Post-Spinel Transition in Fe_2SiO_4

Tomoo Katsura, Atsushi Ueda[1], Eiji Ito, and Koh-ichi Morooka[2]

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

The phase boundary of the dissociation of Fe_2SiO_4 spinel to wüstite+stishovite was investigated at temperatures of 1000-1600 K and pressures of 14-19 GPa using a 6-8 type multianvil apparatus. $FeCl_2$ was used as a catalyst to enhance the reaction rate, and complete the dissociation within 180 min above 1200 K. The catalyst also made it possible to conduct reversal runs. Excess wüstite and iron were added to the starting material in order to minimize the Fe^{3+} contents in spinel and wüstite. The dissociation reaction occurs at 17.3 GPa. No temperature dependence on the transition pressure was observed in the temperature range investigated.

1. INTRODUCTION

$(Mg,Fe)_2SiO_4$ olivine is considered to be the most abundant mineral in the upper mantle [Ringwood, 1979]. The 410-km and 660-km seismic discontinuities are usually accounted for by the olivine - modified spinel transition and the dissociation of spinel to perovskite+magnesiowüstite, respectively, in the system Mg_2SiO_4-Fe_2SiO_4. Hence, a knowledge of the phase relations in this system is indispensable for elucidating the constitution of the Earth's mantle. Accordingly, the phase relations in this system have been studied by many workers [c. f., Yagi et al., 1987; Akaogi et al., 1989; Ito and Takahashi, 1989; Katsura and Ito, 1989; Morishima et al., 1994]. The detailed phase relations of the olivine - modified spinel - spinel transitions have been clarified in the whole compositional range of the system. Those of the post-spinel transitions, however, have not yet been established for the Fe-rich part of the system.

[1] Now at Nikkato Co., Japan.

[2] Now at Mitsubishi Material Co., Japan.

More than 20 years ago, *Basset and Takahashi* [1970] and *Basset and Ming* [1972] reported that Fe_2SiO_4 spinel dissociates to wüstite (Fe_xO) and stishovite (SiO_2). The Fe/O ratio of wüstite is slightly smaller than unity [*Hazen and Jeanloz*, 1984]. Therefore the reaction should be written as

$$Fe_2SiO_4 = 2Fe_xO + SiO_2 + 2(1-x)Fe \quad (1)$$
$$\text{spinel} \quad \text{wüstite} \quad \text{stishovite} \quad \text{iron}$$
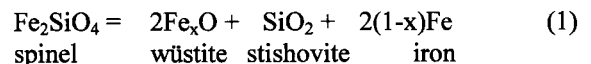
Kawada [1977] and *Ohtani* [1979] attempted to determine the phase boundary of this dissociation reaction. However, their results showed a striking disagreement with each other; *Kawada* [1977] proposed a positive (dP/dT) slope of the phase boundary whereas *Ohtani* [1979] proposed a negative one.

Morooka [1992] tried to determine the phase boundary more precisely by careful examination of the run products using scanning electron microscopy and microfocused X ray diffractometry. However, he observed the presence of three phase, that is, spinel+wüstite+stishovite over a 4 to 5 GPa pressure interval in the range of 15 to 20 GPa (Figure 1). Figure 2 is a typical example of the presence of three phases in a run product, indicating that the dissociation of spinel to wüstite+stishovite was not completed. Because of the sluggishness of the reaction, *Morooka* [1992] was not able to determine the phase boundary precisely.

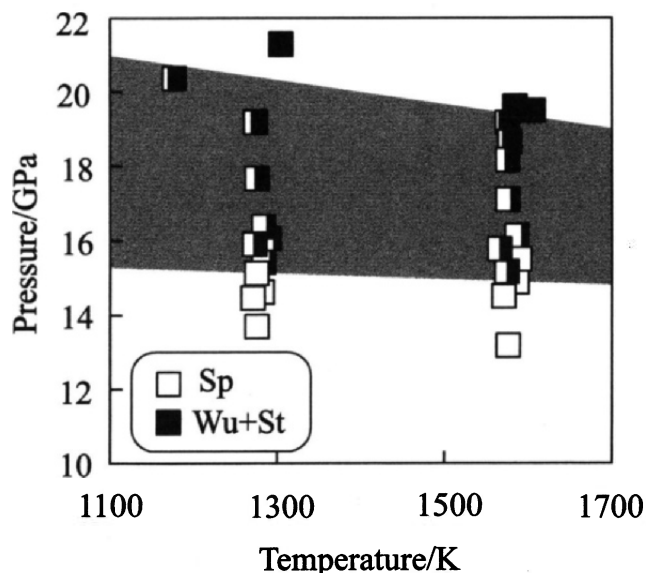One possible reason why the previous workers failed in

