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The effect of water on the high-pressure phase boundaries in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$

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Abstract. The phase boundaries between olivine, wadsleyite and ringwoodite have been studied comparatively under anhydrous and hydrous conditions with a fixed H_2O content of 1 wt% at 1673K. By comparing anhydrous and hydrous samples from the same experimental runs, we determined that two-phase coexisting loop in the olivine-wadsleyite boundary shifted towards lower pressure or lower iron content by the effect of H_2O , which is consistent with our previous work [1]. On the other hand, the loop in the wadsleyite-ringwoodite boundary shifted towards higher pressure or higher iron content, and the pressure width of the loop decreased. Thus, the presence of H_2O in the Earth's mantle will sharpen the 520-km seismic discontinuity, deep the depth of the discontinuity.

1. Introduction

H_2O is an important volatile material in the Earth, which may be transported to the Earth's deep mantle by subducting slabs [e.g. 2-4]. Recent experiments clarified that wadsleyite(β) and ringwoodite(γ), which are high pressure polymorphs of olivine(α) and the major high pressure phases constituting the transition zone (410-660 km), can accommodate significant amounts of H_2O (~2-3 wt%) in their crystal structures [5-9]. Such H_2O should affect the nature of the phase transformation of olivine polymorphs, as it changes the densities and the thermodynamic parameters of the anhydrous forms. Some theoretical and experimental studies have been done to clarify the effect of water on the α - β phase boundary. Wood [10] calculated the boundary theoretically, and clarified that the phase boundary shifts towards lower pressure because greater solubility of H_2O in the β phase implies a lower activity of $(\text{Mg,Fe})_2\text{SiO}_4$ in the β phase. Experimental studies [1, 11] also supported this behaviour, but the loop intervals of α and β are controversial and argued to be narrower [1] or wider [10, 11] caused by the effect of H_2O . Because the 410 km seismic discontinuity is considered to be responsible for the α - β phase transformation, it is very crucial to clarify the possibility of the existence of H_2O around the 410 km seismic discontinuity. In addition, there are no experimental data so far for the effect of H_2O on the β - γ phase transformation boundary, in spite of the importance on the nature of the 520 km seismic discontinuity. We have conducted high pressure experiments to clarify the effect of H_2O on the α - β - γ phase boundaries. On the basis of these experimental data, we discuss the nature of the 520 km seismic discontinuities in the mantle transition zone.

2. Experimental procedure

Three hydrous starting compositions (Mg_2SiO_4 , $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ and $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$) with 1 wt% H_2O were used. The starting materials were prepared with mechanical mixtures of MgO , $\text{Mg}(\text{OH})_2$, SiO_2 , and Fe_2SiO_4 powders with appropriate proportions; thus H_2O was introduced by $\text{Mg}(\text{OH})_2$, and ferrous iron was introduced by Fe_2SiO_4 because wustite (Fe_{1-x}O) has a stoichiometric problem.

The corresponding anhydrous starting compositions were also prepared. Pure forsterite was used with a Mg_2SiO_4 composition, and natural San Carlos olivine, with a composition of $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, was used. For the composition of $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$, the appropriate mechanical mixture of Mg_2SiO_4 and Fe_2SiO_4 powders was used. Both anhydrous and hydrous samples were enclosed into a welded $\text{Au}_{75\%}\text{Pd}_{25\%}$ alloy capsule separately before loading into a high pressure cell.

In all experiments, two capsules containing hydrous and anhydrous starting materials were placed symmetrically in one cell assembly to directly compare the difference between the two materials under the same pressure and temperature conditions.

High pressure experiments were conducted using two MA8-type (KAWAI-type) high pressure apparatus (EUDES-700 and ORANGE-2000) at Ehime University. Below ~ 15 GPa experiments, EUDES-700 press was used, and ORANGE-2000 press was used above ~ 15 GPa experiments. The edge lengths of truncation on the second-stage cubic anvil corner were 3.5 mm for EUDES-700, and 3.0 mm for ORANGE-2000. The pressure mediums are octahedral semi-sintered magnesia doped with 17 wt % CoO with the edge length of 9.5 mm for EUDES-700, and 9.0 mm for ORANGE-2000. We adopted a cylindrical platinum heater with a wall thickness of 30 μm . The cell assembly used in the ORANGE-2000 experiment is shown in Figure 1. The cell assembly used in the EUDES-700 experiment is the almost the same with some dimensional differences.

