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# Water partitioning in the Earth's mantle

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**Abstract** We have conducted H<sub>2</sub>O partitioning experiments between wadsleyite and ringwoodite and between ringwoodite and perovskite at 1673K and 1873K, respectively. These experiments were performed in order to constrain the relative distribution of H<sub>2</sub>O in the upper mantle, the mantle transition zone, and the lower mantle. We successfully synthesized coexisting mineral assemblages of wadsleyite-ringwoodite and ringwoodite-perovskite that were large enough to measure the H<sub>2</sub>O contents by secondary ion mass spectrometry (SIMS). Combining our previous H<sub>2</sub>O partitioning data (Chen et al., 2002) with the present results, the determined water partitioning between olivine, wadsleyite, ringwoodite, and perovskite under H<sub>2</sub>O-rich fluid saturated conditions are 6: 30: 15 : 1, respectively. Because the maximum H<sub>2</sub>O storage capacity in wadsleyite is ~3.3 wt% (e.g. Inoue et al, 1995), the possible maximum H<sub>2</sub>O storage capacity in the olivine high pressure polymorphs are as follows: ~0.7 wt% in olivine (upper mantle just above 410 km depth), ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660 km depth), and ~0.1 wt% in perovskite (lower mantle). If we assume ~0.2 wt% of the H<sub>2</sub>O content in wadsleyite in the mantle transition zone estimated by recent electrical conductivity measurements (e.g. Dai and Karato, 2009), the estimated H<sub>2</sub>O contents throughout the mantle are as follows; ~0.04 wt% in olivine (upper mantle just above 410 km depth), ~0.2 wt% in wadsleyite (410-520 km depth), ~0.1 wt% in ringwoodite (520-660 km depth) and ~0.007 wt% in perovskite (lower mantle). Thus, the mantle transition zone should contain a large water reservoir in the Earth's mantle compared to the upper mantle and the lower mantle.

34 Key words: mantle, olivine, wadsleyite, ringwoodite, perovskite, hydrous wadsleyite,  
35 hydrous ringwoodite, high pressure phase transformation, partitioning of H<sub>2</sub>O

36

## 37 **1. Introduction**

38 Water, the most abundant volatile component on the Earth's surface, has been  
39 supplied to the Earth's mantle by subducting slabs from the lithosphere (e.g. Irifune et  
40 al.,1998; Ohtani et al., 2004). Because water influences the physical properties and  
41 melting temperature of minerals, it is important to constrain the potential amount of  
42 water in nominally anhydrous phases at various depths in the Earth's mantle.

43 Olivine ( $\alpha$ -phase) and the high pressure polymorphs of olivine are the most abundant  
44 minerals in the upper mantle, and the high-pressure polymorphs of olivine, wadsleyite  
45 ( $\beta$ -phase), and ringwoodite ( $\gamma$ -phase), can contain up to 2-3 wt% of H<sub>2</sub>O in their crystal  
46 structures (e.g. Inoue et al., 1995, 1998; Kohlstedt et al., 1996). However, the  
47 partitioning data of H<sub>2</sub>O between these minerals are few except for the  
48 olivine-wadsleyite transformation (Chen et al., 2002) and ringwoodite-perovskite  
49 transformation (Bolfan-Casanova et al., 2003). We have determined the partitioning of  
50 H<sub>2</sub>O between wadsleyite and ringwoodite and between ringwoodite and perovskite at  
51 1673K and 1873K, respectively. These temperatures are close to typical mantle  
52 temperature proposed by Brown and Shankland (1981) and Katsura et al. (2009) at the  
53 520 km and 660 km seismic discontinuity. We have also ascertained the relative  
54 distribution of H<sub>2</sub>O among the upper mantle, the mantle transition zone, and the lower  
55 mantle.

56

## 57 **2. Experimental**

58 High-pressure experiments were conducted in an MA-8 type (Kawai-type)  
59 high-pressure apparatus at Ehime University. The truncation edge lengths (TEL) of the  
60 cubic anvils were 3.5 and 2.5 mm for the experiments on wadsleyite-ringwoodite and  
61 ringwoodite-perovskite, respectively. We used semi-sintered magnesia that was doped  
62 with 17 wt % CoO and LaCrO<sub>3</sub> as the pressure medium, and ZrO<sub>2</sub> was used as the  
63 thermal insulator. We adopted a cylindrical platinum (Pt) or rhenium (Re) heater with a  
64 wall thickness of ~30  $\mu$ m. The typical cell assembly used with TEL of 3.5 mm is shown  
65 in Fig. 1.

66 The starting materials were a mixture of Mg(OH)<sub>2</sub>, Fe<sub>2</sub>SiO<sub>4</sub> and SiO<sub>2</sub> reagent with the

67 chemical composition of  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$  plus 15.8 wt%  $\text{H}_2\text{O}$  (Table 1). Thus,  $\text{H}_2\text{O}$   
68 was introduced by  $\text{Mg}(\text{OH})_2$ , and ferrous iron was introduced by  $\text{Fe}_2\text{SiO}_4$  because  
69 wustite ( $\text{Fe}_{1-x}\text{O}$ ) is non-stoichiometric. The reason we selected such large water content  
70 was to enhance the crystal growth and to make it possible to measure the  $\text{H}_2\text{O}$  content  
71 precisely by secondary ion mass spectroscopy (SIMS). In addition, the reason we  
72 selected the olivine composition of  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$  was to enhance the coexisting  
73 region of wadsleyite-ringwoodite and ringwoodite-perovskite in order to obtain the  
74 sample.

75 A corresponding anhydrous starting material was also prepared. The appropriate  
76 mechanical mixture of  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$  powders was used for the composition of  
77  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ . Both anhydrous and hydrous samples were enclosed in a welded  
78  $\text{Au}_{75\%}\text{Pd}_{25\%}$  alloy capsule separately before loading into a high pressure cell in order to  
79 avoid the loss of both water and iron. Platinum is often used as capsule material, but it  
80 absorbs iron significantly. Therefore, we used  $\text{Au}_{75\%}\text{Pd}_{25\%}$  to make the loss of Fe less,  
81 which is superior to Pt in an iron bearing system, as the capsule material.

82 Temperature was measured with a  $\text{W}_{97}\text{Re}_3$ - $\text{W}_{75}\text{Re}_{25}$  thermocouple junction placed in  
83 the center of the furnace assembly. The fluctuation of temperature throughout the run  
84 was kept within  $\pm 5^\circ\text{C}$  in each condition, but no pressure correction was made for the  
85 emf of the thermocouple.

