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2 # Hydrogen incorporation mechanism in the lower-mantle bridgmanite

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25   **ABSTRACT**

26   Bridgmanite, the most abundant mineral in the lower mantle, can play an essential role in deep-

27   Earth hydrogen storage and circulation processes. To better evaluate the hydrogen storage

28   capacity and its substitution mechanism in bridgmanite occurring in nature, we have synthesized

29   high-quality single-crystal bridgmanite with a composition of $(Mg_{0.88} Fe^{2+}_{0.05} Fe^{3+}_{0.05} Al_{0.03})(Si_{0.88}$

30    $Al_{0.11} H_{0.01})O_3$ at nearly water-saturated environments relevant to topmost lower mantle pressure

31   and temperature conditions. The crystallographic site position of hydrogen in the synthetic (Fe,

32   Al)-bearing bridgmanite is evaluated by a time-of-flight single-crystal neutron diffraction

33   scheme, together with supporting evidence from polarized infrared spectroscopy. Analysis of the

34   results show that the primary hydrogen site has an OH bond direction nearly parallel to the

35   crystallographic *b* axis of the orthorhombic bridgmanite lattice, where hydrogen is located along

36   the line between two oxygen anions to form a straight geometry of covalent and hydrogen bonds.

37   Our modelled results show that hydrogen is incorporated into the crystal structure via coupled

38   substitution of Al^{3+} and H^+ simultaneously exchanging for Si^{4+} which does not require any cation

39   vacancy. The concentration of hydrogen evaluated by secondary-ion mass spectrometry and

40   neutron diffraction is ~0.1 wt% H_2O and consistent with each other, showing that neutron

41   diffraction can be an alternative quantitative means for the characterizations of trace amounts of

42   hydrogen and its site occupancy in nominally anhydrous minerals.

43

44

INTRODUCTION

45

46   Chemically bonded hydrogen in rock-forming minerals of mafic oceanic lithospheres could

47   survive subduction processes and be transported into the deep Earth via plate tectonic motions

48   (Kawakatsu and Watada 2007; Ohtani et al. 2004; Thompson 1992). The total mass of such

49   hydrogen cycle in the present Earth had been proposed to exceed the mass of surface ocean water

50   (Karato et al. 2020). Crystal structures of hydrous and nominally anhydrous minerals in the deep

51   Earth are possible candidates for transporting such hydrogen into the deep mantle. The hydrogen

52   incorporation in these minerals can involve not only covalent hydroxyl (OH) bonds but also

53   moderate to strong hydrogen bonds as determined primarily by neutron diffraction works

54   (Purevjav et al. 2014; 2016; 2018; 2020; Sano-Furukawa et al. 2011; 2018; Tomioka et al. 2016;

55   Trots et al. 2013; Suzuki et al. 2001). These hydrogen bonds in the host minerals allow hydrogen

56   to stay in the host crystal structures even at relevant high-temperature conditions. Among such

57   hydrogen-hosting minerals, wadsleyite and ringwoodite in the mantle transition zone from 410

58   km to 660 km depth are among the most representative ones and relatively well documented;

59   these minerals can have total water storage capacities as high as six ocean masses (Karato et al.

60   2020 and references therein). The actual existence of hydrogen in the transition zone had also

61   been confirmed by the discovery of a natural hydrous ringwoodite crystal in a diamond inclusion

62   (Pearson et al. 2014).

63   As for the fate of hydrogen beyond 660 km depth, it is essential to consider that some of

64   the oceanic lithospheres can penetrate through the transition zone and carry some hydrogen into

65   the lower mantle (Fukao et al. 2009; Fukao and Obayashi 2013; Portner et al. 2020). The lower

66   mantle, the largest volume fraction of the layered Earth, consists of bridgmanite, ferropericlase,

67   and other minor constituent phases. Bridgmanite likely represents approximately 80 % of the

68   lower-mantle volume (Hirose et al. 2017), such that hydrogen capacity and stability in this

69   mineral phase is one of the primary factors in determining the distribution and circulation of

70   hydrogen within the multi-layered Earth. There have been extensive studies on hydrogen in

71   bridgmanite in past decades, including analyses by Fourier-transform infrared (FTIR)

72   spectroscopy and secondary-ion mass spectrometry (SIMS) for synthetic crystals obtained at

73   relevant high pressure and temperature conditions (Bolfan-Casanova et al. 2003; Litasov et al.

74   2003; Meade et al. 1994; Murakami et al. 2002; Liu et al. 2021; Panero et al. 2015). In addition

75   to these studies, Fu et al. (2019) conducted a combined analysis of polarized FTIR and

76   NanoSIMS to characterize hydrogen in (Fe, Al)-bearing bridgmanite synthesized at nearly water-

77   saturated, uppermost lower mantle conditions. They reported that the single-crystal bridgmanite,

78    $Mg_{0.88} Fe^{3+}_{0.065} Fe^{2+}_{0.035} Al_{0.14} Si_{0.90} O_3$, contains ~1,020(±70) ppm of H_2O and displays two

79   pronounced OH^- stretching bands at ~3,230 cm^{-1} and ~3,460 cm^{-1}. Following these works, here

80   we have focused on the analysis of hydrogen's chemical bonding environments in the crystal

81   structure of (Fe, Al)-bearing bridgmanite. For the first time, the high-quality bridgmanite crystals

82   we synthesized here permit time-of-flight (TOF) Laue neutron diffraction analysis. These results

83   allow us to refine the site of chemically-bonded hydrogen and to model its cation exchange

84   mechanism within the crystal structure. We have also conducted polarized FTIR analysis in all

85   three principal crystal orientations. Together with SIMS analysis of the crystals, these results

86   provide new insights in our understanding of the hydrogen substitution site and mechanism in the

87   crystal structure of bridgmanite.

88

89   **CRYSTAL STRUCTURE OF BRIDGMANITE AND**

90   **ITS HYDROGEN EXCHANGE MECHANISM**

91   Here we briefly introduce the crystal structure of bridgmanite and its previously proposed

92   hydrogen substitution mechanism as this information will be used to evaluate the actual

93   experimental data for the hydrogen site occupancy in the present study. Figure 1 shows the

94   crystal structure of (Fe, Al)-bearing bridgmanite (space group *Pbnm*), which is the same as that

95   of $MgSiO_3$ bridgmanite (Horiuchi et al. 1987; Kudoh et al. 1990; Nakatsuka et al. 2021;

96   Sugahara et al. 2006; Ross and Hazen 1989). The A cation site with twelve (or practically eight)

97   oxygen anions (O^{2-}) is occupied by either magnesium (Mg^{2+}), iron ($Fe^{2+/3+}$), or aluminum (Al^{3+}).