Figure 1. The synthesis diagram of Fe_2SiO_4 at pressures of 13-22 GPa and temperatures of 1200-1500 K from *Morooka* [1992]. The open and solid squares denote presence of spinel and wüstite+stishovite, respectively. A 5-GPa pressure interval shows the presence of three phases, that is, spinel+wüstite+stishovite.

determining the phase boundary is that the compositions of spinel and wüstite could have changed during experiments by oxidation. The Fe/O ratio in wüstite can vary, for example, from 0.96 to 0.85 at ambient pressure [*Hazen and Jeanloz*, 1984]. *Tobe* [1995] showed that Fe_2SiO_4 spinel forms a complete solid solution with Fe_2O_3 magnetite above 10 GPa. These facts suggest that when oxidation of the system occurs, iron will disappear from Equation (1), and instead, spinel+wüstite+stishovite will coexist over a certain pressure interval.

A second possible explanation is a slow reaction rate of the dissociation reaction, as implied by Figure 2. Stishovite has a very high melting point, for example, 3300 K at 17 GPa [*Zhang et al.*, 1993], whereas, the temperatures of the experiments made by the previous workers are below 1700 K. This temperature difference suggests that stishovite is very slow to react at temperatures well below its melting point.

The third possible source of uncertainty is a pressure drop while heating. Typically, in usual high-pressure experiments made in a multianvil apparatus, pressure is first applied to a desired value by increasing the oil pressure of the hydraulic press, and then temperature is raised to a desired value while the oil pressure is held. When the sample is heated, the pressure medium and gasket material are also heated and flow from the pressure cell more readily than at room temperature condition. Moreover, sintering

and phase transitions within both the sample and pressure medium decrease the material volume in the pressure cell. Consequently, the sample pressure may decrease during heating, even if the oil pressure is held. If the pressure of the sample before heating is a little above the phase boundary, it will be lowered from the stability field of wüstite-stishovite to that of spinel on heating, resulting in cessation of the reaction.

In order to overcome these problems, we improved the experimental techniques as follows. First, we add excess metallic iron and wüstite to starting materials in order to keep the redox state of samples along the IW buffer, resulting in minimum amounts of Fe^{3+} in spinel and wüstite. Secondly, we add a small amount of catalyst to the staring material; the catalyst adopted here is mainly $FeCl_2$. The catalyst enhances and completes dissociation reaction, and also makes it possible to form spinel from wüstite+stishovite. Thirdly, we use anvils with larger truncated edge length than used in the previous studies. The large truncation makes the heating volume smaller relative to the pressure cell so that the pressure drop on heating will be smaller. The large truncation also enables more efficient thermal insulation, which minimizes the flow of gasket materials.

2. EXPERIMENTAL PROCEDURE

The starting material of 'normal' experiments was a mixture of fayalite, wüstite, iron, and catalyst with molar ratio of 100:20:10:5. The catalyst for the experiments
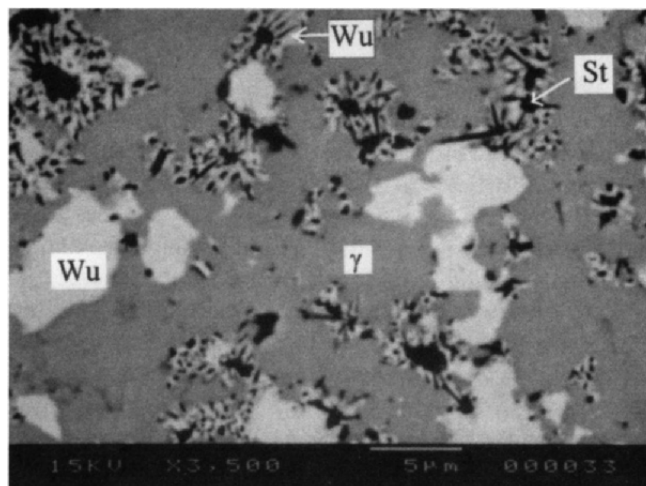