86 Careful pressure calibration was done on the basis of the present anhydrous  
87 experiments of the wadsleyite-ringwoodite phase transition based on the  
88 thermochemical phase diagram (Akaogi et al., 1989) at 1673K, and the postspinel phase  
89 transition (Ito and Takahashi, 1989) at 1873K. Therefore, the pressure conditions for  
90 the coexisting run products wadsleyite-ringwoodite and ringwoodite-perovskite were  
91 determined by fitting our anhydrous compositional data on the loop by Akaogi et  
92 al.(1989) and Ito and Takahashi (1989). In this case, the relative pressure precision in  
93 the runs with the coexisting wadsleyite-ringwoodite and coexisting  
94 ringwoodite-perovskite under anhydrous conditions is estimated to be about 0.05 GPa,  
95 and about 0.2 GPa in runs without co-existing phases.

96 In high-pressure and high-temperature experiments, pressure was applied first to the  
97 target ram loads, then the temperature was kept constant for 20-120 minutes before  
98 quenching by turning off power to the furnace, and then the run was quenched by

99 turning off the electric power. The recovered charges were polished for phase  
100 identification and chemical analysis.

101 The phases were identified by a micro-focused X-ray diffractometer and by  
102 micro-Raman spectroscopy. The chemical compositions were determined by EPMA and  
103 the water content of the minerals was measured by SIMS at Hokkaido University.

104 The SIMS instrument used in the present study was the Cameca IMS-3F ion mass  
105 microanalyzer. The polished samples were coated with a gold film 300 Å in thickness  
106 for SIMS analysis. A primary beam operated at ~10 nA, 12.5 kV  $^{16}\text{O}^-$  was focused to  
107 form an ~30 μm spot on the sample, and the secondary  $^1\text{H}^+$  and  $^{30}\text{Si}^+$  ions were  
108 collected from the center region (10 μm in diameter) of the sputtered area using a  
109 mechanical aperture to minimize artifacts arising from hydrogen adsorption on the  
110 polished sample surface. The  $\text{H}_2\text{O}$  content of samples was calibrated from relative  
111 intensities of  $^1\text{H}^+ / ^{30}\text{Si}^+$  using an empirical linear relationship (Yurimoto et al., 1989). We  
112 used natural amphibole crystal with a water content of 1.66 wt % for a standard, which  
113 was determined by a hydrogen gas manometry method with the accuracy of  $\pm 0.1$  wt%  
114 (Miyagi and Yurimoto, 1995). In addition, San Carlos olivine was used for the  
115 background H intensities, because the H concentration is considerably small (10-60  
116 ppm: Kurosawa et al. 1997), compared with the present H concentration in our samples.

117 We obtained a depth profile of the intensity of  $^1\text{H}^+$  and  $^{30}\text{Si}^+$  with time. The  
118 steady-state hydrogen emission achieved depends on the H concentration, but usually it  
119 is achieved after 30-60 minute bombardments of the primary ions with  $\text{H}_2\text{O}$   
120 concentration of ~1 wt%. The uncertainty of the  $\text{H}_2\text{O}$  content in the present analysis is ~  
121  $\pm 10\%$ , which mainly comes from the scattering of the measured  $^1\text{H}^+ / ^{30}\text{Si}^+$  value for  
122 several standard measurements, probably because of the slightly chemical heterogeneity  
123 of the present natural amphibole standard. More details for the SIMS measurement are  
124 described in Miyagi and Yurimoto (1995), and the water content and the chemical  
125 composition of the present amphibole standard was shown in Table 1 (ICH) of Miyagi  
126 et al. (1998).

127

### 128 **3. Results and discussion**

129 The experimental conditions and results are summarized in Tables 2 and 3. The  
130 experiments were conducted at conditions of 14.6-17.0 GPa and 1673K for the  
131 wadsleyite-ringwoodite experiment and ~23 GPa and 1873K for the

132 ringwoodite-perovskite experiments. The heating durations were 20-120 minutes.

133 All experiments were performed under H<sub>2</sub>O-rich fluid (melt) saturated conditions  
134 where solid phases coexisted with a hydrous melt, as evidenced by fibrous crystals and  
135 spinifex texture in the quench product. These results show the formation of liquid under  
136 all conditions.

137 Note that at the present experimental conditions in the silicate-H<sub>2</sub>O system,  
138 H<sub>2</sub>O-bearing silicate melt (liquid) and H<sub>2</sub>O-rich aqueous fluid cannot be distinguished  
139 from each other because of the existence of the second critical end point (e.g. Mibe et  
140 al., 2007). So the terminology of melt (liquid) and fluid in this paper has the same  
141 meaning.

142

### 143 **3-1. The effect of water on the phase boundary between wadsleyite and** 144 **ringwoodite**

145 We observed the coexistence of wadsleyite and ringwoodite at pressures of 15.6 to  
146 16.5 GPa under anhydrous conditions, whereas the coexistence of both wadsleyite and  
147 ringwoodite were not observed below 16.4 GPa under hydrous conditions (Table 2).  
148 This shows that the phase boundary between wadsleyite and ringwoodite moves to  
149 higher pressure under water-bearing conditions.

150 Table 4 shows the Fe/(Mg+Fe) in wadsleyite and ringwoodite and the corresponding  
151 partition coefficient at each pressure. We define the partition coefficient,  $K_d$ , as  
152  $(Fe/Mg)_\gamma / (Fe/Mg)_\beta$ . The  $K_d$ s were ~1.6-1.7 in both the anhydrous and hydrous systems,  
153 which are consistent with our previous report (Inoue et al, 2010).

154 Figures 2(a) and 2(b) show the high pressure phase diagrams of wadsleyite and  
155 ringwoodite in the Mg<sub>2</sub>SiO<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub> system under anhydrous and hydrous conditions,  
156 respectively, by using the present Fe/(Mg+Fe) data for wadsleyite and ringwoodite.

157 At 15.6 GPa (Run E1766), the coexistence of wadsleyite and ringwoodite starts to  
158 appear in the anhydrous system, but ringwoodite does not appear in the hydrous system.  
159 This trend for the anhydrous and hydrous systems continues up to 16.5 GPa (Run  
160 E1794), and the coexistence of wadsleyite and ringwoodite appears at 16.5 GPa (Run  
161 E1760, E1751) in the hydrous system. In run E1788 (P≈17 GPa), only ringwoodite  
162 was observed under anhydrous conditions, but the coexistence of wadsleyite and  
163 ringwoodite was still observed under hydrous conditions.

164 This result indicates that the loop of the wadsleyite and ringwoodite boundary shifts  
165 towards higher pressure or higher iron content, and the pressure width of the loop  
166 decreased with the effect of H<sub>2</sub>O. The present observation is consistent with our  
167 previous result of 1 wt% H<sub>2</sub>O (Inoue et al., 2010).

168 We have already determined that the phase boundary between olivine and wadsleyite  
169 shifts to lower pressures under water bearing conditions (Chen et al., 2002; Inoue et al.,  
170 2009). Combining the present results with our previous data, it is clear that the stability  
171 region of wadsleyite expands and the pressure width of the divariant loop decreases for  
172 both of the phase boundaries between olivine and wadsleyite, and between wadsleyite  
173 and ringwoodite.

