Melting of bridgmanite under hydrous shallow lower mantle conditions

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Abstract

High pressure and temperature experiments were carried out on bridgmanite under the hydrous shallow lower mantle conditions (24-25 GPa and 1673 - 1873 K with 5 - 10 wt. % of water in the starting material). Bridgmanite investigated include MgSiO₃, (Mg, Fe)SiO₃, (Mg, Al, Si)O₃ and (Mg, Fe, Al, Si)O₃. Melting was observed in all runs. The water content of the melt was estimated from the measurements of the void space using the equation of state of H₂O that occupies the void space and agree reasonably well with the initial water content. Melt is enriched in FeO/MgO and Al₂O₃/SiO₂ compared to the starting materials. As a consequence, the residual solids contain a substantial amount of stishovite particularly for the high FeO/MgO and Al₂O₃/SiO₂ starting materials. Stishovite-rich materials will cause seismic scattering when they are transported to ~1100 km depth where stishovite shows anomalous elastic behavior. The water content in the residual solids was measured by the FTIR and is 50 - 70 ppm wt. in bridgmanite and 26 - 670 ppm wt. in stishovite, depending on the starting composition. However, bridgmanites in these samples contain inclusions of superhydrous phase B. If these inclusions were formed during cooling, water content in bridgmanite co-existing with hydrous melt would be 1000-1500 wt ppm that agrees with the previous experimental results on inclusion-free bridgmanite and with a theoretical study. Some implications of these results are discussed including the nature of chemical evolution associated with melting in the shallow lower mantle.

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15 Abstract

16 High pressure and temperature experiments were carried out on bridgmanite under the hydrous 17 shallow lower mantle conditions (24 - 25 GPa and 1673 - 1873 K with 5 - 10 wt. % of water in 18 the starting material). Bridgmanite investigated include MgSiO₃, (Mg, Fe)SiO₃, (Mg, Al, Si)O₃ 19 and (Mg, Fe, Al, Si) O_3 . Melting was observed in all runs. The water content of the melt was 20 estimated from the measurements of the void space using the equation of state of H_2O that 21 occupies the void space and agree reasonably well with the initial water content. Melt is enriched 22 in FeO/MgO and Al_2O_3/SiO_2 compared to the starting materials. As a consequence, the residual 23 solids contain a substantial amount of stishovite particularly for the high FeO/MgO and 24 Al₂O₃/SiO₂ starting materials. Stishovite-rich materials will cause seismic scattering when they 25 are transported to ~1100 km depth where stishovite shows anomalous elastic behavior. The water 26 content in the residual solids was measured by the FTIR and is 50-70 ppm wt. in bridgmanite 27 and 26 - 670 ppm wt. in stishovite, depending on the starting composition. However, 28 bridgmanites in these samples contain inclusions of superhydrous phase B. If these inclusions 29 were formed during cooling, water content in bridgmanite co-existing with hydrous melt would 30 be 1000-1500 wt ppm that agrees with the previous experimental results on inclusion-free 31 bridgmanite and with a theoretical study. Some implications of these results are discussed 32 including the nature of chemical evolution associated with melting in the shallow lower mantle. 33 34 35 36

38 Plain Language Summary

39 Melting is a major process by which Earth evolves chemically. However, the 40 consequence of melting is not well understood under the deep mantle conditions. This study 41 focuses on melting under the shallow lower mantle conditions that occurs with the help of water. 42 Nature of water distribution between the melt and remaining solids was studied using new 43 approaches. We discovered that when melting occurs for a material with composition similar to 44 oceanic crust, the residual solid is nearly completely stishovite (SiO₂). Stishovite shows 45 anomalous elastic properties at ~1100 km depth. Observed strong seismic scattering in this depth 46 range might be due to the presence of stishovite-rich materials formed by melting in the lower 47 mantle.

48

49 Introduction

50 Due to the large contrast in the solubility of water (hydrogen) between lower mantle 51 minerals and transition zone minerals, it is likely that partial melting occurs in the lower mantle 52 if a substantial amount of water (and other volatiles) is present in the lower mantle (e.g., (Ohtani 53 et al., 2004)). (Liu et al., 2016, 2018; Schmandt et al., 2014) reported seismological observations 54 showing a velocity drop (from the shallow to the deep mantle) at around ~750 km and suggested 55 that this velocity drop might be caused by partial melting caused by the transport of water-rich 56 materials from the transition zone.

Although there have been previous studies on melting in the shallow lower mantle (e.g., (Boujibar et al., 2016; Corgne et al., 2005; Ito et al., 2004; Ito and Takahashi, 1987; Kawamoto, 2004; Litasov and Ohtani, 2002; Nakajima et al., 2019; Panero et al., 2020)), the conditions and the consequence of melting on the composition of the melt and the residual solids are poorly

61 constrained particularly under the hydrous conditions. The composition of the melt (and the 62 residual solid minerals) is important for two reasons. First, the compositional change upon 63 melting controls the way in which Earth evolves chemically and also the contrast in the water 64 content between the melt and the co-existing solids determines the critical amount of water under 65 which melting occurs. Second, the composition of the melt relative to that of the co-existing 66 minerals has a large influence on the density contrast between them that controls the direction to 67 which melt is transported. Particularly important is the contrast in the concentration of Fe and H 68 in the melt and co-existing solids. However, in contrast to extensive studies on the Fe 69 partitioning between the melt and the co-existing solids (e.g., (Irifune et al., 2010; Nishiyama 70 and Yagi, 2003; Nomura et al., 2011; Wood, 2000)), less studies have been made on water 71 (hydrogen) partitioning and large discrepancies remain on the water partitioning between the 72 melt and the solids under the lower mantle conditions.

