 50 GPa smaller than Jeanloz's [1981] value adopted in Bass and Anderson's calculation. More recently, both compressional and shear wave velocities for $\text{Mg}_4\text{Si}_4\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets have been found to be close to those of pyrope [Weidner *et al.*, 1987]. Such large revisions on majorite elastic data inevitably subject the "piclogite" model to substantial modification, because more than 80% of "piclogite" is in the majorite form in the lower half of the transition zone [Irifune and Ringwood, 1987]. Therefore it appears that the peridotitic or pyrolitic model still has special importance as a base for consideration of the state of the deep mantle. In this context, detailed knowledge of transformations in spinel and majorite is of great significance for the interpretation of the 670-km discontinuity.

The present study demonstrates that the spinel phase with compositions from Mg_2SiO_4 to $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ dissociates into perovskite and magnesio-wüstite at 23.1 GPa and 1600°C . The pressure value for the onset of the dissociation is slightly low compared to that at 670 km depth, namely, 23.7 GPa [Dziewonski and Anderson, 1981], but the differ-

ence is in a reconcilable range when uncertainties in both the experimental pressure and in the depth of the discontinuity are considered. The $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ spinel yields $(\text{Mg}_{0.97}\text{Fe}_{0.03})\text{SiO}_3$ perovskite and $(\text{Mg}_{0.83}\text{Fe}_{0.17})\text{O}$ magnesio-wüstite [Ito *et al.*, 1984]. It is noteworthy that the dissociation is completed within a quite small pressure interval (less than 0.15 GPa) or a depth range less than 4 km, contrary to previous expectations [e.g., Lees *et al.*, 1983]. The sharp contrast in acoustic impedance associated with the dissociation could produce an appreciable reflection when a seismic wave passes upward through the discontinuity [Richards, 1972; Nakanishi, 1988].

Recently, it has been revealed that majorite dissociates, in succession to spinel, into perovskites rich in MgSiO_3 and in $\text{CaMgSi}_2\text{O}_6$ [Liu, 1987] or CaSiO_3 [Liu and Ringwood, 1975] and other minor phases; this dissociation proceeds over the fairly large pressure range of 2–3 GPa [Ito, 1989; Ito and Takahashi, 1987a; Takahashi and Ito, 1987; Irifune and Ringwood, 1987]. Therefore both the dissociations of spinel and majorite could be responsible for the 670-km discontinuity. The former makes the discontinuity very sharp in its initial stage, while the latter broadens it toward the deeper region. These features are consistent with the characteristic of the discontinuity shown in recent seismic models in which the sharp increase in velocity is followed by a high-velocity gradient zone extending down to about 750 km depth [Dziewonski and Anderson, 1981; Grand and Helmberger, 1984]. The resultant lower mantle mineralogy is magnesian perovskite (70%), Ca-bearing perovskite (10%), magnesio-wüstite (20%), and a trace amount of accessory phases including stishovite and a dense Al_2O_3 -rich phase [Ito, 1989; Ito and Takahashi, 1987a; Irifune and Ringwood, 1987].

Alternatively, a lower mantle composed almost exclusively of perovskite has been proposed, together with an abrupt change in composition at the 670-km discontinuity [e.g., Kumazawa, 1982; Liu, 1979; Anderson and Bass, 1986]. However, a chemical change between the upper and lower mantle is no longer an inevitable consequence of the sharpness of the 670-km discontinuity. A large-scale chemical layering of the mantle, such as the concentration of perovskite in the lower mantle, might be possible only through the differentiation process during an extensive melting in the early stage of the Earth's history. Recently, Ito and Takahashi [1987b] demonstrated that magnesian perovskite is actually the liquidus phase at lower mantle conditions in melting experiments on a primitive peridotite. However, they also showed that only a small degree of perovskite fractionation (15%) yields an upper mantle composition consistent with geochemical and cosmochemical constraints with respect to the refractory major elements. Therefore the chemically stratified mantle models in which the lower mantle is regarded as perovskite are not substantiated by the melting experiments.