174 In the present study, the experiments were performed under H<sub>2</sub>O-rich fluid saturated  
175 conditions, so note that the width of the loop can only be applied to H<sub>2</sub>O-rich fluid  
176 saturated conditions, and the width of the loop should be narrower than those in  
177 H<sub>2</sub>O-rich fluid undersaturated conditions when considering the phase diagram of the  
178 pure-Mg system (Frost and Dolejs, 2007). However, the important point is that the  
179 amounts of Mg and Fe in the coexisting phases are different between anhydrous and  
180 hydrous conditions (Inoue et al.2010). The present results reflect the system with  
181 Mg-Fe partitioning under H<sub>2</sub>O-rich fluid saturated condition.

182 For the hydrous melting phase relation, clinoenstatite was observed in the liquidus  
183 phase below ~17 GPa, and then changed to stishovite. These results indicate that  
184 MgO-rich (ultrabasic) liquid was formed under hydrous melting conditions, which are  
185 consistent with our previous results (Inoue at al., 1994; Yamada et al., 2004).

186

### 187 **3-2. The effect of water on postspinel phase boundary**

188 The coexisting region of ringwoodite and perovskite was quite narrow in both the  
189 anhydrous and hydrous systems, so it was difficult to determine the exact loop in this  
190 boundary. However, we could observe the coexistence of ringwoodite and perovskite at  
191 pressures of 23.0-23.2 GPa (runs E1784, E1730 and E1695).

192 At 23.0 GPa (E1784), the Fe/(Mg+Fe) ratios in ringwoodite, perovskite, and  
193 magnesiowustite were 0.199, 0.086 and 0.342, respectively, whereas in the hydrous  
194 system, the Fe/(Mg+Fe) ratios in ringwoodite and perovskite were 0.159 and 0.056,  
195 respectively. We could not observe magnesiowustite in the most hydrous run, because  
196 the composition of the hydrous liquid became MgO rich with increasing pressure, as we

197 have already reported (Inoue, 1994; Yamada et al., 2004), and magnesiowustite tends to  
198 dissolve in the liquid. The reason why the Fe/(Mg+Fe) ratios of ringwoodite and  
199 perovskite in the hydrous system is much lower than those in anhydrous conditions is  
200 the existence of the hydrous liquid. The hydrous liquid prefers iron compared to  
201 crystalline phases. Nevertheless, the partition coefficients,  $K_d = (Fe/Mg)_{Pv}/(Fe/Mg)_\gamma$ ,  
202 were almost the same ( $\sim 0.3\sim 0.4$ ) in both anhydrous and hydrous systems.

203 We have already reported the effect of water on the spinel-postspinel transformation  
204 in  $Mg_2SiO_4$ , and reported that the boundary moves to high pressures by  $\sim 0.2$  GPa under  
205 water bearing conditions, compared with anhydrous conditions (Higo et al., 2001). In  
206 the present experiment, we could not observe the phenomena clearly because of the  
207 fluctuation of the generated pressure in each cell assembly. In the hydrous system this  
208 was also caused by the complicated phase assembly in each run. Nevertheless, the main  
209 purpose of the present experiment was to obtain the coexisting sample of ringwoodite  
210 and perovskite to determine the  $H_2O$  content and the partitioning effect. We succeeded  
211 in this purpose, which will be further described later.

212

### 213 **3-3. The $H_2O$ content and partitioning in wadsleyite, ringwoodite and** 214 **perovskite**

215 We succeeded in synthesizing large ( $\sim 50\mu m$ ) crystals of coexisting wadsleyite and  
216 ringwoodite, and of ringwoodite and perovskite. Figures 3 and 4 show the back  
217 scattered electron images of the coexisting run products of wadsleyite and ringwoodite  
218 (E1751, E1760), and of ringwoodite and perovskite (E1748 and E1730), respectively. In  
219 all run products, hydrous liquids coexisted with the minerals. In addition, clinoenstatite  
220 existed in the liquidus phase at  $\sim 16.5$  GPa and 1673K under hydrous melting  
221 conditions.

222 Table 6 shows the  $H_2O$  contents in wadsleyite and ringwoodite at  $\sim 16.5$  GPa and  
223 1673K, and the corresponding partition coefficient. The  $H_2O$  contents in wadsleyite and  
224 ringwoodite at  $\sim 16.5$  GPa and 1673K were 1.8-2.3 wt% and 1-1.25 wt%, respectively.  
225 In E1788, the  $H_2O$  content was higher than that in the other runs, because the  
226 temperature was estimated by the power supply and the generated temperature may  
227 have been lower than 1673K. For this reason, the amount of hydrous melt was small and  
228 the  $H_2O$  contents in the crystals became higher in E1788. In spite of this difference, the  
229 partition coefficient between wadsleyite and ringwoodite ( $K_d = (H_2O)_\beta / (H_2O)_\gamma$ ) was  $\sim 2$ ;

230 this result shows that wadsleyite favors H<sub>2</sub>O twice as much when compared to  
231 ringwoodite.

232 Table 7 shows the H<sub>2</sub>O content in ringwoodite and perovskite at ~23 GPa and 1873K,  
233 and the partition coefficient. The H<sub>2</sub>O content in ringwoodite and perovskite at ~23 GPa  
234 and 1873K were 0.6-0.8 wt% and less than 0.1 wt%, respectively. Because the H<sub>2</sub>O  
235 content in perovskite was quite small, the resulting calculated partition coefficient  
236 between ringwoodite and perovskite exhibits larger scatter. Nevertheless, the results  
237 show that the partition coefficient between ringwoodite and perovskite  
238 ( $K_d = (H_2O)_\gamma / (H_2O)_{Pv}$ ) could be determined to be ~15 in average; this result shows that  
239 ringwoodite favors H<sub>2</sub>O 15 times more compared with perovskite.

240 We have already determined that the partition coefficient between olivine and  
241 wadsleyite ( $K_d = (H_2O)_\beta / (H_2O)_\alpha$ ) was ~5 (Chen et al., 2002). Combining our previous  
242 data with our present data, the partitioning of H<sub>2</sub>O in olivine( $\alpha$ ), wadsleyite( $\beta$ ),  
243 ringwoodite( $\gamma$ ) and perovskite(Pv) could be determined as  $\alpha : \beta : \gamma : Pv = 6 : 30 : 15 : 1$ .  
244 Olivine is the most abundant minerals in the mantle, so the H<sub>2</sub>O partitioning among the  
245 upper mantle, between 410-520 km and 520-660 km of the mantle transition zone, and  
246 the lower mantle can be estimated as 6:30:15:1, respectively.