98   The B cation site with six O^{2-} anions is occupied by either silicon (Si^{4+}) or Al^{3+}. There are two

99   O^{2-} sites (O1 and O2), which were proposed to include a minor fraction of vacant sites ($V^{\bullet\bullet}_O$)

100   (Navrotsky 1999). Each O1 is shared by two BO_6 octahedra with the bonding direction along the

101   *c*-axis, while each O2 is shared by two BO_6 octahedra with the bonding direction normal to the *c*-

102   axis. Based on the aforementioned crystal structure, two types of hydrogen exchange

103   mechanisms had been proposed for the Al-bearing bridgmanite system. These are (1) Al^{3+} (or

104   possibly Fe^{3+}) and H^+ simultaneously exchange for Si^{4+} at a B site (Muir and Brodholt 2018;

105   Townsend et al. 2015), and (2) two Al^{3+} or Fe^{3+} and one $V^{\bullet\bullet}_O$ simultaneously exchange for two

106   Si^{4+} at two B sites, and then some fraction of the generated $V^{\bullet\bullet}_O$ is coupled with another O^{2-} to

107   simultaneously exchange for two OH^- (Litasov et al. 2003; Navrotsky 1999).

108

EXPERIMENTAL AND ANALYTICAL PROCEDURES

110   **Synthesis**

111   In the previous study, we had synthesized high-quality, inclusion-free crystals of (Fe, Al)-

112   bearing bridgmanite at a fixed pressure-temperature condition of 24 GPa and 1800 ºC using a

113   scaled-up Kawai-type cell (Fu et al. 2019; Okuchi et al. 2015). The current synthesis procedure

114   was designed for growing larger crystals several hundreds of μm in sizes while maintaining the

115   quality of the crystals. The starting material was made of a powder mixture of $MgSiO_3$,

116    $Mg(OH)_2$, ^{57}FeO, and Al_2O_3, with 64.8, 20.2, 8.9, and 6.1 wt%, respectively. It contains 6 wt% of

117   H_2O, simulating a water-saturated peridotite system. Approximately 15 mg of the mixture was

118   packed into a Pt capsule with outer and inner diameters of 2.3 and 2.0 mm, respectively. The

119   capsule was sealed by welding, inserted into a 14/6 Kawai-type cell assemblage, and then

120   pressurized to 24 GPa by applying a 19 MN load at the Institute for Planetary Materials (IPM),

121   Okayama University. At the targeted pressure, the capsule was heated to 1820 °C and kept for 10

122   minutes to melt the mixture. Then, the temperature was slowly reduced to 1690 °C with a

123   cooling rate of 0.5 °C/min for 4 hours, and even more slowly decreased to 1590 °C with a rate of

124   0.1 °C/min for 12 hours. Finally, the temperature was kept constant for another 4 hours. After

125   this series of temperature control procedures, the sample was quenched by cutting off the power

126   source under high pressure. The assemblage was then decompressed to ambient pressure.

127

Phase identification and major element analysis

129   After decompression and recovery of the product crystals from the capsule, several crystals

130   were selected and analyzed using micro-focused XRD (Rigaku's RINT RAPID II – CMF) at

131   IPM. The largest dark brownish bridgmanite crystals were ~500 μm in size (Fig. 2a). A small

132   fraction of transparent majorite crystals of ~200 μm sizes were also found to co-exist with the

133   bridgmanite. Fine-powdered and light-greenish quenched aggregates were also occasionally

134   found, which were identified by XRD analysis as a mixture of dense hydrous magnesium silicate

135   (DHMS) phase D and brucite. This indicates that the bridgmanite crystals were grown in a

136   nearly-water-saturated magmatic environment (Fig. 2b).

137   Major-element compositions of the bridgmanite crystals were determined using a JEOL

138   JXA-8800 electron-probe microanalyzer (EPMA), with operating conditions of 15 kV

139   accelerating voltage, 12.1 nA probe current, and 5 μm probe diameter. Two crystals with

140   polished surfaces were measured by taking four data points from each crystal (Table 1). In

141   addition to these point analyses, macroscopic chemical homogeneity of Mg, Si, Fe, Al, and O

142   within these crystals was confirmed by map analysis. An additional double-side polished crystal

143   190 × 170 μm^2 in size and ~200 μm in thickness was prepared for Mössbauer spectroscopy of

144   ^{57}Fe analysis at Advanced Photon Source at the Argonne National Laboratory (Fig. 2c). Ferric

145   iron fraction of the bridgmanite crystal was determined to be $Fe^{3+}/\Sigma Fe = $ ~52 % (Fig. 2d). Based

146   on these results, the major-element chemical formula of bridgmanite was defined as $Mg_{0.88}$

147    $Fe^{2+}_{0.05} Fe^{3+}_{0.05} Al_{0.11} Si_{0.88} O_3$ including all the cation species except hydrogen.

148

Transmission electron microscopy

150   Four bridgmanite crystals of 200 – 400 μm sizes were prepared for transmission electron

151   microscopy (TEM) analysis. They were cross-sectioned and polished to prepare for five

152   independent foils of 100 to 150 nm in thicknesses and lateral sizes of ~12 × ~8 μm^2, using a

153   Hitachi SMI-4050 focused ion beam apparatus. Figure 3 shows representative TEM images of

154   one of the foils using JEOL JEM-ARM200F at the Japan Agency for Marine-Earth Science and

155   Technology (JAMSTEC), which was operated at low magnification TEM mode (Fig. 3a) and

156   high-resolution scanning TEM (HR-STEM) mode (Fig. 3b, c) at 200 kV accelerating voltage.

157   Nano-scale analysis of the samples shows that they are homogeneous and free of inclusions and

158   defects, indicating that hydrogen must be incorporated in the lattice, instead of forming

159   precipitates or inclusions within the crystal. The selected-area electron diffraction patterns also

160   feature sharp spots consistent with a long-range ordered high-quality crystal structure (Fig. 3d).

161

162   **Polarized Infrared and SIMS analysis**

163   Using polarized FTIR spectroscopy, we determined the bonding direction and strength of

164   structural hydroxyls (OH$^-$) within the three-dimensional lattice of the (Fe, Al)-bearing

165   bridgmanite (Fig. 4). Three crystals of ~400 µm sizes were selected for determination of their

166   crystallographic orientations using X-ray precession photography at Osaka Metropolitan

167   University (Fig. 4e and 4f). Double-side polished thin sections of thicknesses from 100 to 350

168   µm were prepared to have orientations normal to the three crystallographic axes of bridgmanite.

169   FTIR spectra of the three sections were taken at IPM using a JASCO FTIR-6200 spectrometer

170   coupled to an IRT-7000 microscope with 10× objective/condenser, a KBr/Ge beamsplitter, an

171   MCT detector, a ceramic infrared light source, and a KRS-5/Al wire-grid polarizer. A series of

172   polarized spectra were collected within each section, where 1,024 scans were accumulated in

173   each spectrum with an aperture size of 50 × 50 µm and a wavenumber resolution of 4 cm^{-1}.

174   Considering the limit of page space, two spectra series from sections normal to *a* and *c* axes are

175   shown in detail, which are essential to determine the orientation of the O–H dipoles (Figs. 4a and

176   4b). Nonlinear peak fitting analysis was conducted for these series to model each band. Pole

177   figures were prepared to show the two most important bands within the two spectra series (Figs.