Figure 2. The back-scattered electron image of the run product from the spinel+wüstite mixture without a catalyst at 1300 K and 21 GPa. The solid bright and gray parts are wüstite and spinel, respectively. The fine grained mixture of white and black grains is an aggregate of wüstite+stishovite.

above 1200 K was $FeCl_2$, whereas, at 1000 K it was an even molar mixture of $FeCl_2$ and CsCl. The starting material of the 'reversal' experiments was a 100:105:120:15 mixture of hematite, iron, quartz, and $FeCl_2$. In these runs we used submicron powders of hematite and quartz which are expected to be very reactive. The hematite+iron and quartz, respectively, will initially become wüstite+iron and stishovite at high-temperature and high-pressure, and then will form spinel.

The high-pressure phase equilibrium experiments were carried out using a 6-8 type multianvil apparatus [*Ito et al.*, 1984]. The truncated edge length of the anvils and the edge length of the octahedral $MgO+5\%Cr_2O_3$ pressure medium were 5.0 and 11.8 mm, respectively, whereas, those used by *Morooka* [1992] were 3.0 and 7.0 mm. The generated sample pressure was calibrated against the oil pressure of the hydraulic press using semiconductor-metal transitions in ZnS and GaAs at ambient temperature and the $\alpha-\beta$ transition in Mg_2SiO_4 at 1400 K. The results of the calibrations at ambient and high temperatures agree well, suggesting a very small temperature effect on pressure generation.

The sample assembly is shown schematically in Figure 3. The starting material is loaded in an Fe capsule. The heater is composed of $LaCrO_3$. The heater and capsule are electrically insulated by a MgO sleeve. The temperature outside the sample is monitored by a $W_3Re_{97}-W_{25}Re_{75}$ thermocouple with 0.05 mm diameter. The thermocouple and heater are electrically insulated by ZrO_2 sleeves.

Sample pressure was increased first by increasing the oil pressure, then the temperature was increased to the desired value at constant oil pressure. Experiments were made in the temperature range of 1000 to 1600 K, and experimental durations were 5-420 min. The sample was quenched by shutting off the supplied electric power, and sample pressure was decreased at a rate of 1 GPa/hour.

Recovered samples were mounted in epoxy resin and made into polished sections cut parallel to the longitudinal axis of the cylindrical heater so that the changes in phases and textures in the run products due to the temperature gradient could be observed. Phases present in the samples were identified by microfocused X ray diffractometry (MFXD). Phase textures and chemical compositions, respectively, were examined using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

3. RESULTS AND DISCUSSION

Experimental conditions and results are summarized in Table 1.
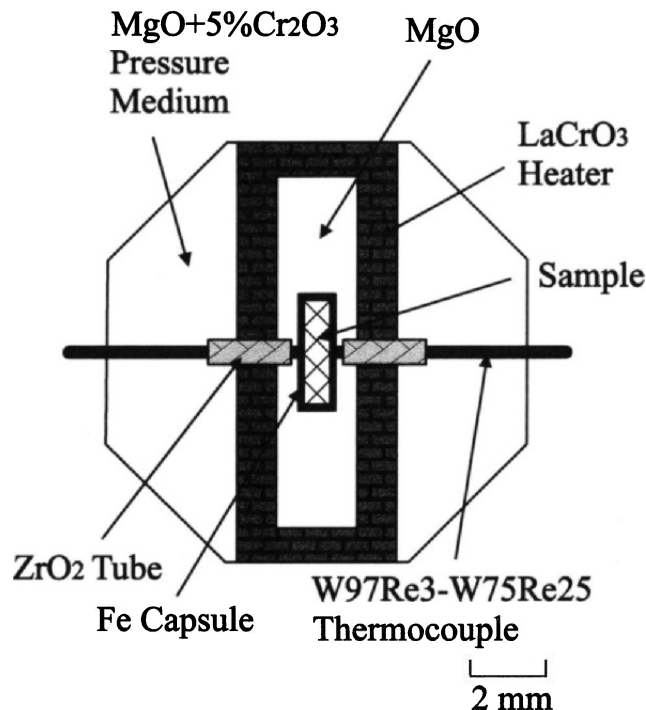
At temperatures above 1200 K, the observed phase