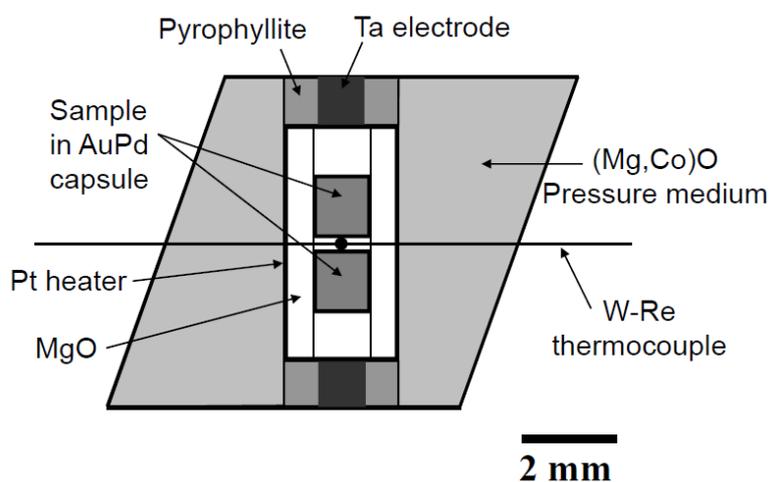


Figure 1. An example of cell assembly used in the present experiment

A careful pressure calibration was done on the basis of the present anhydrous experiments of α - β - γ phase transitions based on the thermochemical phase diagram [12] at 1673K. So the pressure conditions of the coexisting run product of α - β or β - γ were critically constrained by fitting our anhydrous data on the loop by Akaogi et al.[12] (See Figure 2a). In this case, the relative pressure precision is estimated to be about 0.05 GPa, and the others without the coexistence is estimated to be about 0.2 GPa.

Temperature was measured with a W_{97}Re_3 - $\text{W}_{75}\text{Re}_{25}$ thermocouple, whose hot junction was placed in the center of the furnace assembly. The fluctuation of temperature throughout the run was kept within ± 5 $^{\circ}\text{C}$ in each condition, but no pressure correction was made for the emf of the thermocouple.

In high-pressure and high-temperature experiments, pressure was applied first to the target ram loads and then the temperature was kept for mainly 30 minutes, and then the run was quenched by turning off the electric power.

The polished section of the recovered run product was prepared in order to identify the phases present and to measure their chemical compositions. Analysis was done on the sample near the hot junction of the thermocouple. A wave-dispersive electron probe microanalyser (EPMA) and a microfocused X-ray diffractometer were used for these purposes.

3. Results and discussion

The experimental conditions and the results are summarized in Table 1, and the high pressure phase diagrams of α - β - γ in the system Mg_2SiO_4 - Fe_2SiO_4 are shown in anhydrous (Figure 2a) and hydrous (Figure 2b) conditions from our experimental data. The experiments were conducted from 11.6 to 20.6 GPa at a constant temperature of 1673K in the system Mg_2SiO_4 - Fe_2SiO_4 with 1 wt% H_2O .