178   4c and 4d). These spectra within each crystal were highly reproducible at several different

179   aperture positions, indicating homogeneous distribution of hydrogen within the crystal.

180   The hydrogen concentration was quantitatively analyzed by SIMS (CAMECA IMS-6F) at

181   JAMSTEC. The other three crystals of ~250 µm sizes were embedded in an indium pellet

182   together with standard materials. Sample mounts were ultrasonically washed using acetone and

183   pure water, then dried in a vacuum oven overnight before coating. The mount was then coated

184   with gold of 30 nm thickness, and kept in a SIMS sample chamber in a vacuum for more than a

185   day before the analysis. This procedure worked effectively to reduce background of absorbed

186   water on the sample surface. In the SIMS measurements, a primary $^{133}Cs^+$ beam operated at 1 nA

187   and 14.5 keV was focused to a 15 μm spot on the sample surface. Normal incident electron

188   shower was used for electrostatic charge neutralization of the sputtering area. A field aperture

189   was used to permit transmission of ions from the central area of 10 μm in diameter of the

190   sputtered region to minimize the hydrogen signals from remaining absorbed water on the sample

191   surface. The secondary ions of ^1H, ^{12}C, and ^{30}Si were collected from the sputtered area

192   sequentially by an electron multiplier with 1 second × 20 cycles. Total duration of each analysis

193   was ~5 minutes, including 120 seconds of pre-sputtering. For hydrogen standard materials, we

194   used (i) natural amphibole from the Ichinome-gata volcano (Miyagi and Yurimoto 1995) and (ii)

195   aphyric glass of a mid-oceanic ridge basalt EPR-G3 from the East Pacific Rise (Shimizu et al.

196   2017), which were reported to contain 1.66 and 0.22 wt% of H_2O, respectively (Fig. 5). As for

197   the dry silicate standard for background analyses of hydrogen and carbon, San Carlos olivine

198   was used. While we measured ^{12}C for monitoring contaminations from invisible scratches or

199   cracks on the minerals, we did not observe any irregularly-higher $^{12}C/^{30}Si$ ratios than the carbon

200   background. In order to determine the hydrogen concentration in sample crystals, five to seven

201   data points were collected from different portions of each crystal, where we once again

202   confirmed that hydrogen was homogeneously distributed within these crystals, as in the case of

203   FTIR results. Figure 5 shows our procedure to determine the hydrogen concentration as H_2O in

204   the samples assuming a linear relationship between their concentrations and the $^1H/^{30}Si$ ratio. We

205   did not conduct background correction of H_2O because the observed $^1H/^{30}Si$ ratio of San Carlos

206   olivine was negligibly small compared with the sample crystals. The H_2O concentration in the

207   bridgmanite was either 630(40) or 810(50) ppm: the former was obtained using the natural

208   amphibole standard and the latter was obtained using the EPR-G3 glass, respectively. These

209   results are compared with the neutron diffraction results that are described later in this paper.

210

211   **Neutron diffraction and major element distribution**

212   As collaboratively demonstrated by the datasets of EPMA, HR-(S)TEM, FTIR, and SIMS

213   analyses, the synthesized (Fe, Al)-bearing bridgmanite crystals were chemically homogeneous in

214   their major cations and hydrogen distributions (Okuchi et al. 2015). In the present study, we aim

215   to refine the site position of hydrogen in the bridgmanite crystal structure, where neutron

216   diffraction plays the most essential role. To achieve the task, it is essential to find site

217   distributions and occupancies of all major cations and anions in addition to hydrogen, because

218   hydrogen can only become visible after removing all scattering densities of these stronger

219   neutron scatters from the bridgmanite lattice space. One of the largest crystals was selected for

220   neutron diffraction, which was $0.4 \times 0.5 \times 0.15$ mm^3. The crystal was exposed to the neutron

221   beam for ~2.5 days in total at a TOF Laue diffractometer TOPAZ installed at the Spallation

222   Neutron Source (SNS), Oak Ridge National Laboratory, which was operated at 1.4 MW proton

223   beam power (Schultz et al. 2014). The crystal was cooled down to 100 K by cold nitrogen gas,

224   where the signal-to-noise ratio of higher-order reflections was enhanced (Purevjav et al. 2016,

225   2018, 2020). For covering the full reciprocal space, we sequentially reoriented the crystal to have

226   25 different orientations with the help of the CrystalPlan software (Zikovsky et al. 2011). The

227   obtained *hkl*-intensity dataset was refined using the General Structure Analysis Software (Larson

228   and Von Dreele 2004). The optimized structure parameters are summarized in Table 2. The

229   refined space group of the bridgmanite crystal is *Pbnm*, consistent with the previous studies. The

230   lattice constants determined at 100 K are $a = 4.8071(2)$ Å, $b = 4.9473(1)$ Å, and $c = 6.9141(2)$ Å.

231   Based on the EPMA analysis, we have obtained the total occupancies of A and B sites for

232   Mg, Fe, Al, and Si cations. Upon defining their relative distributions between A and B sites (Fig.

233   1), we considered their preferences reported in the previous crystal-chemical studies of

234   aluminous and/or ferrous bridgmanite: (i) Mg and Fe strongly prefer the A site, (ii) Si strongly

235   prefers the B site, and (iii) Al moderately prefers the B site, which are all due to the relations

236   between the relevant site volumes and ionic radii (Lin et al. 2016; Nakatsuka et al. 2021; Nishio-

237   Hamane et al. 2005). In addition, Al can be distributed into the A site when the capacity of the B

238   site is exceeded, as confirmed by the stability of the bridgmanite structure along the solid

239   solution of $MgSiO_3$ and $Mg_3Al_2Si_3O_{12}$ (Hirose et al. 2001; Kubo and Akaogi 2000). Therefore,

240   in our structural refinements, Mg and Fe were all fixed in the A site and Si was fixed in the B site,

241   whereas Al occupancies were refined between the A and B sites while constraining their total to

242   be equal with the bulk analytical result from EPMA. As shown in Table 2, this constrained

243   refinement procedure for cation occupancies provided a very reasonable solution: the neutron

244   coherent scattering length of ^{57}Fe (=2.3), Al (=3.45), Si (=4.15), and Mg (=5.38) are all

245   substantially different from each other, guaranteeing that their site distribution was solidly

246   constrained as long as the scattering intensity dataset had enough quality. We found that the total

247   occupancy of the A site was 1.01 as the sum of Mg, Fe, and Al nuclear site occupancies, where

248   its total cation charge was 2.11 as the sum of Mg^{2+}, Fe^{2+}, Fe^{2+}, and Al^{3+} valences. We also found

249   that the total occupancy of the B site was 0.99 as the sum of Al and Si nuclear site occupancies,

250   where its total cation charge was 3.84 as the sum of Al^{3+} and Si^{4+} valences. The total cation

251 valence charge at the A and B sites was 2.11 + 3.84 = 5.95, which was smaller than the total

252 anion charge of 6.00, as necessarily expected when hydrogen cations were additionally involved

253 within the crystal structure. From these results on the nuclear site occupancies, we concluded that

254 Fe^{2+} or Fe^{3+} did not substantially exist in the B site, which was in contrast to some previous

255 reports (Frost and Langenhorst 2002; Hummer and Fei 2012; Litasov et al. 2003). We note that

256 the results were obtained along with the refined scale factor that assured full occupancies of the

257 two oxygen sites (Table 2). Unreasonable cation site deficiencies in both the A and B sites would

258 be necessary if we instead assumed nontrivial oxygen site vacancies, as previously proposed

259 (Navrotsky 1999).