Figure 3. Schematic drawing of the furnace assembly.

assemblages of the normal runs were stishovite+wüstite+iron above 17.4 GPa (Figure 4a) and spinel+wüstite+iron below 17.2 GPa (Figure 4b). The texture observed by *Morooka* [1992], showing the incomplete dissociation reaction stops, was not seen in experiments made at conditions above 1200 K, suggesting that the $FeCl_2$ catalyst completes the dissociation reaction. No Cl-bearing phase could be found by SEM and EPMA observations. This is probably because most of the Cl-bearing phase was removed and/or dissolved in water while polishing. The area analysis by EPMA, however, showed a small amount of Cl present along the grain boundaries of the primary phases. It is noted that no variation in the phase assemblage associated with the temperature gradient was observed in any run product.

In contrast, the dissociation reaction was not completed in the experiments at 1000 K. The MFXD showed that the products at 17.7 and 18.4 GPa contain stishovite+spinel+ wüstite+iron whereas that at 17.2 GPa contains only spinel+ wüstite+iron. In these low temperature runs, the mixture of $FeCl_2$+CsCl was used for a catalyst instead of $FeCl_2$ for further enhancement of the reaction rate. Nevertheless, the reaction was not completed. The experimental temperature of 1000 K is too low to complete the dissociation reaction using the present method.
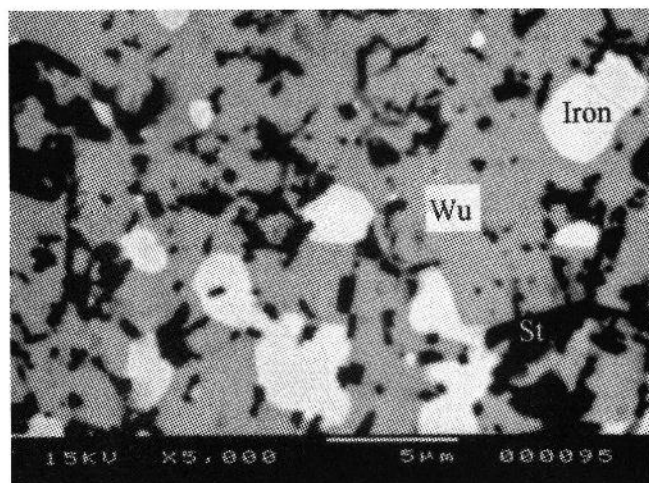
a
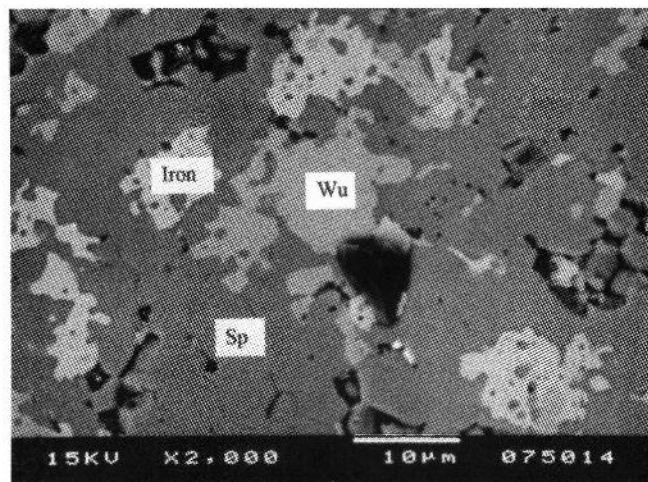
b
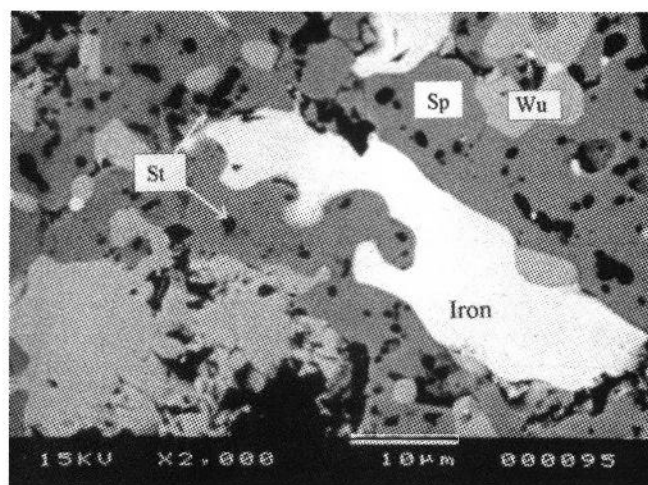
c