Table 1. Experimental conditions and the results (T=1400°C)

Run No.	P (GPa)	dry	wet	dry (Fe/(Mg+Fe)%)				wet (Fe/(Mg+Fe)%)			
				α	β	γ	<i>Kd</i>	α	β	γ	<i>Kd</i>
<i>Mg₂SiO₄ system</i>											
E-1394	12.3	α	α	0	-	-	-	0	-	-	-
E-1398	13.2	α	α	0	-	-	-	0	-	-	-
E-1401	14.4	α	α	0	-	-	-	0	-	-	-
E-1403	14.6	α	α	0	-	-	-	0	-	-	-
E-1405	14.8	β	β	-	0	-	-	-	0	-	-
OS-481	15.9	β	β	-	0	-	-	-	0	-	-
OS-484	18.5	β	β	-	0	-	-	-	0	-	-
OS-494	19.0	β	β	-	0	-	-	-	0	-	-
OS-498	19.2	β	β	-	0	-	-	-	0	-	-
OS-509	19.4	γ	γ	-	-	0	-	-	-	0	-
OS-491	19.5	γ	γ	-	-	0	-	-	-	0	-
OS-488	20.6	γ	γ	-	-	0	-	-	-	0	-
<i>(Mg_{0.9}Fe_{0.1})₂SiO₄ system</i>											
E-1558	12.3	α	α	8.8	-	-	-	8.7	-	-	-
E-1419	12.6	α	α	8.9	-	-	-	10.4	-	-	-
E-1559	13.0	α	α	8.4	-	-	-	8.5	-	-	-
E-1570	13.7	α + β	α + β	8.7	16.4	-	2.1	5.7	17.6	-	3.5
E-1582	13.8	α + β	α + β	7.2	13.9	-	2.1	4.8	11.9	-	2.7
E-1424	13.9	α + β	β	5.8	12.6	-	2.3	-	10.4	-	-
E-1579	14.1	β	β	-	10.0	-	-	-	10.0	-	-
E-1413	14.3	β	β	-	9.1	-	-	-	10.3	-	-
E-1409	14.8	β	β	-	8.5	-	-	-	10.1	-	-
E-1567	15.2	β	β	-	7.7	-	-	-	11.2	-	-
E-1406	15.3	β	β	-	9.5	-	-	-	10.2	-	-
OS-535	15.7	β	β	-	8.7	-	-	-	10.4	-	-
OS-547	16.7	β	β	-	8.6	-	-	-	10.4	-	-
E-1563	17.1	β + γ	β	-	9.0	14.6	1.7	-	11.3	-	-
OS-542	17.4	β + γ	β	-	8.1	14.1	1.9	-	10.4	-	-
OS-550	17.5	β + γ	β	-	8.0	13.0	1.7	-	10.4	-	-
OS-530	18.4	γ	γ	-	-	8.6	-	-	-	10.3	-
OS-524	19.5	γ	γ	-	-	8.9	-	-	-	10.4	-
OS-521	20.6	γ	γ	-	-	8.7	-	-	-	9.7	-
<i>(Mg_{0.8}Fe_{0.2})₂SiO₄ system</i>											
E-1417	11.6	α	α	19.7	-	-	-	20.8	-	-	-
E-1415	12.3	α	α	21.1	-	-	-	19.2	-	-	-
E-1439	12.5	α + γ	α	20.7	-	43.1	2.9	20.5	-	-	-
E-1435	12.8	α + γ	α + γ	16.2	-	42.0	3.7	17.8	-	44.7	3.7
E-1412	13.8	β	β	-	21.6	-	-	-	21.1	-	-
E-1410	14.7	β + γ	β	-	20.6	30.9	1.7	-	21.0	-	-
OS-629	15.3	β + γ	β	-	17.7	26.0	1.6	-	20.8	-	-
E-1408	15.4	β + γ	β + γ	-	17.6	26.9	1.7	-	20.1	28.2	1.6
OS-634	16.6	γ	β + γ	-	-	20.1	-	-	14.6	20.5	1.5

All annealing times were 30 minutes except for OS-498 and E1559 (15 minutes).