260

261 **Neutron diffraction and hydrogen site analysis**

262 Normal hydrogen (^{1}H) generates negative scattering length density distribution of neutrons,

263 whereas all other atoms generate positive densities. Therefore, even if the concentration of

264 hydrogen is much smaller than the other atoms, its position can still be detectable as a unique

265 negative anomaly in the three-dimensional scattering density map (Fourier map). To find such an

266 anomaly in our data, we obtained a difference-Fourier map similar to the case of our previous

267 work (Purevjav et al. 2018). We calculated this map using the difference between all major

268 cation and anion densities and the observed neutron scattering densities. In order to discriminate

269 the hydrogen site, we refined the coordinates, the occupancy, and the Debye-Waller factors of

270 each candidate position step-by-step as suggested from each apparently negative anomaly in the

271 difference map. These procedures in finding the candidate site were made for sixty-three

272 candidate positions located at distances of 0.7 Å to 1.3 Å measured from the nearest oxygen site.

273 As explained later in the discussion, only one of them, shown in Figure 6, was fully consistent

274   with the other analytical results, such that we defined it as the primary hydrogen site shown in

275   Table 2.

276

277   **Neutron diffraction and hydrogen concentration**

278   After finding the primary site, we try to evaluate its occupancy which is equivalent to the

279   hydrogen concentration in the crystal structure. This is a much more challenging task than

280   finding the site, because of its small occupancy, low site symmetry, and very large Debye-Waller

281   factors, all consistently make the quantitative evaluation of scattering density of hydrogen

282   difficult. We previously reported that the accuracy of refined hydrogen occupancy is secured by

283   its stability as a function of resolution in space, where the resolution increases with increasing

284   number of reflections at smaller d-spacings (Purevjav et al. 2016; 2018). Following this

285   methodology, we evaluated the hydrogen occupancy in bridgmanite (Fig. 7). It was proved to be

286   stable throughout the whole resolution range to provide best-effort site occupancy of

287   0.010±0.003 (Table 2).

288

289   **RESULTS AND DISCUSSION**

290   **Primary site position deduced from infrared and neutron results**

291   Using the polarized FTIR results, here we discuss the most-plausible hydroxyl bonding

292   strength and direction in the bridgmanite. It was suggested that multiple bonding geometries

293   coexisted within the crystal structure, because of such broad and orientation-dependent infrared

294   absorption profiles, which ranged from 2300 cm^{-1} to 3800 cm^{-1} (Fig. 4). The bonding geometries

295   must also be highly anisotropic within the bridgmanite structure. By carefully evaluating the

296   orientational dependence of the profiles, we assigned four coexisting vibration bands, which

297   have peak wavenumbers at 3480($\pm$40) cm^{-1}, 3160($\pm$20) cm^{-1}, 2880($\pm$20) cm^{-1}, and 2680($\pm$50) cm$^-$

298   ^{1}, respectively. The integrated area intensity of the 3160 cm^{-1} band was much more significant

299   than the 3480 cm^{-1} band (Figs. 4c and 4d) and also than the other two. Therefore, even

300   considering the negative correlation between the molar absorption coefficient and the OH

301   stretching wavenumber (Libowitzky and Rossman, 1997), the most intense 3160 cm^{-1} band still

302   showed the property of the most important hydrogen site. The next strongest 3480 cm^{-1} band

303   showed the property of the second site. When the section normal to the *a* axis was analyzed (Fig.

304   4c), these two bands had common strong pleochroism with the largest absorbances along the *b*

305   axis and very small absorbances along the *c* axis. Therefore both of these OH dipoles were

306   oriented normal to the *c* axis. When the section normal to the *c* axis was analyzed (Fig. 4d), the

307   two bands showed reversing moderate pleochroism. While the 3160 cm^{-1} band showed the

308   largest absorbance around the *b* axis, the 3480 cm^{-1} band showed the largest absorbance around

309   the *a* axis. Their wavenumbers were reported to quantitatively reflect hydrogen bonding strength;

310   it is reasonable to assume that the 3160 cm^{-1} band was from hydroxyls with a moderately-strong

311   hydrogen bond, while the 3480 cm^{-1} band was from that with a very weak hydrogen bond

312   (Libowitzky 1999). While the crystal orientation information was less clarified than in the

313   current case, the coexistences of these two bands and their coherent behavior against crystal

314   orientation were already observed by infrared analysis of (Fe, Al)-bearing bridgmanite (Fu et al.

315   2019; Litasov et al. 2003). Considering the features of the two strong bands, we conclude that the

316   most important hydrogen site formed hydroxyls approximately aligned along the *b* axis with

317   moderately-strong hydrogen bonding, whereas the second site approximately aligned along the *a*

318   axis with very weak hydrogen bonding.

319   With the new insights from these infrared results, it follows that the primary hydrogen site is

320   located between two O1 oxygen anions, which is the most-consistent solution among the

321   possible candidates suggested from the neutron diffraction results. These two O1 oxygens form

322   an edge of the A site dodecahedron, where the hydrogen is installed with a hydrogen bonding

323   angle of 179(6)° (Fig. 6), forming a straight bonding geometry along the edge. The covalent

324   hydroxyl bond has a distance of 1.03(7) Å and the counterpart hydrogen bond has a distance of

325   1.81(7) Å. The hydrogen sites related to the other three bands at 3480, 2880, and at 2680 cm^{-1} are

326   not yet clearly resolved by neutron diffraction. Nonetheless, they show substantial pleochroism

327   as a function of orientation, making them definable as independent bands. We currently do not

328   have any conclusive solution on their crystallographic geometry. A suggestion may come from

329   previous infrared evidence for another nominally anhydrous mineral having an octahedrally-

330   coordinated Si cation site. For example, a remarkably-similar infrared band of very weak

331   absorption at 2659–2667 cm^{-1} was reported for both Al-free and Al-bearing stishovite, where

332   either reaction of $Si^{4+} \leftrightarrow Al^{3+} + H^+$ or $Si^{4+} \leftrightarrow 4H^+$ was proposed to generate its wide variety of

333   hydroxyl absorption bands (Litasov et al. 2007). In addition, a combination of two broad but

334   distinct bands at around 2900 cm^{-1} and 2650 cm^{-1} were reported to exist in Al-free stishovite

335   experiencing $Si^{4+} \leftrightarrow 4H^+$ hydration reaction (Spektor et al. 2016). Thus, the bands at the lower

336   wavenumbers observed in bridgmanite could come from clustered hydrogen around the vacant B

337   site, although further studies are necessary to clarify the nature of such hydrogen clusters in the

338   crystal structure of bridgmanite.