247 Because the maximum H<sub>2</sub>O solubility in wadsleyite is 3.3 wt% (e.g. Inoue et al,  
248 1995), the possible maximum H<sub>2</sub>O storage capacities in the olivine high pressure  
249 polymorphs are as follows; ~0.7 wt% in olivine (upper mantle just above 410 km  
250 depth), ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660  
251 km depth) and ~0.1 wt% in perovskite (lower mantle). With this consideration, we  
252 adopted the maximum H<sub>2</sub>O solubility in wadsleyite to discuss the maximum H<sub>2</sub>O  
253 storage capacity in the mantle. However, it was reported that the H<sub>2</sub>O solubility  
254 becomes lower with increasing temperature (e.g. Demouchy et al. 2005). The  
255 temperature in the mantle transition zone is important to estimate the H<sub>2</sub>O content.

256 In spite of the effect of temperature, the mantle transition zone should be a large  
257 geochemical reservoir of water in the Earth's interior, and the maximum water storage  
258 capacity in the mantle transition zone is ~4 times relative to the amount of sea water.  
259 Note that the H<sub>2</sub>O content in olivine was determined at ~13.5 GPa (just above 410 km  
260 depth), and we know that the H<sub>2</sub>O solubility in olivine increases with increasing  
261 pressure as shown in Kohlstedt et al. (1996) and Hauri et al. (2006). In the shallower  
262 mantle below 410 km depth, the H<sub>2</sub>O content in olivine should become less with

263 decreasing pressure.

264

### 265 **3-4. Geophysical implication**

266 Knowledge of absolute water contents in the mantle is important because hydration  
267 affects various physical properties of mantle minerals (e.g. Inoue et al, 1998; Jacobsen  
268 et al., 2004; Huang et al., 2005). Therefore, many researchers have made an effort to  
269 estimate the absolute water content in the mantle. Especially, seismological and  
270 electrical conductivity observations combined with laboratory measured values enable  
271 us to estimate the water content in the mantle. Mantle transition zone minerals,  
272 wadsleyite and ringwoodite, can accommodate significant amount of H<sub>2</sub>O (up to 2-3  
273 wt%) in their crystal structures, so these minerals should be key minerals to contain  
274 water in the mantle.

275 Suetsugu et al. (2006) and Yamada et al. (2009) tried to estimate temperature  
276 anomalies and water content in the mantle transition zone just above the 660 km  
277 discontinuity beneath the Japan Islands and the Philippine Sea from tomographically  
278 determined P-velocity anomalies and the depth of the 660-km discontinuity determined  
279 by the receiver function method. The water content beneath the Philippine Sea and  
280 western Japan, where the Pacific slab is subducted, was estimated to be in the range of  
281 1-1.5 wt% H<sub>2</sub>O, and the west Philippine basin, away from the Pacific slab, did not have  
282 any significant water content. This estimated H<sub>2</sub>O content shows the relative water  
283 content anomaly with respect to average values in their study regions, because  
284 tomographically determined P-velocity anomalies were used as mentioned in Yamada et  
285 al. (2009). They observed the apparently unreasonable negative values of water content  
286 (-0.5 wt%) beneath northern Japan, and interpreted that the average H<sub>2</sub>O content could  
287 be regarded as ~0.5 wt% in the region, when it is regarded as a situation of absolutely  
288 null water (dry). Recently, Suetsugu et al. (this issue) applied the same method by  
289 using a new data set of ocean bottom geophysical observations beneath the Philippine  
290 Sea and the northwestern Pacific Ocean, and revised the water content and estimated  
291 that there was less than 0.2 wt% H<sub>2</sub>O beneath these areas. Although they mentioned that  
292 the estimated water content had an uncertainty of about 0.2-0.3 wt% H<sub>2</sub>O, the average  
293 H<sub>2</sub>O content in these areas was considered to be ~0.1 wt% H<sub>2</sub>O from Figure 7 in  
294 Suetsugu et al. (this issue). Note that this estimated H<sub>2</sub>O contents reflects that in  
295 ringwoodite.

296 On the other hand, the electrical conductivities of wadsleyite and ringwoodite in  
297 anhydrous and hydrous forms were measured (Huang et al., 2005; Yoshino et al., 2008;  
298 Manthilake et al., 2009; Dai and Karato, 2009), and compared to the geophysical  
299 observations to estimate the water content. Though there are some arguments about the  
300 estimated water content (Karato and Dai, 2009; Yoshino and Katsura, 2009), their recent  
301 conclusions show that some water (~0.1–0.3 wt% in the Pacific) is required to explain  
302 the observed electrical conductivity (Dai and Karato, 2009). In addition, though Yoshino  
303 et al. (this issue) mentioned that the present conductivity-depth profiles in the transition  
304 zone agreed with that obtained from the geophysical observations beneath the Pacific in  
305 the case of the mantle transition zone, 0.1-0.2 wt% H<sub>2</sub>O explains the recent geophysical  
306 reference model (Shimizu et al., submitted) from Figure 6 in Yoshino et al. (this issue).  
307 Still more, Yoshino et al. (this issue) mentioned that the presence of water in the  
308 transition zone minerals is required to explain the high conductivity beneath the  
309 Philippine Sea and northeastern China (Baba et al., this issue).

310 In this study, we determined the partitioning of H<sub>2</sub>O among olivine high pressure  
311 polymorphs. When we apply ~0.2 wt% of the H<sub>2</sub>O content in wadsleyite in the mantle  
312 transition zone estimated by the recent electrical conductivity measurements (e.g. Dai  
313 and Karato, 2009), the estimated H<sub>2</sub>O content in the mantle is as follows; ~0.04 wt% in  
314 olivine (upper mantle), ~0.2 wt% in wadsleyite (410-520 km depth), ~0.1 wt% in  
315 ringwoodite (520-660 km depth), and ~0.007 wt% in perovskite (lower mantle). These  
316 estimated values satisfy, within the error, the recently estimated H<sub>2</sub>O content in mantle  
317 transition zone minerals (i.e. wadsleyite and ringwoodite) by different methods based on  
318 seismological and electrical conductivity observations.

319 Thus, the mantle transition zone should be a large geochemical reservoir of water in  
320 the Earth's mantle compared with the upper and lower mantle. Additionally, the amount  
321 of water in the mantle transition zone is ~0.3 times more relative to that of sea water,  
322 when mantle wadsleyite contains ~0.2 wt% H<sub>2</sub>O.

323

#### 324 **4. Conclusions**

325 We have determined the water partitioning between wadsleyite and ringwoodite, and  
326 ringwoodite and perovskite. The results are as follows; olivine : wadsleyite :  
327 ringwoodite : perovskite = 6: 30: 15 : 1. In addition, the phase boundary of  
328 olivine-wadsleyite, wadsleyite-ringwoodite, and postspinel transformations move to the

329 low, high, and high pressure side, respectively, with the effect of water, when we  
330 combine the present data with our previous data (Higo et al., 2001; Chen et al., 2002;  
331 Inoue et al., 2010). The resultant H<sub>2</sub>O partitioning of  $[H_2O]_{\alpha} < [H_2O]_{\beta} > [H_2O]_{\gamma} >$   
332  $[H_2O]_{pv}$  is consistent with the results of the effect of water on the high pressure phase  
333 boundary of olivine.