$Kd = (\text{Fe/Mg})_{\text{high pressure phase}} / (\text{Fe/Mg})_{\text{low pressure phase}}$

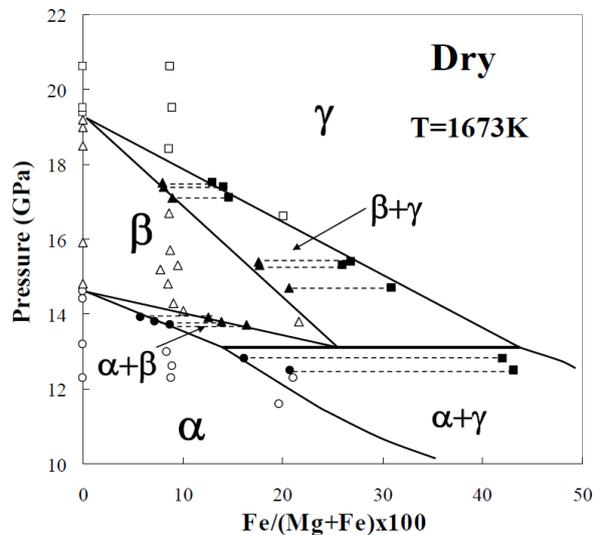


Figure 2a. High pressure phase diagram of olivine in anhydrous condition. The solid line is from Akaogi et al [12] (See text).

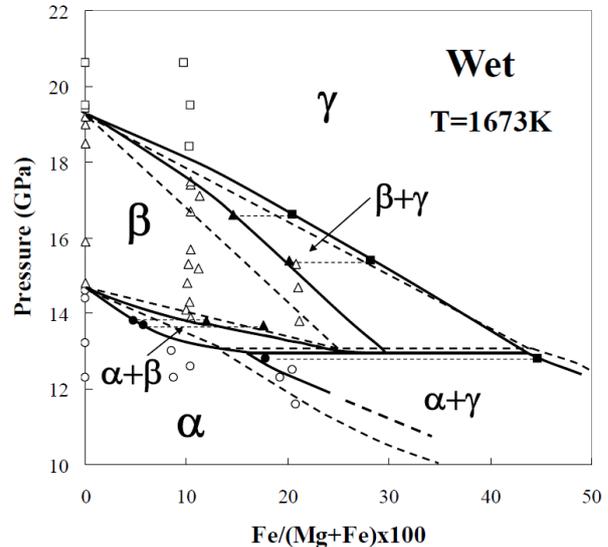


Figure 2b. High pressure phase diagram of olivine in hydrous condition (H₂O 1 wt%). The broken line is from Akaogi et al [12] under anhydrous condition.

In the Mg₂SiO₄ system, no difference in the phase boundaries of the α - β and β - γ between the anhydrous and hydrous (H₂O 1 wt%) systems is observed within the pressure interval of 0.2 GPa, indicating that the phase boundary change caused by H₂O is not greater than 0.2 GPa.

In the (Mg_{0.9}Fe_{0.1})₂SiO₄ system, however, significant change in the α - β and β - γ coexisting loop boundaries are observed by the effect of H₂O 1 wt%. Coexistence of α and β phases appears at pressure of 13.7 GPa (Run E-1570) in both anhydrous and hydrous system, but the iron concentration in the α phase in the hydrous system ((Fe/Mg+Fe)%=5.7) is much smaller than that in the anhydrous system ((Fe/Mg+Fe)%=8.7). Consequently the iron partitioning (Kd) between the α and β phases in the hydrous system ($Kd=3.5$) is much larger than that in the anhydrous system ($Kd=2.1$). At 13.8 GPa (Run E-1582), the coexistence is still observed in both the anhydrous and hydrous systems, but the iron concentration in the α and β phases in the hydrous system is much smaller than that in the anhydrous system. Still more, at 13.9 GPa (Run E-1424), coexistence of the α and β phases is still observed in the anhydrous system, whereas only the β phase starts to exist above this pressure.

Thus, the phase boundary between α and β in the hydrous condition with 1 wt% H₂O shifted towards the lower pressure side compared to the anhydrous boundary; this result is consistent with that reported by Chen et al. [1].