339

340   **Hydrogen substitution mechanism**

341   In previous works using neutron diffraction, we successfully determined full structure

342   parameters of several dense hydrogen-bearing minerals occurring in the mantle transition zone,

343   including both nominally hydrous and anhydrous types (Purevjav et al. 2014; 2016; 2018; 2020).

344   It has been demonstrated that octahedrally coordinated Mg^{2+} or Fe^{2+}, as well as tetrahedrally

345   coordinated Si^{4+}, were removed to exchange for hydrogen. That is, hydrogen clusters are

346   generated around the sites originally filled by Mg^{2+}, Fe^{2+}, and Si^{4+} cations. On the other hand, in

347   the bridgmanite structure in the lower mantle, these major cations remain even after the

348   hydration reaction. In other words, it is preferred to avoid creating any cation vacancy as well as

349   hydrogen clusters. By simply referring to the total cation occupancy of 1.01 and its valence

350   charge of 2.06 in the A site, it is clear that hydrogen clustering around such a fully filled site with

351   such an excess charge is energetically unfavorable. We thus conclude that one hydrogen around

352   one filled cation is the unique solution most consistent with the neutron diffraction result (Fig. 6

353   and Table 2). On the other hand, the total cation charge of 3.94 in the B site must be

354   compensated by such an addition of hydrogen around oxygen anions surrounding the site. Since

355   Al^{3+} causes the smaller charge in the B site, the major hydrogen exchange reaction in (Fe, Al)-

356   bearing bridgmanite must be (1') Al^{3+} and H^+ simultaneously exchanging for Si^{4+} in the B site

357   (Muir and Brodholt 2018; Townsend et al. 2016). We note that the addition of hydrogen only

358   increases the total cation charge to 5.96, which is still smaller than the total anion charge of 6.00.

359   The origin of the remaining difference (0.04 per formulation) is still not clear; it is not reasonable

360   to assume a far larger concentration of hydrogen in this site, as explained later. While we may

361   ascribe some fraction of this difference by possible uncertainty of EPMA analysis and

362   Mössbauer results, further research is necessary to solve this issue on the missing cation valence

363   charge.

364

Hydrogen concentration

366   To provide a reliable hydrogen concentration in aluminous bridgmanite which has been

367   greatly debated so far (Fu et al. 2019; Litasov et al. 2003; Liu et al. 2021; Murakami et al. 2002),

368   and also to evaluate the technical limit of single-crystal neutron diffraction for a trace amount of

369   hydrogen, we finally compare and discuss the concentration values obtained by neutron

370   diffraction and SIMS schemes to each other. Our SIMS results show that the H_2O concentration

371   is between 630($\pm$40) and 810($\pm$50) ppm (Fig. 5). On the other hand, our neutron diffraction

372   results show that the hydrogen site occupancy is 0.010($\pm$0.003) which corresponds to its bulk

373   concentration of 870($\pm$260) ppm (Fig. 7). These results are rather consistent with each other,

374   suggesting that single-crystal neutron diffraction can be an alternative means for a quantitative

375   evaluation of hydrogen concentration as low as 900 ppm = 0.09 wt% of H_2O. We also note that

376   our infrared results suggest the existence of minor hydrogen site(s) which were not revealed in

377   the analysis of neutron diffraction data, but could still be detected in the SIMS analysis results.

378   Further neutron diffraction research using even larger crystals with significantly larger volumes

379   could be useful to address other remaining questions in hydrated bridgmanite.

380

IMPLICATIONS AND CONCLUSIONS

382   In this study, we have determined the full crystallographic parameters of hydrous (Fe, Al)-

383   bearing bridgmanite, including its hydrogen site position and occupancy, using the TOF Laue

384   neutron diffraction scheme. The diffraction experiments were proved successful due to the use of

385   large and high-quality bridgmanite crystal synthetically grown in a nearly water-saturated

386   environment. Together with the complementary dataset of polarized infrared spectroscopy, our

387   results show that both the hydroxyl covalent bond and the hydrogen bond are directed nearly

388   parallel to the crystallographic *b* axis. The water concentration in bridgmanite has been

389   quantitatively evaluated by SIMS analysis, in addition to the neutron diffraction scheme. These

390   results for water concentration are self-consistent and complementary to each other, showing that

391   neutron diffraction can be used to detect its trace amount as low as ~0.1 wt% H_2O.

392   It was demonstrated that hydrogen is incorporated into the bridgmanite crystal structure via

393   the coupled exchange reaction of H^+ and Al^{3+} for Si^{4+} ($H^+ + Al^{3+} \leftrightarrow Si^{4+}$), which does not require

394   the presence of a cation vacancy. That is, hydration in bridgmanite is not accompanied with the

395   creation of any vacancies or any hydrogen clusters, which is in marked contrast to the previously

396   reported hydrogen substitution mechanisms in hydrous minerals in the upper mantle, such as

397   wadsleyite, ringwoodite, and DHMS phase E (Purevjav et al. 2014; 2016; 2018; 2020; Sano-

398   Furukawa et al. 2011; Tomioka et al. 2016). We consider that this contrast is due to the densely-

399   packed nature of the bridgmanite structure, where larger numbers of oxygen anions coordinate

400   single cation. Therefore, it is energetically unfavorable to remove such a cation to create a

401   vacancy while keeping the structure. Multiple hydrogen occupancy within one vacant site

402   (Purevjav et al. 2014; 2016) or creation of hydrogen clusters (Purevjav et al. 2018) are prohibited

403   in the structure of bridgmanite without vacancies, implying that its hydrogen concentration is

404   much more limited than the upper mantle minerals which can have numerous cation vacancies.

405   We thus reinforce the prevailing concept that the upper mantle, including the transition zone,

406   keeps more water than the lower mantle (Karato et al, 2020). In addition, the absence of cation

407   vacancy in hydrous bridgmanite in the lower mantle is important for considering its rheological

408   behavior. We confirmed the result of Muir and Brodholt (2018) by first principle calculation,

409 where hydration of bridgmanite cannot promote hydrolytic weakening because the prevailing

410 $Al^{3+} + H^+$ coupling mechanism does not create any cation vacancies.

411   It had been previously proposed that the geometry of chemical bonding around hydrogen

412 atoms in the hydrogen-bearing deep-mantle minerals are determined with high accuracy by using

413 smaller *d*-spacings in the TOF single-crystal experiments (Okuchi et al., 2015). Our study here

414 demonstrates that the distances of covalent and hydrogen bonding and the angle between them

415 can be measured even for the trace amount of hydrogen in the bridgmanite single crystal. This

416 result opens a new window of research opportunity to analyze hydrogen positions and

417 concentrations in other deep-mantle nominally anhydrous minerals by making full use of such

418 neutron diffraction instruments. This type of future studies can help to understand the hydrogen

419 substitution mechanism and water solubility in wide variety of minerals in the deep Earth.