73 The main reason for the poor constraints on partitioning of water (hydrogen) is the 74 difficulties in determining the water content in both melts and solids formed under the lower 75 mantle conditions. Melts formed under the lower mantle conditions are unquenchable and there 76 has been no well-established method to determine the water content of these melts. A commonly 77 used practice is to assume that less than 100% of compositional measurements by EPMA 78 (electron-probe micro-analyzer) correspond to the water content. For example, if the EPMA 79 analysis gives 70% total, it is often assumed that water content is 30% (e.g., (Hirschmann et al., 80 2009; Nakajima et al., 2019)). The physical basis for this method is unclear because the density 81 of void space is different from the rest. Also, the measurement of water (hydrogen) content in a 82 mineral is not trivial. There is a wide range of reports for the water solubility in bridgmanite 83 (e.g., (Bolfan-Casanova et al., 2003; Fu et al., 2019; Litasov et al., 2003; Meade et al., 1994;

Murakami et al., 2002; Panero et al., 2015)). The reason for this large discrepancy is not well
understood but it is partly caused by the influence of inclusions (e.g., (Bolfan-Casanova et al.,
2003; Fu et al., 2019; Schmandt et al., 2014)). A recent work by (Fu et al., 2019) on inclusionfree (Al, Fe)-bearing bridgmanite single crystal, grown from hydrous melt, shows large water
solubility (~1000 ppm wt. water), under the shallow lower mantle conditions.

The main purpose of this study was to investigate the compositions of melts and coexisting solid minerals formed by hydrous melting under the shallow lower mantle conditions with the emphasis on those of Fe and H.

92

93 Experimental Procedure

94 In this study, we focus on the melting behavior of bridgmanite. We synthesized several 95 hydrous compositions of bridgmanite. For hydrous $MgSiO_3$, we used MgO, SiO_2 and $Mg(OH)_2$ 96 oxide starting materials whereas for Al- and Fe-bearing MgSiO₃ bridgmanite were synthesized 97 by adding appropriate amounts of Al_2O_3 and FeO (**Table 1**). All the oxides used had purities of 98 99.99%. Oxide powders were mixed and ground by grinding the mixture in an agate mortar to 99 make nearly homogenous mixture of fine powders (typical grain size was less than 1µm). A fine-100 grained mixture was loaded and sealed in a platinum capsule (we did some experiments with Fe-101 Pt capsule to test the degree of Fe loss). A 1000-ton Kawai type multi-anvil press was used for 102 these experiments. A sample assembly was compressed to pressures of ~25 GPa and annealed at 103 a temperature of ~1873K for 3-5 hours. The pressure was estimated from the load, based on the 104 calibration using the phase transformation of majorite to bridgmanite at 1600°C. Temperatures 105 were measured using W-5/26% Re thermocouple wire. The uncertainties in pressure estimate are 106 0.5 GPa, and that of temperature are 100°C.

After annealing, the heater was shut-off and the pressure was slowly reduced (2.0
GPa/hour). After shutting off the furnace, temperature drops from 1600°C to 1000°C in ~10
seconds. The samples were polished down to ~200 µm and Raman spectroscopy was carried out
to determine the phases present. FTIR spectra were then recorded on the solid phases using a
Varian FTIR spectrometer with an internal IR source. Scanning electron microscopy (SEM) as
well as electron microprobe analyses (EPMA) were also carried out to determine the
compositions of both the synthesized products.

114

115 **Results**

116 Under the current experimental conditions, melts are not quenchable. However, the remnant of 117 melt can be identified unambiguously from the texture (Figure 1, 2 and 4), where we observed 118 remnant of melt, in the central part of the capsule. We observed remnant of melt in all the 119 samples investigated in this study. The temperature gradients generated from the design of the 120 assemblies used resulted in the segregation of quenched liquids in the highest temperature 121 regions within the capsule. Phase separation between bridgmanite and stishovite was also 122 observed. This was also observed in diamond anvil melting experiments (Baron et al., 2017). 123 The left-hand side of **Figure 1** shows a back-scattered image from SEM on a polished 124 MgO-SiO₂-FeO-H₂O system containing 10% wt. H₂O in the starting mixture (K1157). We 125 estimated the melt fraction, F, by successively polishing the sample capsule and calculating the 126 melt area at each step of the polish. The samples were first sectioned and after taking optical 127 images they were polished to roughly 200 µm and optical images taken again. This procedure 128 was repeated several time for the entire sample. The areas of the melt and solid phases were 129 calculated from the optical images using an imaging software (ImageJ), and the respective

130 volume of each phase calculated using the thickness that was polished off (200 μ m). From these,

131 the overall melt and solid volume were then estimated. Figure 2 shows an example of this

132 procedure for sample K1217, where the sample thicknesses at each stage of the polish are

133 included. F was estimated to be about 40% (\pm 5 %), in this case.

- 134
- 135 Raman spectroscopy measurement

136 In the solid part (judged from the texture), several minerals were identified including 137 bridgmanite, stishovite and super hydrous phase B (**Table 2**). In the run without Fe, only 138 bridgmanite and melt were formed. When the starting compositions contain Fe and Al, stishovite 139 is observed. In the case where the Fe content was 5 wt. %, only stishovite is formed (Figure 1, 140 Right). Raman spectra on pure MgSiO₃-bridgmanite showed strong clean peaks identifiable to 141 the mineral. The MgSiO₃-bridgmanite synthesized with Al also showed the same Raman peaks with an additional peak at 1096 cm^{-1} at some locations. This peak is identified with superhydrous 142 143 phase B (Figure 3, left) (Koch-Muller et al., 2005; Liu et al., 2002). The superhydrous phase B 144 is observed inside bridgmanite (but not stishovite) as small inclusions in the optical micrograph 145 (Figure 4). The origin of this phase will be discussed in relation to the interpretation of FTIR 146 observations. Figure 5 summarizes the observed phases in the residual solids. Volume fraction 147 of bridgmanite and stishovite depends on Al₂O₃ and FeO content: fraction of stishovite increases 148 as $Al_2O_3/(Al_2O_3 + SiO_2)$ and FeO/(FeO + MgO) increase. In case of $Al_2O_3/(Al_2O_3 + SiO_2) = 0.09$ 149 and FeO/(FeO + MgO) = 0.19, the residual material is pure stishovite.