While in the β - γ transition in (Mg_{0.9}Fe_{0.1})₂SiO₄ with 1 wt% H₂O, the boundary shifted towards the higher pressure side of ~0.8 GPa compared to the anhydrous boundary. At 17.1 GPa (Run E-1563), coexistence of the β and γ phases starts to appear in the anhydrous system, but the β phase still appears in the hydrous system. This combination in the anhydrous and hydrous systems continues up to 17.5 GPa (Run OS-550), and the single γ phase appears at 18.4 GPa (Run OS-530) in both anhydrous and hydrous systems. This result also shows that the pressure width of the coexisting loop of β and γ phases in the composition of (Mg_{0.9}Fe_{0.1})₂SiO₄ decreases to ~0.5 GPa under hydrous conditions with 1 wt% H₂O, whereas that under anhydrous conditions has the intervals of ~1.0 GPa [12].

Thus, the loop in the β - γ boundary shifted towards higher pressure or higher iron content, and the pressure width of the loop decreased with the effect of H₂O.

In $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ system, coexistence of α and γ phases appears at a pressure of 12.5 GPa (Run E-1439), whereas only the α phase still exists at this pressure. At 12.8 GPa (Run E-1435), coexistence of α and γ phases exist, and transformed to the single β phase at 13.8 GPa (Run E-1412) in both anhydrous and hydrous conditions.

At 14.7 GPa (Run E-1410), however, coexistence of β and γ phases appears in the anhydrous condition, whereas only the β phase still exists under hydrous conditions at this pressure. This combination continues to 15.3 GPa (Run OS-629), but at 15.4 GPa (Run E-1408), coexistence of β and γ phases starts to appear under hydrous conditions.

Finally at 16.6 GPa (Run OS-634), single γ phases start to exist under anhydrous conditions, whereas coexistence of β and γ phases still exists under hydrous conditions.

These results indicate that the loop of the β - γ boundary shifted towards higher pressure or higher iron content, and the pressure width of the loop decreased with the effect of H_2O similarly to the $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ system. Thus, the stability region of the β phase expands and the pressure width of the loop decreased in both phase boundaries of α - β and β - γ .

The interpretation of the above results can be made by the partition behaviour of H_2O between α - β - γ , i.e. $[\text{H}_2\text{O}]_\alpha < [\text{H}_2\text{O}]_\beta > [\text{H}_2\text{O}]_\gamma$. Chen et al. [1] has already reported that the partitioning coefficient of H_2O between α and β ($[\text{H}_2\text{O}]_\beta/[\text{H}_2\text{O}]_\alpha$) is ~ 5 within the α - β coexisting loop, indicating that the β phase can take up to 5 times more water than the α phase at the same P-T condition. In addition, we have already confirmed the β phase can take up to ~ 2 times more water than the γ phase at the same P-T conditions [13]. These results are quite consistent with the present phase boundary changes under hydrous condition.

The present result shows that the β - γ transition in mantle olivine Fe content (~ 10 mol%) with H_2O 1 wt% occurs at higher pressure (~ 0.7 GPa, which is corresponding to the depth of ~ 20 km) relative to anhydrous conditions, and the width become sharper (~ 0.5 GPa, which corresponds to a depth interval of ~ 15 km) compared to that of anhydrous conditions (~ 1.0 GPa, which corresponds to a depth interval of ~ 30 km). Some seismological studies observed discontinuity at about 520 km depth, which is considered to be caused by the phase change between β and γ (e.g. 14, 15). Especially, Deuss and Woodhouse [15] reported that the previously observed discontinuity at about 520 km depth is confirmed in many regions, but is found to be absent in others. In addition, they reported that there are a number of regions in which two discontinuities at about 500 and 560 km depth are found.

Combining the present result with seismological observations, the discontinuity at around 560 km depth may correspond to the high pressure phase transition of olivine in the hydrous region of the mantle. The explanation of the existence of the discontinuity at around 500 km is difficult, but the non-olivine component, such as garnet, should exist in the mantle transition zone, and the transformation from garnet to Ca-perovskite may attribute to the discontinuity.

Thus, the present result should give us critical information to understand the distribution of water in the mantle transition zone, by comparing with the seismological observations.

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