The reversal runs, using hematite+iron+quartz+FeCl$_2$ as the starting material, were conducted at 1200 K and 16.9 GPa, and at 1580 K and 16.7 GPa. At the former conditions, wüstite, iron, and a silica mineral were observed by SEM and EPMA analysis, but spinel was not found. However, a small amount of spinel was detected by MFXD. On the contrary, the run product at 1580 K shows that a large amount of spinel was formed, although a small amount of stishovite is still present (Figure 4c). Generally, reversal runs are very difficult to conduct for high-pressure dissociation reactions. One reason for this difficulty is that each of the dissociated phases (in this case, wüstite and stishovite) is stable in the stability field of the original phase (spinel). Another reason is that each of the dissociated phases usually has a higher melting point than the original phase if the dissociated phases have a eutectic relationship. In this study, the first successful reversal run for the post-spinel transition was achieved.

The phase diagram constructed on the basis of the observations described above (Figure 5) shows that the dissociation of Fe$_2$SiO$_4$ spinel to wüstite+stishovite occurs at 17.3 GPa with no temperature effect on the transition pressure. A very small or non-existent temperature dependence on the transition pressure is also suggested by the observation that there was no variation in phase assemblage due to the temperature gradient across the sample.

The present phase boundary is located at a lower pressure than those of *Kawada* [1977] and *Ohtani* [1979], and higher pressure than that of *Morooka* [1992]. One possible explanation for the discrepancy between this study and *Ohtani* [1979] is that *Ohtani* [1979] was not able to observe precisely the beginning of the dissociation reaction because of the sluggish kinetics. The kinetic effect should decrease with increasing temperature, and, therefore, the over-pressure needed to enhance the dissociation reaction should also decrease with increasing temperature. This could explain why *Ohtani* [1979] observed a negative pressure dependence.

The reason for the discrepancy between this study and

Figure 4. Back-scattered electron images of the run products with the FeCl$_2$ catalyst. (a) at 17.4 GPa and 1200 K from the mixture of fayalite, wüstite, and iron with FeCl$_2$. The run product is composed of stishovite, wüstite and iron with FeCl$_2$. (b) at 17.2 GPa and 1200 K from the mixture of fayalite, wüstite, and iron with FeCl$_2$. The run product is composed of spinel, wüstite, and iron. (c) at 16.2 GPa and 1575 K from the mixture of quartz, hematite, and iron with FeCl$_2$. The run product is composed mainly of spinel, wüstite, and iron, although a small amount of stishovite is found.

TABLE 1.   Experimental Conditions and Results

Run#	Temperature (K)	Pressure (GPa)	Duration (min)	Phases Present
(Normal Run)				
64	1200	19.8	180	St-Wu-I
67	1200	14.8	180	Sp-Wu-I
68	1200	17.4	180	St-Wu-I
70	1200	16.2	180	Sp-Wu-I
71	1200	16.9	180	Sp-Wu-I
75	1400	17.2	20	Sp-Wu-I
77	1400	17.7	60	St-Wu-I
88	1000	18.4	18	St-Sp-Wu-I
89	1000	17.2	300	Sp-Wu-I
90	1000	17.7	300	St-Sp-Wu-I
95	1600	17.4	10	St-Wu-I
(Reversal Run)				
97	1200	16.9	420	St-Sp-Wu-I
98	1580	16.7	10	St-Sp-Wu-I

Sp, St, Wu, and I in the column 'phases present' denote spinel, stishovite, wüstite and iron, respectively.