150

151 Electron microprobe analysis

152 Quantitative electron microprobe analysis of both the solid and melt parts of the run 153 products was carried out on all samples. Measurements were made using a 15 KeV acceleration 154 voltage with 30 µm diameter defocused beam. The total of EPMA analyses of the "melt" part 155 yield 50 - 70 % due to the presence of void space (Table 2). The (Mg + Fe)/Si molar ratio of the 156 melt ranges from 2.0 - 4.1, up from an initial value of ~1, thus the melt is more mafic than the 157 bridgmanite crystals. The partitioning of Fe is also strongly dependent of Al concentration. The 158 (Mg + Fe)/Si molar ratio in Al-free bridgmanite ($(Mg, Fe)SiO_3$ composition) increases to 2.7 159 from ~2 indicating that Al increases the partition of Fe into the melt. 160 We define the partition coefficients of Fe and Si between the mineral (bridgmanite) and melt by $K_D^{Fe} = \frac{(Fe/Mg)_{mineral}}{(Fe/Mg)_{melt}}$ and $K_D^{Si} = \frac{(Si/Mg)_{mineral}}{(Si/Mg)_{melt}}$, respectively where concentration is in the 161 molar fraction (mineral in this case is bridgmanite). Our measurements show that K_D^{Fe} is 1.05 (in 162

163 K1161), approximately a factor of 4 larger than the Al-free, Fe-bearing bridgmanite ($K_D^{Fe} = 0.25$) 164 (in K1157). This result is qualitatively consistent with previous melting experiments on dry Fe-165 and Al-bearing bridgmanite that suggests that Al enhances Fe partitioning into bridgmanite 166 (Boujibar et al., 2016; Corgne et al., 2005; Ito et al., 2004).

167

168 Estimating the water content in the melt

Because the melt produced in these experiments were not quenched to a glass, water content cannot be directly determined from the sample. Rather, the "melt" in the recovered sample is made of small crystals and voids. We interpret that these small crystals were formed during cooling, and voids are the space that were filled with the volatiles (water in this case) that was present in the melt but expelled from the melt during crystallization. In this model, the plausible processes to form such a texture are as follows: (1) Upon cooling at high pressure,

175 crystals are formed from the hydrous melt. Because these crystals have low water solubility, the 176 water content in the melt increases. (2) With further cooling, the water content in the melt will 177 exceed the solubility limit and water-filled voids will be formed. When temperature reaches 178 room temperature, crystallization is completed and the regions that were originally filled with the 179 melt are now filled with small crystals and a void pace filled by water at a given pressure and 180 room temperature. (3) Now at room temperature, we reduce pressure. During the isothermal 181 pressure reduction, the volume of water will change but some elastic relaxation will occur that 182 modifies the volume of voids. (4) When a capsule is opened, water will evaporate and the void 183 space will be left.

184 Therefore, in order to estimate the water content in the melt from the microstructure of a 185 recovered sample containing crystals and voids, one needs to measure the volume fraction of 186 voids and the mass of water that filled the voids. Images of the regions containing small crystals 187 and voids (regions that were melt at high pressure and temperature) were collected by scanning 188 electron microscopy (SEM) then analyzed using ImageJ to estimate the porosity (volume fraction 189 of void space) in the melt. Figure 6 shows examples of SEM images with different starting 190 compositions alongside their digitized images that were used. As shown in **Figure 6** SEM image 191 show solid region and void region with different grayness. To separate void space and solid 192 space, we convert the gray image into a black and white (binary) image in which black is the 193 void and white is the solid. This conversion assumes some threshold value. We explored various 194 threshold values to find optimum threshold value for which uncertainties in the estimated 195 volumes are less than $\sim 5\%$.

196 The mass of water that occupied the void space was estimated using the equation of state 197 of water (Hemley et al., 1987). The simplest assumption is that the pressure of water in the void

198 space in the recovered sample is room pressure. This would be the case when the void space is 199 connected. In this case, the mass of water can be estimated by the specific volume of water at 200 ambient condition. However, when void space occurs as isolated inclusions, then the water in the 201 void space could have a higher pressure. Consequently, we have considered a range of pressure 202 of water in the void space, from room pressure to the maximum pressure during an experiment 203 (24 - 25 GPa). In these calculations, the equation of state of water determined by (Hemley et al., 204 1987) was used (Figure 7(a)). The volume of voids estimated on the recovered and polished 205 samples may not be exactly the same as the volume of voids in the sample at room temperature 206 and pressure in the sample before polishing if the pressure of water in the void was high. 207 However, the difference in the volume of voids is small, less than 10%, because this volume 208 change occurs by the elastic deformation of minerals surrounding the voids. The water content in 209 the sample estimated from this method is compared to the initial water content of the sample 210 (Figure 7, Table 3).

211

212 Water content measurement in minerals

213 A summary of the infrared absorption peaks observed in the different compositions of 214 bridgmanite is given in **Table 4**. FTIR measurements of pure MgSiO₃-bridgmanite at ambient pressure showed a dominant absorption peak at 3446 cm⁻¹ (Figure 8(a)). Calculation of the 215 216 water content on this spectrum using the Paterson's equation (Paterson, 1982) gave a value of 70 217 ppm wt. % H₂O. This value is of the same order as that determined by (Meade et al., 1994). 218 FTIR spectra of the solubility in Al-bearing MgSiO₃ bridgmanite was dominated by peaks at 3346, 3405 and 3695 cm⁻¹ wavenumbers. They are likely attributed to superhydrous phase B 219 inclusions (Cynn et al., 1996), while the peak at 3695 cm⁻¹ may also be attributed to brucite 220

(Braterman and Cygan, 2006; de Oliveira and Hase, 2001), (Figure 8(b)). Quantification of
water in this sample was estimated by assuming that water in superhydrous phase B was initially
in bridgmanite. The volume fraction of superhydrous phase B in the quenched sample is
estimated to be about 2-3 vol. % (using Figure 4). Given that under saturation conditions
superhydrous phase B contains about 5 - 6 wt. % water (Bolfan-Casanova et al., 2003; Ohtani,
2005), we can therefore approximate the initial amount of water in the bridgmanite phase to be
about 1000 - 1500 ppm wt. water.