420

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579

580   **Figure and Table captions**

581

582   Table 1. Major-element composition of two representative bridgmanite crystals analysed by

583   EPMA. The weight percent of each oxide component is listed, where FeO* is determined

584   assuming all Fe is Fe^{2+}. Total average# values of the two crystals were used for the neutron

585   structure refinement.

586

587   Table 2. Refined structure parameters of the (Fe, Al)-bearing bridgmanite. Initial atomic

588   coordinates in the refinements were taken from Horiuchi et al. (1987). See the text for the

589   refinement procedure in detail.

590

591   Figure 1. The crystal structure of (Fe, Al)-bearing bridgmanite with an orthorhombic symmetry

592   (space group *Pbnm*). The bridgmanite structure consists of A site cations, B site cations, and

593   oxygen anions with an ABO_3 perovskite-type framework. In the illustration, the A sites are

594   visible as brown spheres while the B sites are hidden inside blue-colored BO_6 octahedra. The

595   illustration was produced using VESTA3 (Momma and Izumi, 2011).

596

597   Figure 2. Synthesis and characterizations of the (Fe, Al)-bearing bridgmanite crystals. All scale

598   bars shown with black color are 100 μm in length. (a) A stereo microscope image of the

599   recovered bridgmanite crystals with dark-brownish color and subhedral to euhedral forms. (b) A

600   micro-focused X-ray diffraction pattern of the recovered aggregates with a mixture of the

601   bridgmanite (asterisks), brucite (Br), and DHMS phase D (D), respectively, indicating that the

602   bridgmanite crystals were grown under nearly water-saturated condition. The inset shows the

603   appearance of the aggregates. (c) Double-side polished crystal of the (Fe, Al)-bearing

604   bridgmanite with a thickness of ~200 μm. The red circles indicate the areas for Mössbauer

605   measurements. (d) Mössbauer spectrum of the bridgmanite crystal. The spectrum was collected

606   using a ^{57}Co point source with a beam size of 300 μm and a collection time of ~40 hours. The

607   spectrum was fit with two doublets, corresponding to Fe^{2+} (green) and Fe^{3+} (blue) using the

608   MossA program (Prescher et al., 2012). Analysis of the spectrum shows ~52 % $Fe^{3+}/\Sigma Fe$ and

609   ~48 % $Fe^{2+}/\Sigma Fe$.

610

611   Figure 3. TEM/STEM micrographs of the (Fe, Al)-bearing bridgmanite crystal. (a) A bright-field

612   TEM image of a representative thin foil which shows homogeneous crystal without visible

613   inclusions or defects. (b) A bright-field STEM image showing the lattice fringes of (001). (c) A

614   Fourier-noise-filtered image of (b) which confirmed high-quality lattice spaces without

615   disturbances. (d) A selected-area electron diffraction (SAED) pattern along the [1-10] zone axis

616   for a selected area of the crystal. The SAED pattern shows sharp reflection spots of the

617   bridgmanite structure.

618

619   Figure 4. Polarized infrared absorption spectra, pole figures, and photographs of the oriented

620   crystal sections of bridgmanite. (a) A series of spectra measured from the section cut normal to

621   the *a*-axis and double-side polished into 350(±10) μm thickness. It was measured along the

622   orientation from 0º (the polarization of the IR beam parallel to the *c*-axis) via 90º (parallel to the

623   *b*-axis) to 180º (again parallel to the *c*-axis). (b) A series of spectra measured from the section cut

624   normal to the *c*-axis and double-side polished into 100(±10) μm thickness. It was measured along

625   the orientation from 0º (the polarization of the IR beam parallel to the *a*-axis) via 90º (parallel to

626   the *b*-axis) to 180º (again parallel to the *a*-axis).

627   (c, d) The couple of pole figures corresponding to the series of spectra (a) and (b). These show

628   intensity trend of integrated absorbances of 3480 cm^{-1} (open circle) and 3160 cm^{-1} (filled circle)

629   bands, respectively. (e, f) The measured crystal sections cut normal to the *a* and *c* axes,

630   respectively.

631   For each specrum shown in (a) and (b), a baseline for the window of O-H stretching region (2300

632   to 3800 cm^{-1}) was defined as a spline finction covering the original spectrum from 1500 to 4000

633   cm^{-1}, and was subtracted from tne original. This baseline was close to linear in the window of the

634   O-H stretching region. For definig each point shown in (c) and (d), a nonlinear peak-fitting

635   analysis was conducted to resolve overlapped Gaussian peaks within the series of spectra (a) and

636   (b).

637

638   Figure 5. Results of hydrogen concentration analysis for the bridgmanite (Bdg) crystals by SIMS.

639   The solid and broken lines show correlations between ^{1}H/^{30}Si count ratios and water

640   concentrations using natural amphibole (Amp) and basaltic glass (EPR-3G) as the standards,

641   respectively. San Carlos olivine (SC) was used as the dry reference standard. Two independent

642   H$_2$O concentrations from the two crystals (an enlarged region is shown in the inset) were

643   obtained using the averages of all data points from each crystal.

644

645   Figure 6. A difference-Fourier map sectioned normal to the *c*-axis of the bridgmanite. The map

646   shows residual nuclear density distribution after removing scattering contributions from all major

647   cations and anions other than hydrogen. The A sites (shown in brown color) are occupied by Mg,

648   Fe, and Al cations, whereas the B sites (shown in gray color) are occupied by Al and Si cations.

649   This map simultaneously shows positive (blue color) and negative (yellow and red colors)

650   residuals of the scattering density. We evaluated each of the apparent negative residual in the

651   three-dimensional map volume, including those not shown in this section, for finding the

652   possible hydrogen site position (see the text for details). After the evaluation, a negative residual

653   of -1.16 fm/Å^3, as highlighted by the black-dashed circle, was determined as the primary

654   hydrogen site position. The hydrogen is located between two O1 oxygen anions, with OH

655   covalent bonding direction close to the b axis.

656

657   Figure 7. The refined hydrogen site occupancies as a function of the resolution in space. The

658   hydrogen site was refined as (x, y, z = 0.288, 0.143, 0.25) (see Table 2). These occupancies were

659   determined one by one for a series of reflection intensity datasets with different minimum d-

660   spacings from 0.40 Å to 0.60 Å.