Kawada [1977] could be that his samples were more oxidized than the IW buffer. Fe_2SiO_4 spinel can make a complete solid solution with Fe_3O_4 spinel, whereas, the maximum Fe^{3+} content in wüstite is much less than Fe_3O_4 spinel [*Hazen and Jeanloz*, 1984]. Therefore, once the system is oxidized, the Gibbs's free energy of spinel is decreased by $RT\ln(a^{Spinel}_{Fe2SiO4})$, whose absolute value is much larger than $RT\ln(a^{Wüstite}_{FeO})$, where R and T are the gas constant and absolute temperature, and a^x_y denotes the activity of component y phase x. Hence, the stability field of spinel increases to higher pressures with increasing oxidation of the system. This hypothesis also explains the positive pressure dependence of *Kawada* [1977], because the absolute value of $RT\ln(a^{Spinel}_{Fe2SiO4})$, increases with increasing temperature. In fact, the Fe capsules used in this study were found to be partially oxidized. Without excess iron, the spinel and wüstite in the present study would be more oxidized than those along the IW buffer as well.

The reason why the boundary obtained by *Morooka* [1992] is located at a lower pressure than the present study is probably because the pressures in *Morooka's* [1992] samples were decreased while heating as a result of his smaller truncated edge length (3.0 mm) than that used in the present study (5.0 mm).

4. CONCLUDING REMARKS

1)   The dissociation of Fe_2SiO_4 spinel to wüstite (FexO)+stishovite (SiO_2) has a very slow reaction rate. In order to determine the phase boundary of this reaction at high pressure, use of a catalyst was required. In this study,
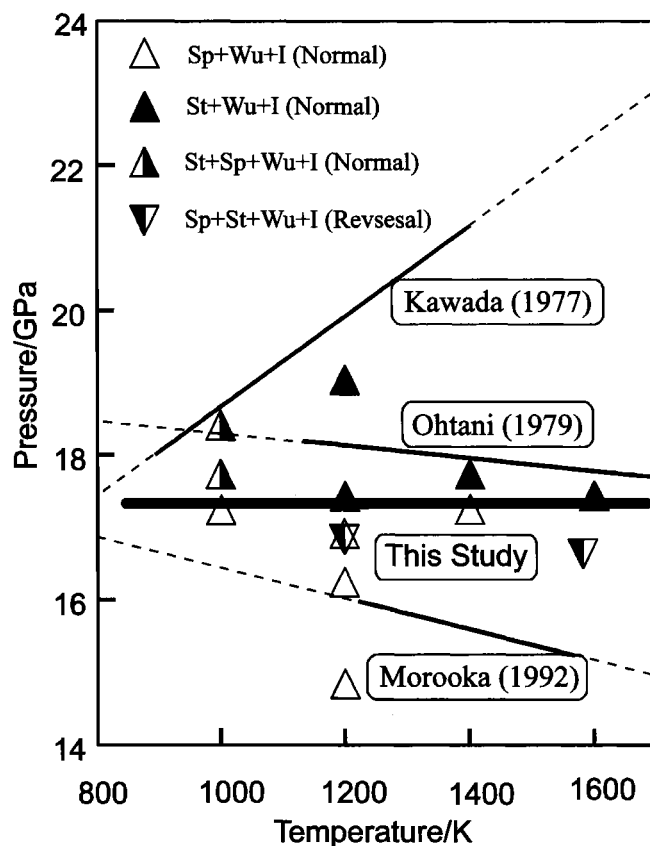

Figure 5. The phase diagram of the dissociation of Fe_2SiO_4 spinel to wüstite and stishovite. Open and solid symbols denote presence of spinel and stishovite in the run products, respectively. Upper and lower triangles denote the normal and reversal runs, respectively.

the FeCl$_2$ catalyst was used to enhance and complete the dissociation reaction above 1200 K, and also made it possible to conduct a reversal experiment at 1580 K. Generally, in high-pressure dissociation reactions, such as post-spinel transitions, accurate determination of the phase relations is very difficult because the dissociated phase are slow to react. Therefore, use of a catalyst is useful to study the phase relations of the post-spinel transitions [c. f. Katsura and Ito, 1996].