228 Bolfan-Casanova et al. (Bolfan-Casanova et al., 2003)'s also showed that infrared 229 absorption for Al-bearing bridgmanite was dominated by spectra from superhydrous phase B 230 inclusions, and when they removed water in superhydrous phase B, they obtained essentially no 231 detectable water (hydrogen). In contrast, (Litasov et al., 2003) synthesized inclusion free Al-232 bearing bridgmanite (4 - 7 wt. % Al_2O_3) and determined the water content in the bridgmanite to be 1000 - 1500 ppm wt. water with a major broad band at 3448 cm⁻¹. (Fu et al., 2019) have also 233 234 determined the water concentration in (Al, Fe)-bearing bridgmanite, where they determined 1020 235 ppm wt. water in single crystal, inclusion-free bridgmanite, grown from hydrous melt. They observed two FTIR water absorption peaks at 3230 cm⁻¹ and 3460 cm⁻¹ wavenumbers. 236 237 In FeO bearing but Al-free sample (K1157), we observed both bridgmanite and stishovite 238 in the solid phase. Stishovite was mostly located at the boundary between the bridgmanite and 239 melt. No inclusions of superhydrous phase B were seen in this composition. FTIR measurement 240 of water solubility was made, separately for stishovite and bridgmanite phases (**Figure 8**(\mathbf{c})). 241 Absorption peaks in stishovite were observed at 3113, 3238, and 3311 cm⁻¹ those agree with the 242 previous report (Pawley et al., 1993), and give a water content of 26 wt. ppm H_2O after 243 subtraction of the baseline. Meanwhile absorption peaks in bridgmanite were observed at 3296

244	and 3394 cm ⁻¹ and gave a total water content of 44 wt. ppm H_2O . Both spectra show a peak at
245	3687 cm ⁻¹ similar to the OH absorption peak in Mg(OH) ₂ . (Bolfan-Casanova et al., 2003) report
246	only one absorption peak at 3388 cm ⁻¹ in a (Mg, Fe)SiO ₃ bridgmanite sample that amounts to a
247	water content of 2 wt. ppm H_2O .
248	Several bridgmanite compositions containing both iron and aluminum were also
249	investigated. These are shown in Table 1. For the same conditions of pressure and temperature
250	experiment K1161 produced bridgmanite, stishovite and melt in the assemblage while K1182,
251	K1217 and K1222 produced both stishovite and melt with no trace of bridgmanite phase (K1182,
252	Figure 1, Right). FTIR absorption peaks observed in K1161 are consistent with those seen in
253	(Mg, Fe)SiO ₃ and (Mg, Al)SiO ₃ compositions for both the bridgmanite and stishovite phases
254	(Figure 8(d)). The absorption peaks at 3242 cm ⁻¹ and 3479 cm ⁻¹ are consistent with those
255	observed by (Fu et al., 2019), at 3230 cm ⁻¹ and 3460 cm ⁻¹ , respectively. In the experiments where
256	only stishovite and melt were observed, the water solubility peaks measured in the stishovite
257	phase corresponds to absorption peaks at 2661 and 3128 cm^{-1} and is about 670 wt. ppm H ₂ O
258	(Figure 8(e)). This is an order of magnitude higher than that measured in the stishovite produced
259	where no aluminum was present in the starting composition.
260	
261	Discussion
262	Fe loss

All experiments were carried out using platinum as a capsule material. When studying systems containing iron, usually some iron is lost to the capsule material, hence iron loss must be examined. This is why numerous investigations have been carried out so as to minimize Fe loss

by alloying the platinum capsule material with iron (Balta et al., 2011; Grove, 1981;

267 Gudmundsson and Holloway, 1993; Kessel et al., 2001; Vanderlaan and Vangroos, 1991).

268 Surprisingly, in our experiments that contained Fe in the starting composition, we did not 269 find any detectable Fe in the Pt capsules by the EPMA. Composition profiles measured across 270 the thickness of the capsule of the polished samples yielded no Fe (less than the detectability, 271 ~ 0.1 wt. %). Contrary to the Fe loss to a capsule, diffusion of Fe into the sample from the 272 capsule was observed when we used a Pt-Fe alloy capsule. This was confirmed by mass balance 273 analysis when we considered the amount of Fe in the starting composition as well as those 274 measured in the solid and melt phases. We interpret that the cause of little Fe loss to a Pt capsule 275 is due to high oxygen fugacity in our sample assembly due to the presence of a large amount of 276 water (according to (Rubie et al., 1993), the solubility of Fe in Pt decreases with oxygen 277 fugacity).

Further, the mass balance analysis confirmed a melt fraction of 36 - 40 % that is consistent with the estimation of melt fraction obtained from the successive polishing of the capsule and calculating the melt fraction using image analysis discussed earlier. The mass balance results for sample K1157 are shown in **Table 5**.

282

283 A comparison to previous method of water content estimate of unquenchable melts

Figure 7(a) shows a comparison of the water content of the recovered sample (estimated from the water content in the unquenchable melt as described before) and the water content of the starting materials. The agreement is reasonable, and we conclude that (i) not much water escaped from the sample during an experiment, and (ii) our new method of estimating water content in an unquenchable melt is valid.