Crystal	1					2					1 and 2
Point	1	2	3	4	average	1	2	3	4	average	average[#]
SiO_2	51.6	51.5	52.0	51.9	51.8(2)	49.4	51.2	51.3	50.9	50.7(9)	51.2(8)
Al_2O_3	7.1	7.5	7.1	6.9	7.1(3)	6.8	7.5	7.6	7.5	7.4(4)	7.2(3)
MgO	34.7	34.5	34.6	34.7	34.6(1)	33.6	34.6	34.4	34.3	34.2(5)	34.4(4)
FeO*	6.6	6.8	6.5	6.5	6.6(1)	8.9	7.1	7.2	7.1	7.6(9)	7.1(8)
Total	100.0	100.3	100.2	99.9	100.1(2)	98.6	100.5	100.5	99.7	99.8(9)	100.0(6)

Table 1

Wyckoff positions	Atoms	Coordinates			Occupancies	Debye-Waller factors (x10^2), Å^2						
		x	y	z		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
	Mg				0.877						0	
4b (A-site)	Fe	0.51446(7)	0.55654(5)	0.25	0.101	0.370(10)	0.352(7)	0.601(8)	0.080(7)	0		
	Al				0.034(1)							
4b (B-site)	Si	0.5	0	0	0.875	0.150(10)	0.143(8)	0.174(8)	0	0	0.013(6)	
	Al				0.113(1)							
4c	O1	0.10543(5)	0.46321(4)	0.25	0.998(1)	0.346(8)	0.356(6)	0.320(6)	0	0	0	
8d	O2	0.19497(4)	0.20015(3)	0.55449(2)	1.000(1)	0.365(6)	0.372(4)	0.419(5)	0.070(4)	0.069(4)	0.084(4)	
4c	H	0.288(14)	0.143(13)	0.25	0.010(3)							3(1)

Table 2

y
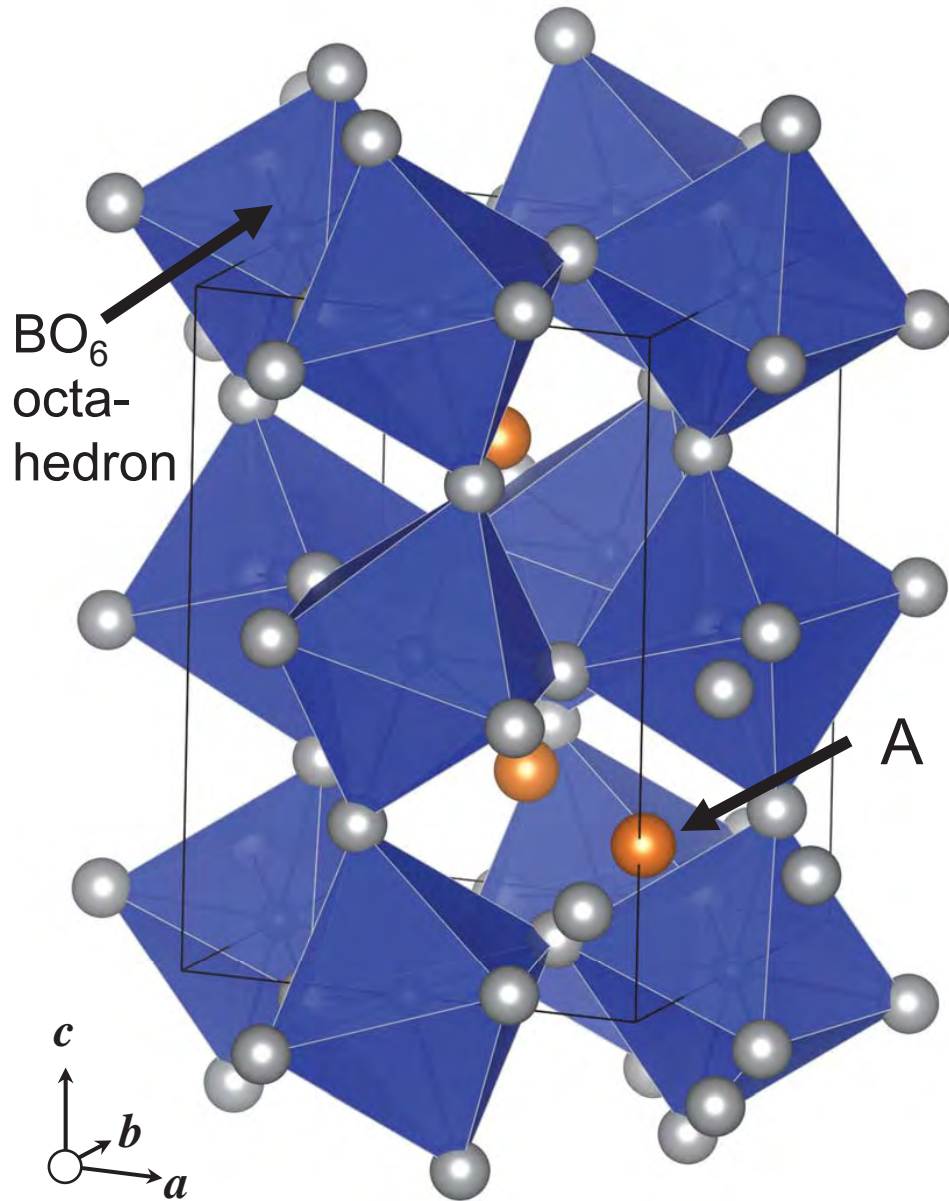
Figure 1
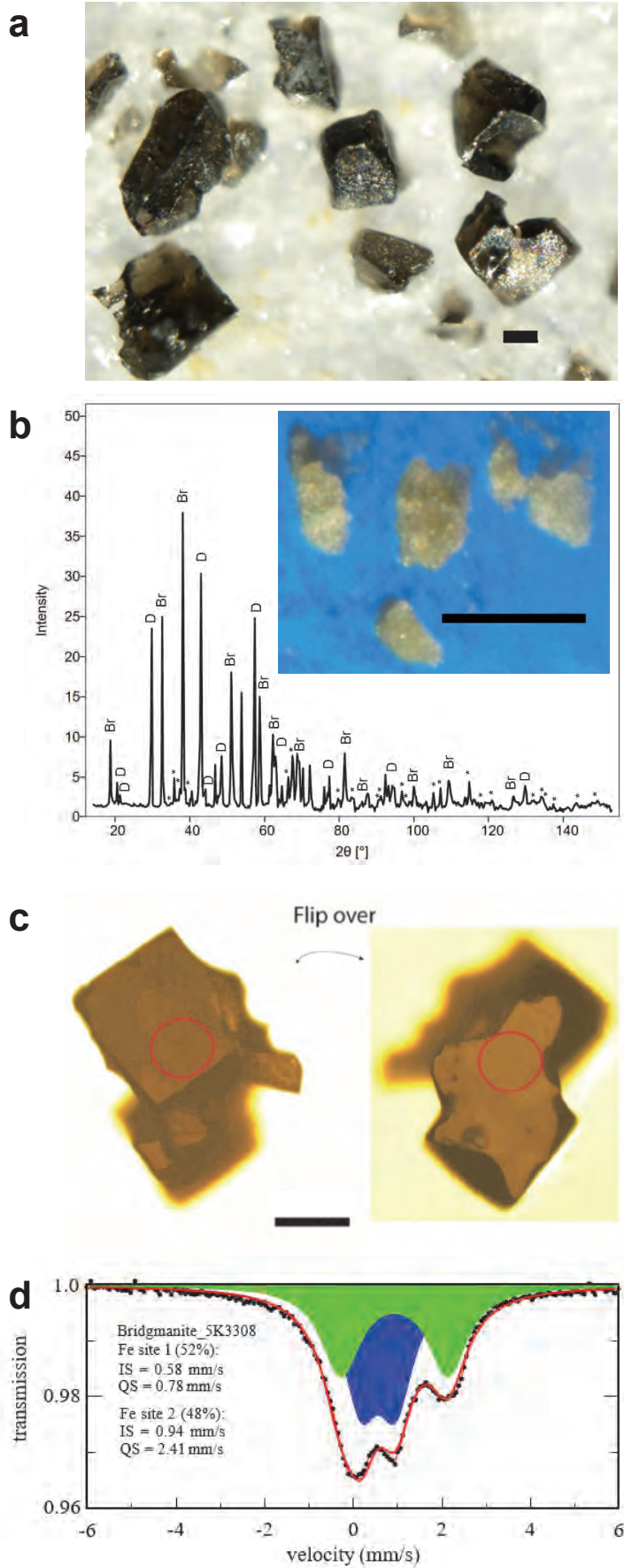
Figure 2