334 Because the maximum H<sub>2</sub>O solubility in wadsleyite is 3.3 wt% (e.g. Inoue et al,  
335 1995), the possible maximum H<sub>2</sub>O storage capacity in the olivine high pressure  
336 polymorphs are as follows; ~0.7 wt% in olivine (upper mantle just above 410 km depth),  
337 ~3.3 wt% in wadsleyite (410-520 km depth), ~1.7 wt% in ringwoodite (520-660 km  
338 depth), and ~0.1 wt% in perovskite (lower mantle).

339 When we apply ~0.2 wt% of the H<sub>2</sub>O content in wadsleyite in the mantle transition  
340 zone, the estimated H<sub>2</sub>O content through the mantle are as follows; ~0.04 wt% in  
341 olivine (upper mantle just above 410 km depth), ~0.2 wt% in wadsleyite (410-520 km  
342 depth), ~0.1 wt% in ringwoodite (520-660 km depth), and ~0.007 wt% in perovskite  
343 (lower mantle).

344 Thus, the mantle transition zone should contain a large water reservoir in the Earth's  
345 mantle when compared to the upper and lower mantle. Additionally, if mantle  
346 wadsleyite contains ~0.2 wt% H<sub>2</sub>O then the mantle transition zone would contain  
347 approximately one-third the H<sub>2</sub>O mass of Earth's oceans.

348

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356

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459

460 **Figure captions**

461

462 Figure 1. An example of the cell assembly used in the present experiments for the  
463 wadsleyite-ringwoodite transformation.

464

465 Figure 2. (a) High pressure phase diagram of olivine high pressure polymorphs under  
466 anhydrous condition at T=1673K. The solid line represents the phase boundary from  
467 Akaogi et al. (1989) under anhydrous condition. Using this plot, the run pressures were  
468 determined.

469 (b) High pressure phase diagram of olivine high pressure polymorphs under hydrous  
470 condition at T=1673K. The broken line represents the phase boundary from Akaogi et al.  
471 (1989) under anhydrous condition, and the solid line represents that under hydrous  
472 condition from Inoue et al. (2010). The present results are consistent with our previous  
473 boundary of Inoue et al. (2010).

474 Open triangles and squares show the assemblages of the single wadsleyite phase and  
475 that of the single ringwoodite phase, respectively, and filled triangles and squares show  
476 the wadsleyite coexisting with ringwoodite, and the ringwoodite coexisting with  
477 wadsleyite, respectively.  $\alpha$ : olivine,  $\beta$ : wadsleyite,  $\gamma$ : ringwoodite.

478

479 Figure 3. Back scattered electron image of run products (a) E1751 and (b) E1760.  $\beta$ :  
480 wadsleyite,  $\gamma$ : ringwoodite, CEn: clinoenstatite, L: liquid.

481

482 Figure 4. Back scattered electron image of run products (a) E1784 and (b) E1730.  $\gamma$ :  
483 ringwoodite, Pv: perovskite, L: liquid.

484

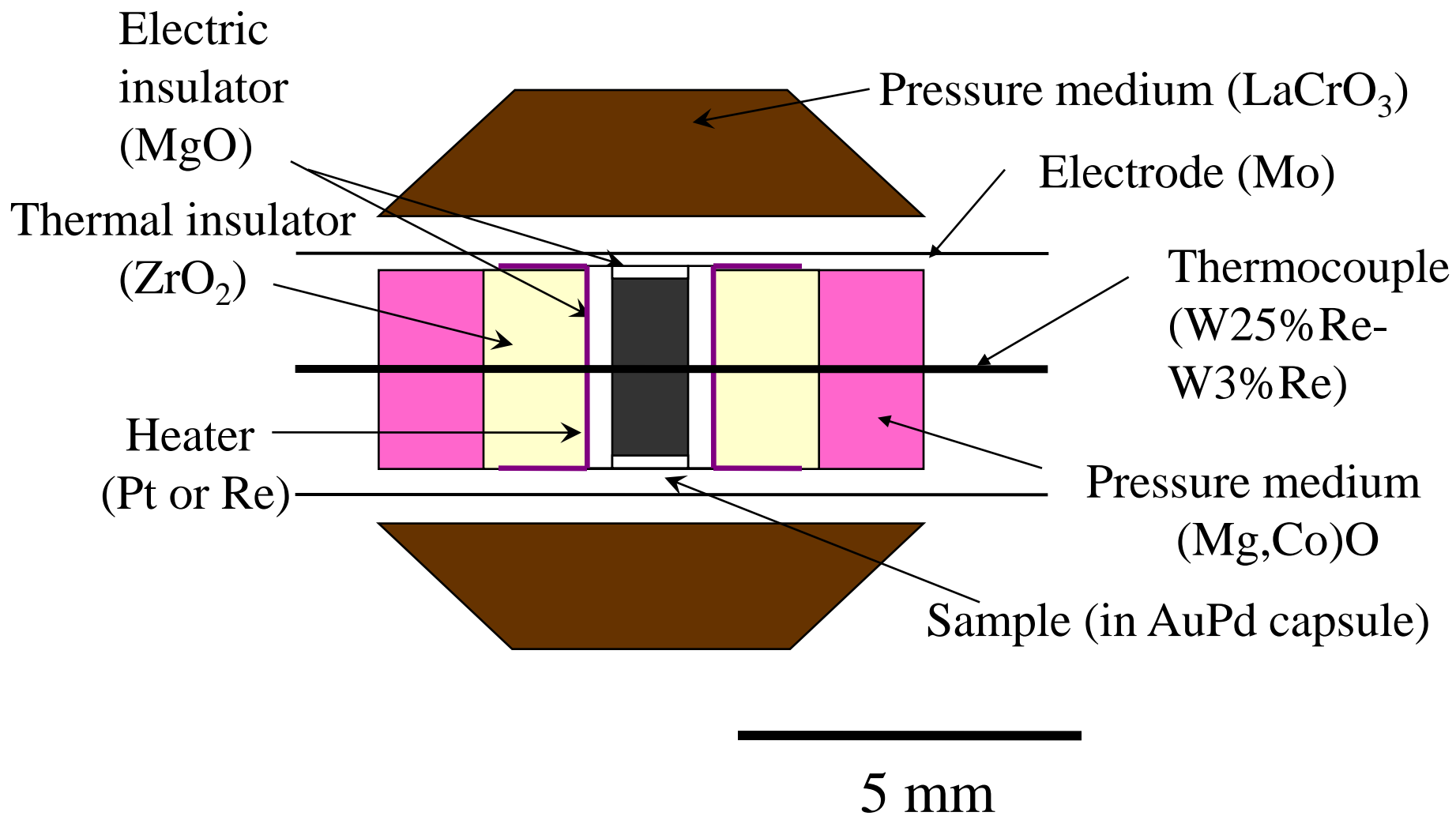


Fig. 1 Inoue et al.