289 There is no well-established method to estimate the water content of melt when melt 290 cannot be quenched to a glass. A commonly used practice of estimating volatiles is to identify 291 the deficit of EPMA measurements from 100% (e.g., (Hirschmann et al., 2009), see also 292 (Nakajima et al., 2019)). We compare the results of estimates of water content based on the void 293 space and equation of state with the results of this conventional method (Figure 7(b)). It is seen 294 that the conventional method gives systematically higher water content, and that in many cases, 295 the water content estimated by this conventional method exceeds the water content of the starting 296 material indicating that this method is not appropriate. This is most likely caused by the fact that 297 the density of materials (water) filling the void space is substantially less than the density of the 298 rest of a sample. The difference in the estimated water content is very large and it has an 299 important implication for the density of the melt.

However, our method also has a large uncertainty regarding the physical status of thevoid space during depressurization.

302

303 A comparison to the previous studies on hydrogen dissolution in lower mantle minerals

304 There has been a large discrepancy in the water solubility in bridgmanite in previous 305 studies (e.g., (Bolfan-Casanova et al., 2003; Fu et al., 2019; Litasov et al., 2003; Litasov et al., 306 2007)). One plausible cause for this discrepancy is the presence of water-rich "inclusions". For 307 instance, (Schmandt et al., 2014) reported that water-rich melt inclusions in bridgmanite caused a 308 broad absorption similar to those observed by (Bolfan-Casanova et al., 2003; Murakami et al., 309 2002), and suggested that a large water solubility reported by (Murakami et al., 2002) is caused 310 by these inclusions. Similarly, water-rich inclusions such as superhydrous phase B (in cases of 311 bridgmanite) (Bolfan-Casanova et al., 2003) or brucite (in case of (Mg, Fe)O) (Bolfan-Casanova

et al., 2002) could lead to high solubility. Our results on water content in bridgmanite are similarto those studies where some superhydrous phase B was reported.

314 In contrast to these results, (Fu et al., 2019) reported a substantially higher amount of 315 water solubility in inclusion-free bridgmanite synthesized from a hydrous melt under the shallow 316 lower mantle conditions (P = 24 GPa, T = 1873 K) (see also (Litasov et al., 2003)). Since 317 inclusions of hydrous phase such as superhydrous phase B are often observed in our study and 318 most previous studies but not in (Fu et al., 2019) and (Litasov et al., 2003), it is likely that this 319 difference is caused by inclusions. However, the reason why inclusions of superhydrous phase B 320 cause small water content in bridgmanite is not clear. Note that superhydrous phase B is not 321 stable under the conditions from which samples are annealed (P = 25 GPa and T = 1873 K). 322 Consequently, it is likely that those inclusions were formed during quenching, and if this is the 323 case, water (hydrogen) content in these inclusions should not be subtracted when calculating the 324 water solubility in bridgmanite. Indeed, if we use diffusion coefficient of hydrogen in olivine as 325 a guide (e.g., (Kohlstedt and Mackwell, 1998)), we find that time needed to diffuse hydrogen to 326 form inclusions of superhydrous phase B with ~10 micron distance is less than one second. 327 Indeed a computational study by (Hernandez et al., 2013) on (Fe and Al free bridgmanite

at the similar P-T conditions reported similar water solubility (1000 ppm wt), suggesting that the
true water solubility in bridgmanite is of the order of 1000 ppm wt but the effect of Fe and Al
should be explored in more detail.

We also note that because our results suggest that hydrogen location in bridgmanite (and other minerals) is unquenchable, interpretation of the peak position and the breadth of infrared absorption is complicated. For example, hydrogen location (crystallographic site) may change during cooling, and hydrogen may form hydrous minerals such as superhydrous phase B or small

water bubbles. A wide variety of observed infrared spectra likely reflects different processes
during cooling in addition to the variety of crystallographic site where hydrogen may be located
at high pressure and temperatures. It would be interesting to explore the role of cooling processes

on the nature of infrared absorption to understand the role of cooling processes.

339

340 A comparison to the previous studies on the major element (Fe and Al) partitioning

We now compare the results on major element partitioning between bridgmanite and coexiting melt of our experiments. The previous results we will compare include those under dry conditions (Boujibar et al., 2016; Corgne et al., 2005; Ito et al., 2004) and under wet conditions (Kawamoto, 2004; Nakajima et al., 2019). The results are summarized in **Table 6.**

345 (Boujibar et al., 2016) starting compositions are 68 wt. % silicate and 32 wt. % metal, 346 with variable sulfur and silicon contents in the metal and an Al_2O_3 content of 2.6 % in the silicate 347 starting composition. (Corgne et al., 2005) contains Al_2O_3 content of 1.96 % in their starting 348 composition, whereas (Ito et al., 2004) have an Al_2O_3 content of 4.26 % in their starting 349 composition. In our case the Al_2O_3 content in the starting composition ranged between 4.6 – 350 5.0%. Also (Boujibar et al., 2016; Corgne et al., 2005; Ito et al., 2004) started with non-hydrous 351 compositions, and had to raise their samples to a temperature of at least 2000°C in order to obtain 352 melt. In our case, since all our starting compositions contained water, we were able to achieve 353 melt at 1600°C. (Boujibar et al., 2016) use graphite sample capsules in their study, which 354 equilibrates their experiment at a lower oxygen fugacity than in our studies while (Ito et al., 355 2004) and (Corgne et al., 2005) use rhenium metal capsules which equilibrate their systems at 356 higher fugacity than in our study.

The appropriate partition coefficients from (Boujibar et al., 2016) to compare with our studies are those in which bridgmanite equilibrated with melt near the liquidus and had large melt fractions of ~40%, comparable to those observed in our studies. Unlike in the near-solidus bridgmanite compositions, which had much less melt fractions, no corrections on the EPMA results are necessary.

The aluminum-free Fe partition coefficients in all the studies are the same, irrespective of the initial non-hydrous or hydrous conditions. The Fe partition coefficient, therefore, is not affected by the $Fe^{3+}/\Sigma Fe$ ratio in bridgmanite, even with change in oxygen fugacity.