2) To study precisely the phase relations of Fe-rich phases, an oxygen buffer is necessary in order to keep redox condition. Without a buffer, samples are easily oxidized or reduced during experiments. Even though experimental temperatures in this study were relatively low for the multianvil experiment, oxidation of iron was clearly observed.

3) The experimental pressure of small pressure cells can become lowered by heating. To keep experimental pressure constant while heating, use of the largest possible pressure cells is desirable.

4) The transition pressure of the dissociation of Fe$_2$SiO$_4$ spinel is 17.3 GPa at temperatures of 1000-1600 K. Although the post-spinel transition in Mg$_2$SiO$_4$ has a negative (dP/dT) slope of the phase boundary, that in Fe$_2$SiO$_4$ has a flat (dP/dT=0) slope.

REFERENCES

Akaogi, M., E. Ito, and A. Navrotsky, The olivine-spinel transformations in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$; calorimetric measurements, thermochemical calculation, and geophysical application, *J. Geophys. Res.*, 94, 15671-15685, 1989.

Basset, W. A. and L. Ming, Disproportionation of Fe$_2$SiO$_4$ to 2FeO+SiO$_2$ at pressures up to 250 kbar and temperatures up to 3000 °C, *Phys. Earth Planet. Int.*, 6, 154-160, 1972.

Basset, W. A., and T. Takahashi, Disproportionation of Fe$_2$SiO$_4$ to 2FeO+SiO$_2$ at high pressure and temperature, *EOS Trans. AGU*, 51, 828, 1970.

Hazen, M. R. and R. Jeanloz, Wüstite (Fe$_{1-x}$O): a review of its defect structure and physical properties, *Rev. Geophys. Space. Phys.*, 122, 37-46, 1984.

Ito, E., and E. Takahashi, Y. Matsui, The mineralogy and chemistry of the lower mantle: an implication of the ultrahigh-pressure phase relations in the system MgO-FeO-SiO$_2$, *Earth Planet. Sci. Lett.*, 67, 238-248, 1984.

Ito, E. and E. Takahashi, Postspinel transitions in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ and some geophysical implications, *J. Geophys. Res.*, 94, 10,637-10,646, 1989.

Katsura, T., and E. Ito, The system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ at high pressures and temperatures: precise determination of stabilities of olivine, modified spinel, and spinel., *J. Geophys. Res.*, 94, 15663-15670, 1989.

Katsura, T. and E. Ito, Determination of Fe-Mg partitioning between perovskite and magnesiowüstite, *Geophys. Res. Let.*, 23, 2005-2008, 1996.

Kawada, K., The system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$ at high pressures and temperatures and the earth's interior, *Ph. D. thesis of University of Tokyo*, pp. 187, 1977.

Morishima, H., T. Kato, M. Suto, E. Ohtani, S. Urakawa, W. Utsumi, O. Shimomura, and T. Kikegawa, The phase boundary between α-and β-Mg$_2$SiO$_4$ determined by in situ X-ray observation, *Science*, 265, 1202-1203, 1994.

Morooka, K., Dissociation of γ-Fe$_2$SiO$_4$ and the reaction between molten iron and silicate melts at high-pressure and high-temperature, *Master thesis of Okayama University*, pp. 57, 1992.

Ohtani, E., Melting relation of Fe$_2$SiO$_4$ up to about 200 kbar, *J. Phys. Earth.*, 27, 189-208, 1979.

Ringwood, A. E., *Origin of the Earth and Moon*, Springer-Verlag, New York, pp. 295, 1979

Tobe, H., *Master thesis of Osaka University*, pp.61, 1995. (in Japanese)

Yagi, T., M. Akaogi, O. Shimomura, T. Suzuki, and S.-I. Akimoto, In situ observation of the olivine-spinel transformation in Fe$_2$SiO$_4$ using synchrotron radiation, *J. Geophys. Res.*, 92, 6207-6213, 1987.

Zhang J., R. C. Liebermann, T. Gasparik, C. T. Herzberg, and Y. Fei, Melting and subsolidus relations in SiO$_2$ at 8-14 GPa, *J. Geophys. Res.*, 98, 19785-19793, 1993.

Tomoo Katsura, Atsushi Ueda, Eiji Ito, and Koh-ichi Morooka, Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken, 682-01 Japan