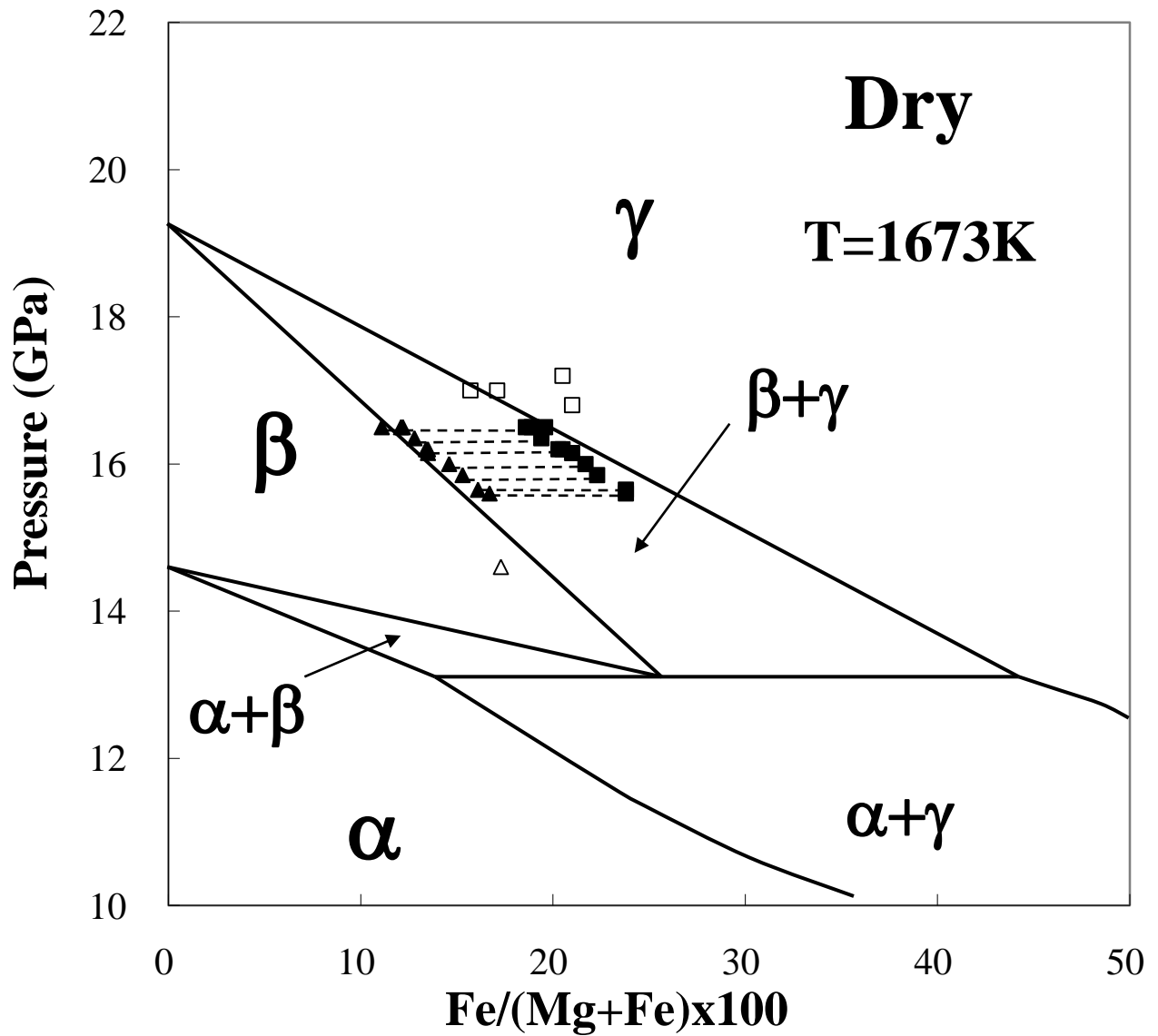


Fig. 2 (a) Inoue et al.

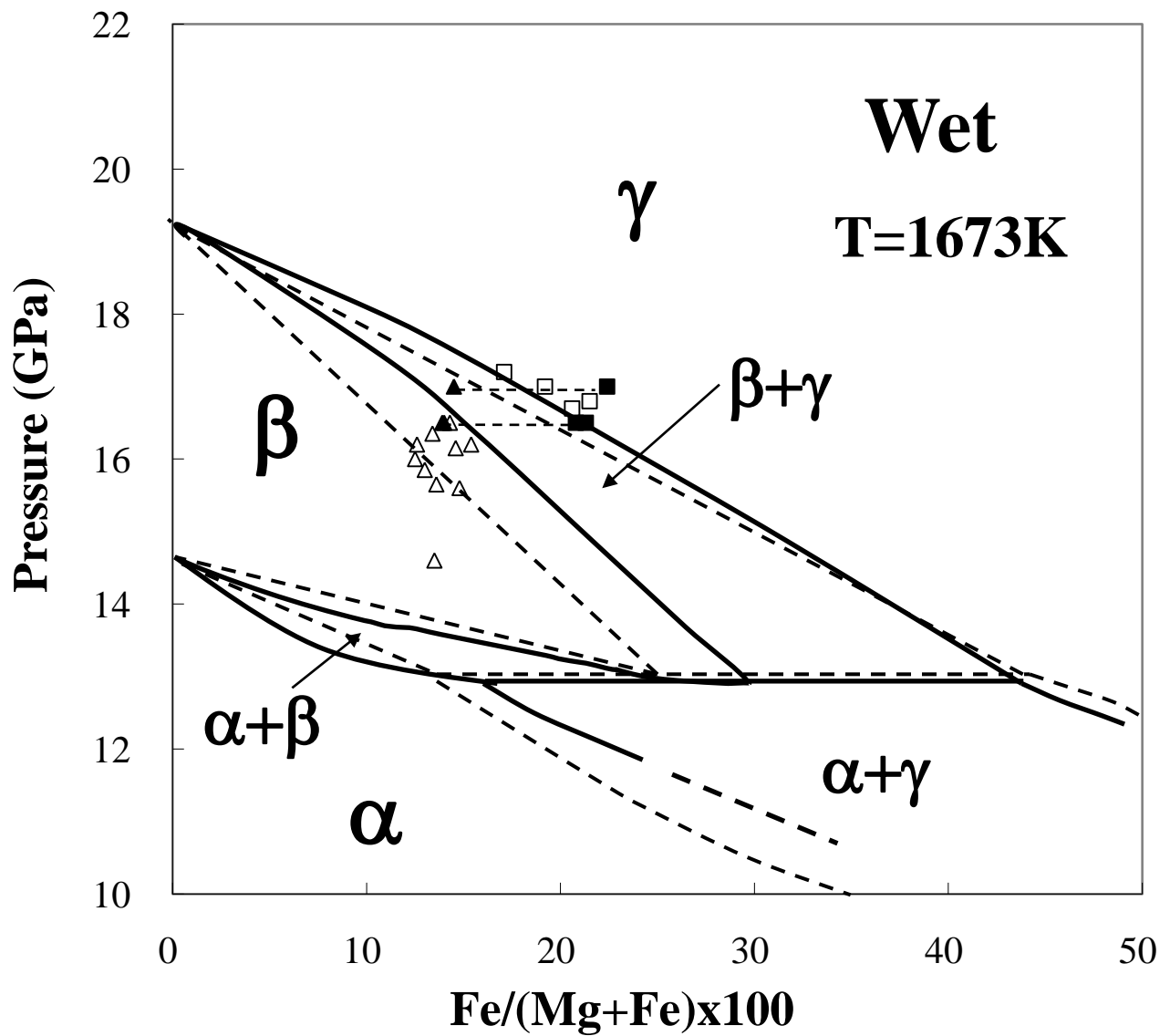
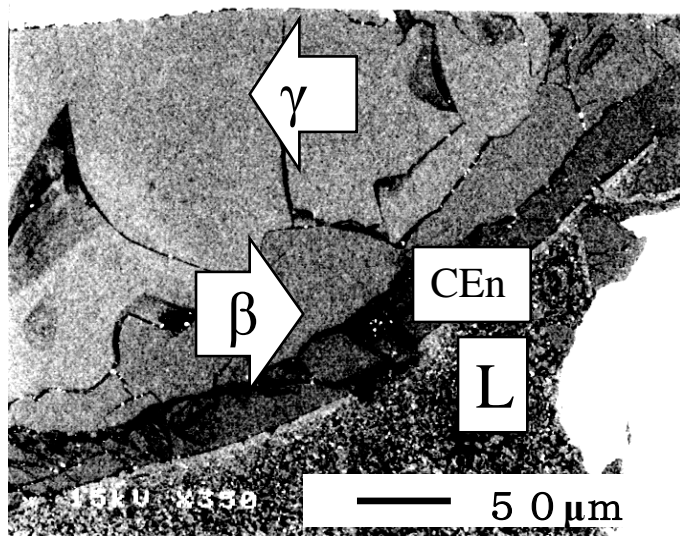