In the case of the aluminum-bearing experiments, on the other hand, the $Fe^{3+}/\sum Fe$ ratio in bridgmanite is enhanced by the presence of aluminum. To a first approximation, therefore, we would conclude that the difference might be as a result of the differences in oxygen fugacities. The oxygen fugacity in our study is higher than that in (Boujibar et al., 2016) and lower than in (Corgne et al., 2005) and (Ito et al., 2004), but we obtained the highest Fe partition coefficient in all the experiments. We could therefore conclude that the presence of water may also have contributed to the high Fe partition coefficient.

372 Meanwhile, when we compare the silica partition coefficients, our Si partition coefficient 373 is on average twice that in all the other three studies conducted under dry conditions. We 374 attribute this primarily to the presence of water. Our results are in good agreement with those by 375 (Kawamoto, 2004), where they carried out hydrous experiments under similar P-T conditions, 376 and also reported the presence of some stishovite. (Kawamoto, 2004) reviewed literature and 377 showed that melts formed from peridotite tend to have a low (Mg + Fe)/Si ratio (more silicic) at 378 low pressures (e.g., (Kushiro, 2001; Mibe et al., 2006; Takahashi, 1986)) whereas (Mg + Fe)/Si 379 ratio becomes higher as pressure increases (e.g., (Mibe et al., 2006; Ohtani, 1987; Takahashi,

1986)). At low pressures, the addition of water *decreases* (Mg + Fe)/Si ratio (more silicic magmas are generated by hydrous melting; (Kushiro, 1972)). In contrast, existing data suggest that at higher pressures (P > 15 GPa), the addition of water *increases* (Mg + Fe)/Si of the melt (e.g., (Kawamoto, 2004; Litasov and Ohtani, 2002)). We found a similar trend in our study: the melt formed by hydrous melting has a higher (Mg + Fe)/Si ratio, leaving SiO₂-enriched residual materials including large crystals of stishovite (**Figure 1 and 5**).

(Nakajima et al., 2019) carried out similar experiments to (Kawamoto, 2004) and
reported a broad range of a Si partition coefficients, but at 1600°C their results are approximately
what was observed by (Kawamoto, 2004) and in our study. But our results show larger amount
of stishovite than these studies. This is presumably due to the difference in the composition of
starting materials: our starting materials have higher SiO2/(MgO + FeO) than Kawamoto (2004)
and Nakajima et al. (2019).

392

393 Some geophysical implications

394 Melting in the lower mantle is possible in two cases. First, in the early stage of Earth 395 evolution, magma ocean was likely present. In this case, water content in the melt is small and 396 consequently the results from dry melting experiments (e.g., (Boujibar et al., 2016)) would be 397 applicable. Second, in the later stage of Earth evolution, temperature in the lower mantle is 398 substantially lower than the dry solidus (e.g., (Andrault et al., 2011)), and therefore, partial 399 melting would occur only at the presence of volatiles such as water. Consequently, our results 400 would be applicable to melting that might occur currently in the (shallow) lower mantle that has 401 been suggested by seismological studies (Liu et al., 2016, 2018; Schmandt et al., 2014).

402

With likely composition determined in the present study, those melts are lighter than the

403 co-existing minerals and hence migrate upward to the bottom of the mantle transition zone (see 404 also (Karki et al., 2018; Nakajima et al., 2019; Sakamaki, 2017)). This provides a mechanism to 405 keep the mantle transition zone wet (Karato et al., 2020). Because these hydrous melts are less 406 dense than surrounding minerals, they will rise up and eventually be incorporated into the mantle 407 transition zone and change to solid aggregates. These materials will have lower seismic wave 408 velocities than the surrounding typical mantle minerals because these frozen melts are FeO and 409 H₂O rich. Similarly, high FeO and H₂O content also suggest high attenuation. Observed low 410 seismic wave velocity regions in the mantle transition zone (e.g., (Wang et al., 2019)) and low Q 411 regions in the mantle transition zone reported by (Zhu et al., 2013) may be caused by these 412 materials derived from the melts formed in the shallow lower mantle.

413 In Figure 9 we compare compositions of residual solids after partial melting under the 414 shallow lower mantle conditions from various studies including (Hart and Zindler, 1986; Javoy 415 et al., 2010; Kawamoto, 2004; Lyubetskaya and Korenaga, 2007a, b; Mcdonough and Sun, 1995; 416 Nakajima et al., 2019; Palme and O'Neill, 2003) where we also include compositions of mid-417 ocean ridge basalt (MORB) and bulk silicate Earth (BSE). Figure 9 (a) is a diagram for SiO2-418 rich composition such as bridgmanite or MORB. For MORB composition, silica-rich materials 419 will be formed as a result of melting in the shallow lower mantle. Therefore the amount of 420 stishovite in the deeply subducted oceanic crust will increase after the partial melting in the 421 lower mantle. In contrast, if the initial composition is nearly BSE, the amount of stishovite is 422 much less after partial melting.

Formation of silica-rich materials has possible geochemical and seismological
implications. There are some reports of SiO₂ inclusions in diamond of deep mantle origin (e.g.,
(Kaminsky, 2020)). Given the deep origin, SiO₂ is likely stishovite in the deep mantle but

426 explaining the presence of pure stishovite is difficult assuming the pyrolytic composition (close
427 to BSE). It is possible that those stishovites are the remnant of lower mantle melting of
428 subducted MORB.

429 Stishovite itself has not much different seismic wave velocities from other minerals down 430 to ~1200 km, but when stishovite is transported into deeper lower mantle by convection, it will 431 transform to a CaCl₂ structure and before the transformation it shows large reduction of C₁₂ that 432 causes large seismic anisotropy and reduction in average velocity (shear wave velocity reduction 433 of ~50%, anisotropy in shear velocity exceeding 100 %) (Karki et al., 1997). Consequently, if 434 there is a substantial amount of stishovite, that will cause substantial seismic scattering. 435 Observed seismic scattering in the depth range of 1000 to 1500 km reported by (Kaneshima and 436 Helffrich, 2010) might be due to the presence of stishovite.