SUMMARY AND CONCLUSIONS

The stability of MgSiO_3 perovskite in magnesium silicates have been reinvestigated at temperatures from 1000°C to 1600°C and pressures from 22 to 25 GPa. The phases present within 100 μm from the thermocouple junction of the run products have been examined by a microfocused X ray diffractometer to minimize ambiguity in phase stability determination due to the steep temperature gradient in the sample chamber. Results of individual runs are much clearer

than previously [Ito and Yamada, 1982]. The phase boundary curves both between ilmenite and perovskite in MgSiO_3 and between spinel and the assemblage of perovskite plus periclase in Mg_2SiO_4 have been confirmed to have negative Clapeyron slopes and are expressed by the equations $P(\text{GPa}) = 26.8 - 0.0025T(^{\circ}\text{C})$ and $P(\text{GPa}) = 27.6 - 0.0028T(^{\circ}\text{C})$, respectively.

In order to understand the nature of the 670-km discontinuity, the postspinel transformations in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ have been investigated at 1100°C and 1600°C and at pressures varying from 22 to 25.5 GPa. At 1100°C, the postspinel assemblage varies as follows according to bulk iron content: perovskite + magnesiowüstite ($0 \leq \text{Fe}/(\text{Fe} + \text{Mg}) \leq 0.26$), perovskite + magnesiowüstite + stishovite ($0.26 \leq \text{Fe}/(\text{Fe} + \text{Mg}) \leq 0.46$), and magnesiowüstite + stishovite ($0.46 \leq \text{Fe}/(\text{Fe} + \text{Mg}) \leq 1.0$) (Figure 5a). The univariant boundary of spinel - perovskite + magnesiowüstite is located at about 24.5 GPa for $0.22 \leq \text{Fe}/(\text{Fe} + \text{Mg}) \leq 0.46$. The stability relations at 1600°C are similar to those at 1100°C. However, all phase boundaries of the perovskite-forming reactions shift both to lower pressures and to higher $\text{Fe}/(\text{Fe} + \text{Mg})$ with increasing temperature, and the univariant boundary at 1600°C is located at about 23.0 GPa for $0.26 \leq \text{Fe}/(\text{Fe} + \text{Mg}) \leq 0.58$ (Figure 5b). The magnesian spinel (with $\text{Fe}/(\text{Fe} + \text{Mg}) \leq 0.22$ at 1100°C and ≤ 0.26 at 1600°C) dissociates into perovskite + magnesiowüstite after passing through the transitional three-phase region of spinel + perovskite + magnesiowüstite. The pressure interval of the transitional region is less than 0.15 GPa for composition with $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.2$ at 1600°C.

The dissociation pressure in magnesian spinel is in agreement with that at the 670-km discontinuity. The dissociation is complete within a so small depth range (less than 4 km) that it could act as an effective reflector of seismic waves. In a peridotitic mantle model, the dissociations of both spinel and majorite could be responsible for the 670-km discontinuity. The former makes the discontinuity very sharp in its initial stage, while the latter broadens it toward deeper region. These features are consistent with the character shown in recent seismic models. Alternative models in which the 670-km discontinuity is regarded as a chemical change may not be necessary to account for the sharpness of the discontinuity and are not supported by the recent melting experiment on a primitive peridotite either.

Acknowledgments. We are grateful to S. Akimoto for his critical reading of the manuscript and valuable comments. We thank Y. Matsui for his support. Critical reading of manuscript by K. Leinenweber is much appreciated. Comments from two reviewers, C. R. Bina and A. Navrotsky, were of great help in improving the manuscript. This research was partially supported by grants 61213011 and 62540621 from the Ministry of Education, Science and Culture, Japan.

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- E. Ito, Institute for Study of the Earth's Interior, Okayama, Misasa, Tottori-ken 682-02, Japan.
- E. Takahashi, Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152 Japan.

(Received August 12, 1988;
revised March 15, 1989;
accepted April 10, 1989.)