Fig. 2 (b) Inoue et al.

(a) E1751 WET  
16.5GPa, 1673K



(b) E1760 WET  
16.5GPa, 1673K

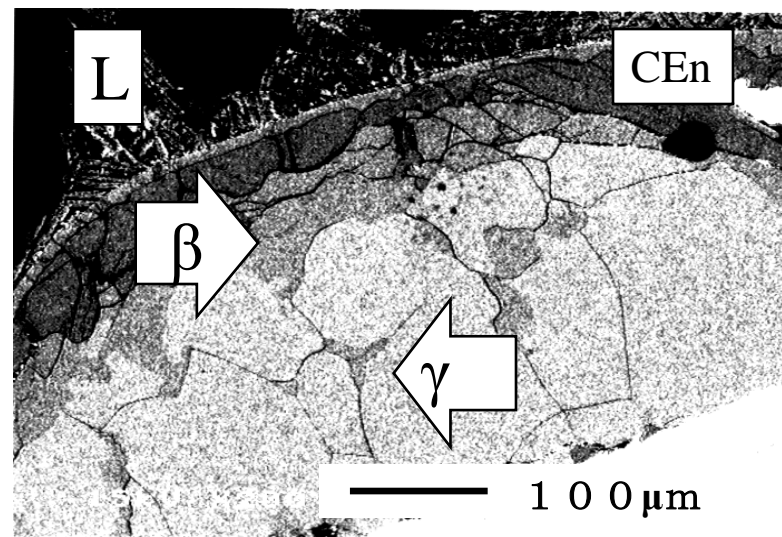
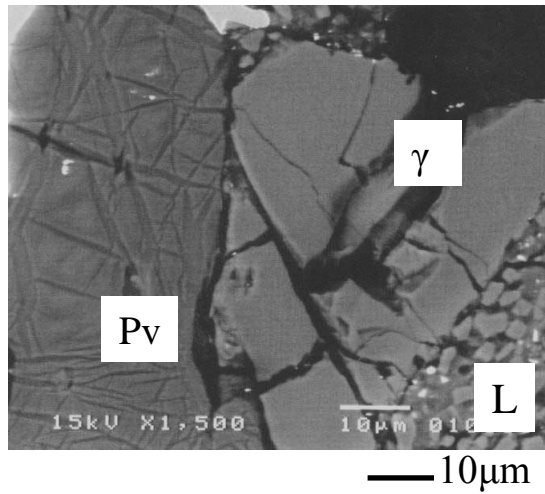


Fig. 3 Inoue et al.

(a) E1784 WET  
23.0GPa, 1873K



(b) E1730 WET  
23.1GPa, 1873K

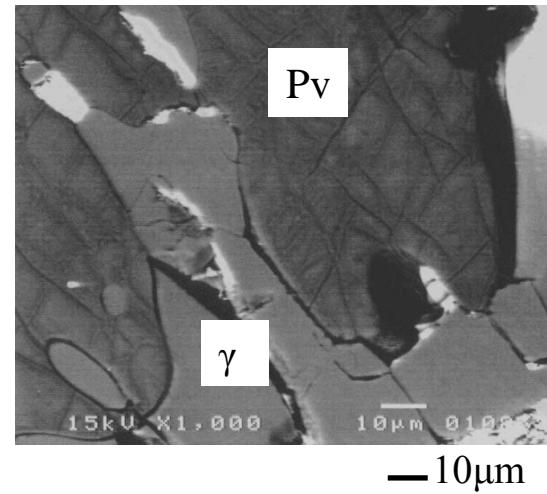


Fig. 4 Inoue et al.