437

438 Summary and concluding remarks

439 High-pressure melting experiments were performed for bridgmanite with a range of 440 composition under water-saturated conditions at P = 25 GPa and $T = 1600^{\circ}C$ equivalent to the 441 shallow lower mantle. We developed a new method of estimating the water content of 442 unquenchable melt via the estimate of the void space in the unquenchable melts. Water 443 (hydrogen) content in the residual solids is determined by FTIR. In most of bridgmanite, there 444 are inclusions of super-hydrous phase B. If these inclusions are formed during cooling water 445 content in hydrous phase B must be included when we estimate water solubility in bridgmanite. 446 Water solubility in the bridgmanite at high pressure and temperature would be ~1000-1500 ppm 447 wt that agrees with the results on inclusion-free bridgmanite reported by (Fu et al., 2019).

However the hypothesis that these inclusions are formed during cooling needs to be tested byfurther experimental studies.

450 Our studies confirm some of the earlier studies in showing that the chemical composition of melts formed under high pressure and hydrous conditions are remarkably different from those 451 452 formed at low pressures. A majority of FeO (and a large fraction of MgO) goes to melt under 453 high-pressure conditions such as the lower mantle conditions. As a consequence, a substantial 454 amount of stishovite is formed in the residual material. The amount of stishovite depends on the 455 composition of the starting materials and is large if the starting material has a MORB-like 456 composition (high FeO/(FeO + MgO) and $Al_2O_3/(Al_2O_3+SiO_2)$). Thus our results provide an 457 explanation for the stishovite paradox discussed by (Kaminsky, 2020). Although the elastic 458 properties of stishovite are not so different from those of other minerals down to ~1000 km, 459 stishovite becomes highly anisotropic and its average velocities become low before the 460 transformation to CaCl₂ structure at \sim 1200 km. This will cause seismic scattering in this depth 461 range.

462

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- 618

Table 1. Starting Compositions of synthesized hydrous bridgmanite (in wt. %), (Mg + Fe)/Si ratios and expected stoichiometry of

Starting materials (Run number)	MgO	Mg(OH) ₂	SiO ₂	Al ₂ O ₃	FeO	(Mg + Fe)/Si	Initial water content*
						(mole ratio)	
Pure MgSiO ₃ Bridgmanite. Excess	24.0	17.0	59.0	0.0	0.0	0.90	5 wt. % H ₂ O
SiO ₂ (K994)							
Pure MgSiO ₃ Bridgmanite. Excess	22.0	33.0	45.0	0.0	0.0	1.48	10 wt. % H ₂ O
MgO (K1073, K1077)							
Al- Bearing MgSiO ₃ Bridgmanite	14.5	32.0	49.5	4.0	0.0	1.10	10 wt. % H ₂ O
(K1098)							
Fe- Bearing MgSiO ₃ Bridgmanite	11.0	32.0	47.0	0.0	10.0	1.23	10 wt. % H ₂ O
(K1157)							
Al- and Fe – Bearing MgSiO ₃	11.0	32.0	47.0	5.0	5.0	1.14	10 wt. % H ₂ O
Bridgmanite (K1161)							
Al- and Fe – Bearing Bridgmanite	8.9	32.0	46.7	4.6	7.2	1.12	10 wt. % H ₂ O
(K1182, 1217, 1222)							

* Water content was calculated from brucite

	K10)77	ŀ	K1098		K1157			K1161		K1	182	K1	222
	MgSiO ₃		(Mg, Al)SiO ₃		(Mg, Fe)SiO ₃		(Mg, Al, Fe)SiO ₃		(Mg, Al, Fe)SiO ₃		(Mg, Al, Fe)SiO ₃			
	Bdg	Melt	Bdg	Melt	Bdg	St	Melt	Bdg	St	Melt	St	Melt	St	Melt
MgO	43.4	41.6	30.1	27.8	36.5	0.0	31.6	35.9	0.1	35.2	0.0	26.9	0.0	26.5
SiO ₂	63.4	35.4	47.8	21.5	56.7	97.8	22.6	53.1	94.1	27.3	93.2	13.4	88.4	13.4
Al ₂ O ₃	0.1	0.1	18.0	0.6	0.0	0.0	0.0	4.2	1.6	3.5	3.0	4.7	2.8	5.2
FeO	0.0	1.0	0.0	0.01	5.0	0.1	17.2	5.4	0.2	5.1	0.1	18.3	0.0	16.9
Oxide totals	105.8	77.2	96.0	49.9	98.2	98.0	71.6	98.7	95.9	71.5	96.3	63.2	91.3	62.0
Mg	2.0	2.5	1.6	2.6	1.9	0.0	2.2	1.9	0.0	2.4	0.0	2.2	0.0	2.2
Si	2.0	1.5	1.7	1.4	2.0	3.0	1.1	1.8	2.9	1.2	2.9	0.7	2.9	0.7
Al	0.0	0.0	0.7	0.1	0.0	0.0	0.0	0.2	0.1	0.2	0.1	0.3	0.1	0.3
Fe	0.0	0.0	0.0	0.0	0.1	0.0	0.7	0.2	0.0	0.2	0.0	0.8	0.0	0.8
Cations per 6 O	4	4	4	4	4	3	4	4	3	4	3	4		4
(Mg + Fe)/Si	1.0	1.8	0.9	1.9	1.0		2.7	1.1		2.0		4.2		4.0

Table 2. Composition of run products (hydrous bridgmanite (Bdg), stishovite (St) and melt) in wt. %.

 Table 3: Porosity estimation and calculated water measurement results from starting water contents

Composition (Experiment number)	Starting Water Content (wt. %)	Porosity (%)	Wt. % water in melt					
			0 GPa	5 GPa	10 GPa	25 GPa	100 – EPMA Total	
MgSiO ₃ (K1003)	5	16	7.8	8.8	9.4	10.4	-	
MgSiO _{3 (} K1077)	5	15	7.4	8.4	8.9	9.9	22.8	
(Mg, Al, Si)O ₃ (K1098)	10	21	10.6	11.9	12.7	14.1	50.1	
(Mg, Fe, Si)O ₃ (K1157)	10	18	8.7	9.8	10.5	11.6	28.4	
(Mg, Al, Fe, Si)O ₃ (K1217)	10	18	9.1	10.2	10.9	12.1	-	
(Mg, Al, Fe, Si)O ₃ (K1222)	10	19	9.6	10.9	11.6	12.8	38.0	
(Mg, Al, Fe, Si)O ₃ (K1270)	5	16	7.8	8.8	9.4	10.4	-	
MgSiO ₃ (K1279)	1	4	1.9	2.2	2.4	2.6	-	
MgSiO ₃ (K1283)	0.1	2	1.0	1.1	1.2	1.4	-	
MgSiO ₃ (K1298)	3	3	1.5	1.7	1.8	2.0	-	

63	2

Composition (Experiment number)	Wavenumber cm ⁻¹					
MgSiO ₃ (K994)					3446	3697
(Mg, Al, Si)O ₃ (K1098)			3346	3405		3695
(Mg, Fe, Si)O ₃ (K1157)		3296	3394			3687
(Mg, Al, Fe, Si)O ₃ (K1161)	3109	3242	3351	3402	3479	3690

Table 4: Summary of the FTIR peak positions in the different bridgmanite compositions studied

 Table 5: Fe mass balance analysis of sample K1157 using EPMA results given in Table 2

Wt. % of Initial FeO	Wt. % FeO in Bdg	Wt. % FeO in Melt	Vol. % Bdg	Vol. % Melt	Total Fe
10	*5.0	*17.2	60	40	
Wt. % of Initial Fe	Wt. % Fe in Bdg	Wt. % Fe in Melt	Wt. % of Fe in Bdg	Wt. % of Fe in Melt	
7.8	3.9	13.4	2.3	5.7	7.7
				% Iron Loss	1.30

643 *EPMA measurements are given in FeO content

Table 6: A comparison on FeO and Al₂O₃ partition coefficient between bridgmanite and co-existing melt

648
$$K_D^{Fe(Si)}$$
 is defined as $K_D^{Fe(Si)} = \frac{(Fe(Si)/Mg)_{bridgmanite}}{(Fe(Si)/Mg)_{melt}}$

Reference	(Boujibar et al	., 2016)	(Ito et al.,	(Corgne et	(Kawamoto,	(Nakajima	This Study
			2004)	al., 2005)	2004)	et al., 2019)	
Experimental	25 GPa		31 GPa	25 GPa	24 GPa	23.5 - 26	25 GPa
Conditions	1900 - 2050°C		2500°C	2350°C	1400°C	GPa	1600°C
	Graphite cap.		Rhenium cap.	Rhenium cap.	Gold cap.	1300 - 1600	Platinum
	Dry conditions		Dry	Dry	Wet conditions	°C	cap.
Partition			conditions	conditions		Gold cap.	Wet
Function	Near liquidus	Near	Near solidus			Wet	conditions
	_	solidus				conditions	
K_D^{Si} Al-Bearing	1.10	1.10	1.26	-	1.98	2.43 - 4.36	2.05
K_D^{Si} Al-Free	1.22	1.10	-	1.15	-	-	1.69
K_D^{Fe} Al-Bearing	0.30	1.10	0.42	0.37	0.69	1.13	1.05
K_D^{Fe} Al-Free	0.27	1.10	-	0.26	-	-	0.25



Figure 1. Back-scattered electron SEM images of a polished MgO-SiO₂-FeO-H₂O system containing ~10 wt. % H₂O in the starting
 mixture (K1157; left), and MgO-SiO₂-FeO-Al₂O₃-H₂O system containing ~10 wt. % H₂O in the starting mixture (K1182; right).
 Bridgmanite (Bdg), stishovite (St) and melt regions are labeled. The scale bars are 200 µm. See Table 1 for sample compositions and
 Table 2 for synthesis conditions.

- 657
- 658
- 659
- 660



0.811 mm

0.680 mm

0.509 mm

0.361 mm

- 661
- 662
- **Figure 2**. Optical images of a sample after successive polishing for melt fraction analysis. Also shown are the total sample thickness

at each stage of polishing. Roughly each polishing step removed 200 micron (K1217).

664

- 00-



Figure 3. Raman spectra of Mg, Al - bearing bridgmanite, K1098, at two different locations at ambient conditions. The red curve is
 from a region containing an inclusion showing evidence for a superhydrous phase B inclusion. X-ray diffraction spectra on left from
 pure MgSiO₃ bridgmanite crystal collected from assemblage showing bridgmanite structure.





Figure 4: Superhydrous Phase B inclusions in (Mg, Al, Si)O₃-bridgmanite (K1098)



Figure 5: Diagram showing the mineralogy of the residual solids for the different starting compositions. Amount of stishovite depends strongly on the composition of the starting material.





Figure 7: (a) A comparison of the water content in the samples with the initial water content, calculated from the void space and
 bridgmanite water content, (b) Comparison of the water content in the melt calculated from the porosity with that determined as less
 than 100% of the total of the oxides from EPMA measurement.



(c)









Figure 8: FTIR spectra of the bridgmanite compositions (a) Fe-Al free bridgmanite (K994) (b) Al-bearing bridgmanite (K1098). The peaks are attributed to superhydrous B. The peak at 3695 cm⁻¹ may also be attributed to brucite. (c) K1157. The black spectrum shows absorption peaks from the stishovite phase while the red, shows the absorption peaks from (Mg, Fe, Si)O₃ bridgmanite phase. (d) (Mg, Fe, Al)SiO₃ (e) K1182. Both peaks at 2661 cm⁻¹ and 3128 cm⁻¹ wavenumbers are from stishovite.





(a) Results for which starting material is bridgmanite (MORB-like composition) and (b) Results for which the starting material has
 bulk silicate Earth composition.