Table 1. Chemical composition of starting material

	Dry	Wet
MgO	42.1	35.4
FeO	18.7	15.8
SiO <sub>2</sub>	39.2	33.0
H <sub>2</sub> O	-	15.8
Total (wt%)	100.0	100.0
(Mg+Fe)/Si	2.0	2.0
Fe/(Mg+Fe)	0.2	0.2



Table 2. Experimental conditions and the results (T=1673K)

Run No.	Load (ton)	Pressure (GPa)	Time (min)	Dry	Wet
E1672	412	14.6	60	$\beta$	$\beta+L$
E1766	480	15.6	120	$\beta+\gamma$	$\beta+CEn+L$
E1748	470	15.7	60	$\beta+\gamma$	$\beta+CEn+L$
E1678	500	15.9	60	$\beta+\gamma$	$\beta+CEn+L$
E1789	490	16.0	60	$\beta+\gamma$	$\beta+L$
E1786	483	16.2	90	$\beta+\gamma$	$\beta+CEn+L$
E1805	506	16.2	90	$\beta+\gamma$	$\beta+CEn+L$
E1744	505	16.2	60	$\beta+\gamma$	$\beta+CEn+L$
E1807	506	16.4	90	$\beta+\gamma$	$\beta+CEn+L$
E1794	500	16.5	90	$\beta+\gamma$	$\beta+L$
E1760	485	16.5	90	$\beta+\gamma$	$\beta+\gamma+CEn+L$
E1751	510	16.5	120	$\beta+\gamma$	$\beta+\gamma+CEn+L$
E1788 <sup>*</sup>	485	~17#	60	$\gamma$	$\beta+\gamma+CEn+L$
E1758	508	~17#	60	$\gamma$	$\gamma+St+L$
E1738 <sup>*</sup>	520	16.7	60	$\gamma$	$\gamma+L$
E1731	525	16.8	60	$\gamma$	$\gamma+L$
E1683	550	17.2	60	$\gamma$	$\gamma+L$

$\beta$ : wadsleyite,  $\gamma$ : ringwoodite, CEn: clinoenstatite, St: stishovite, L: liquid

\* Temperatures were estimated by power supply.

# These pressure should have large uncertainty.

Table 3. Experimental conditions and the results (T=1873K)

Run No.	Load (ton)	Pressure (GPa)	Time (min)	Dry	Wet
E1720	435	22.9	60	$\gamma$	Pv + L
E1767	435	22.9	120	$\gamma\#$	SuB+D+Mw+L
E1749*	440	23.0	120	$\gamma\#$	Pv + L
E1759*	440	23.0	120	$\gamma\#$	Pv+Mw+SuB+L
E1770	440	23.0	120	Pv + Mw	Pv + Mw + L
E1784*	440	23.0	20	$\gamma$ + Pv + Mw	$\gamma$ + Pv + L
E1730	445	23.1	60	$\gamma$ + Pv + Mw	$\gamma$ + Pv + L
E1787	445	23.1	60	$\gamma$	Pv + L
E1688	450	23.2	60	$\gamma$ + Pv + Mw	Pv + L
E1695	450	23.2	30	$\gamma$ + Pv + Mw	$\gamma$ + Pv + L
E1796	450	23.2	60	$\gamma\#$	$\gamma$ +Mw+SuB+D+L

$\gamma$ : ringwoodite, Pv: perovskite, Mw: magnesiowustite, St: stishovite

SuB: superhydrous phase B, D: phase D, L: liquid

\*Temperatures were estimated by power supply.

#Small amounts of magnesiowustite and stishovite exist in the run charge.

Table 4. Fe/(Mg+Fe) in  $\beta$  and  $\gamma$  and the partitioning (T=1673K)

Run No.	Pressure (GPa)	Dry			Wet		
		Fe/(Mg+Fe)		Kd	Fe/(Mg+Fe)		Kd
		$\beta$	$\gamma$		$\beta$	$\gamma$	
E1672	14.6	0.173(6)	----		0.135(5)	----	
E1766	15.6	0.167(1)	0.238(4)	1.56	0.148(28)	----	
E1748	15.7	0.161(4)	0.238(11)	1.62	0.136(3)	----	
E1678	15.9	0.153(1)	0.223(2)	1.59	0.130(4)	----	
E1789	16.0	0.146(2)	0.217(2)	1.62	0.125(1)	----	
E1786	16.2	0.135(7)	0.210(6)	1.71	0.146(3)	----	
E1805	16.2	0.134(6)	0.205(5)	1.67	0.154(7)	----	
E1744	16.2	0.135(1)	0.203(6)	1.64	0.126(5)	----	
E1807	16.4	0.128(3)	0.194(2)	1.65	0.134(2)	----	
E1794	16.5	0.122(1)	0.186(5)	1.65	0.143(11)	----	
E1760	16.5	0.121(5)	0.189(6)	1.70	0.139(4)	0.213(8)	1.68
E1751	16.5	0.111(4)	0.196(3)	1.95	0.140(5)	0.208(3)	1.62
E1788*	~17#	----	0.157(6)		0.145(3)	0.224(3)	1.70
E1758	~17#	----	0.171(5)		----	0.192(6)	
E1738*	16.7		N.A.		----	0.206(4)	
E1731	16.8	----	0.210(2)		----	0.215(2)	
E1683	17.2	----	0.205(2)		----	0.171(14)	

( ): standard deviation; N.A. not analyzed; \* Temperatures were estimated by power supply.

Kd =  $(\text{Fe}/\text{Mg})_{\gamma} / (\text{Fe}/\text{Mg})_{\beta}$ ; # These pressure should have large uncertainty.

Table 5. Fe/(Mg+Fe) in  $\gamma$  and perovskite and the partitioning (T=1873K)

Run No.	Pressure (GPa)	Dry				Wet	
		Fe/(Mg+Fe)				Fe/(Mg+Fe)	
		$\gamma$	Pv	Mw	Kd	$\gamma$	Pv
E1784*	23.0	0.199(9)	0.086(1)	0.342(2)	0.38	0.159(1)	0.056(3)
E1730	23.1	0.188(1)	N.A.	N.A.		0.135(2)	0.063(4)
E1695	23.2	0.178(4)	0.084(6)	N.A.	0.42	0.087(2)	0.049(3)

( ): standard deviation; N.A. not analyzed; \* Temperatures were estimated by power supply.

$$Kd = (Fe/Mg)_{Pv} / (Fe/Mg)_{\gamma}$$

Table 6. H<sub>2</sub>O partitioning between wadsleyite ( $\beta$ ) and ringwoodite ( $\gamma$ )  
 T=1673K

Run No.	Pressure (GPa)	H <sub>2</sub> O wt%		Kd
		$\beta$	$\gamma$	
E1788*-1	~17	3.72	1.69	2.2
E1760-1	16.5	2.28	1.11	2.05
E1760-2	16.5	2.24	1.25	1.79
E1751-1	16.5	1.88	1	1.88
E1751-2	16.5	1.79	1.1	1.63
average				1.9(2)

\* Temperature was estimated by power supply.

( ): standard deviation,  $Kd=(H_2O)_\beta/(H_2O)_\gamma$

Table 7. H<sub>2</sub>O partitioning between ringwoodite ( $\gamma$ ) and perovskite (Pv)

T=1873K

Run No.	Pressure (GPa)	H <sub>2</sub> O wt%		Kd
		$\gamma$	Pv	
E1784*	23	0.76	0.06	13
E1730	23.1	0.71(25)	0.03	24(8)
E1695	23.2	0.63(11)	0.07(3)	9(5)
average				15(8)

\* Temperature was estimated by power supply.

(): standard deviation,  $Kd=(H_2O)_{\gamma}/(H_2O)_{Pv}$