Figure 3

Figure 4

(c) section ⊥*a*

(d) section ⊥*c*

(e)

(f)
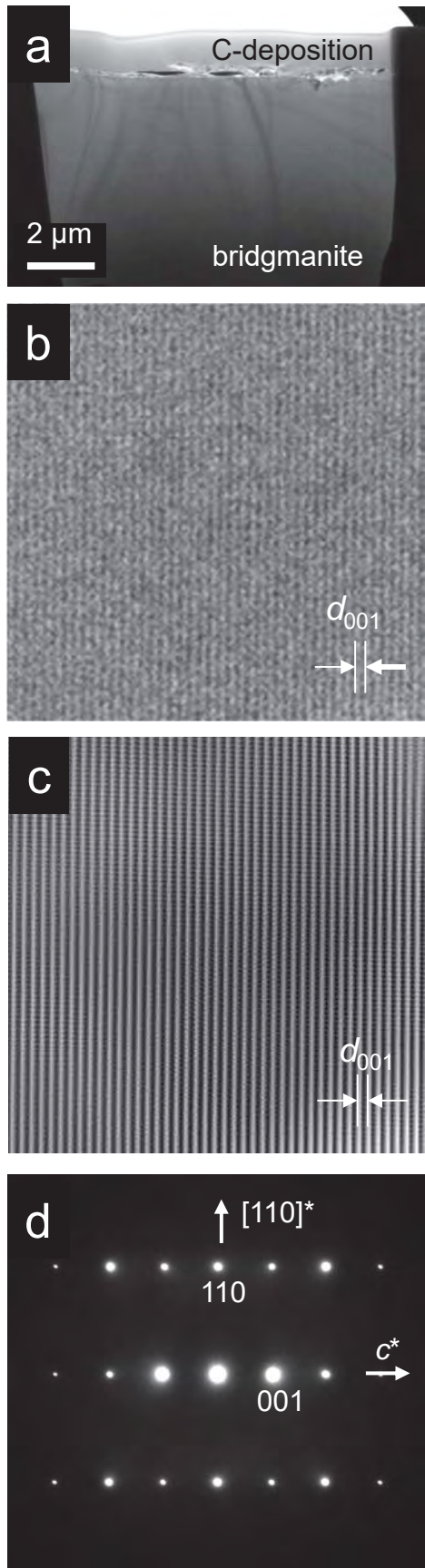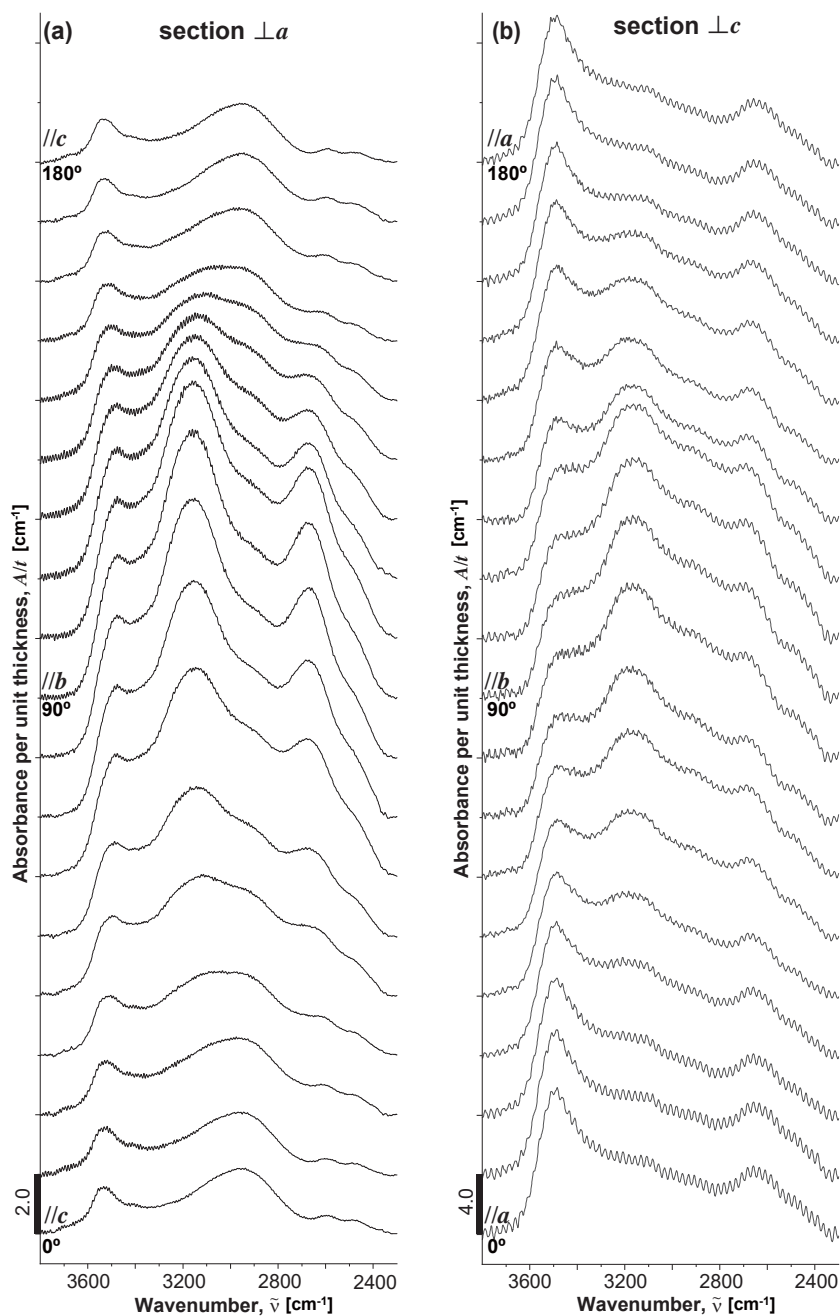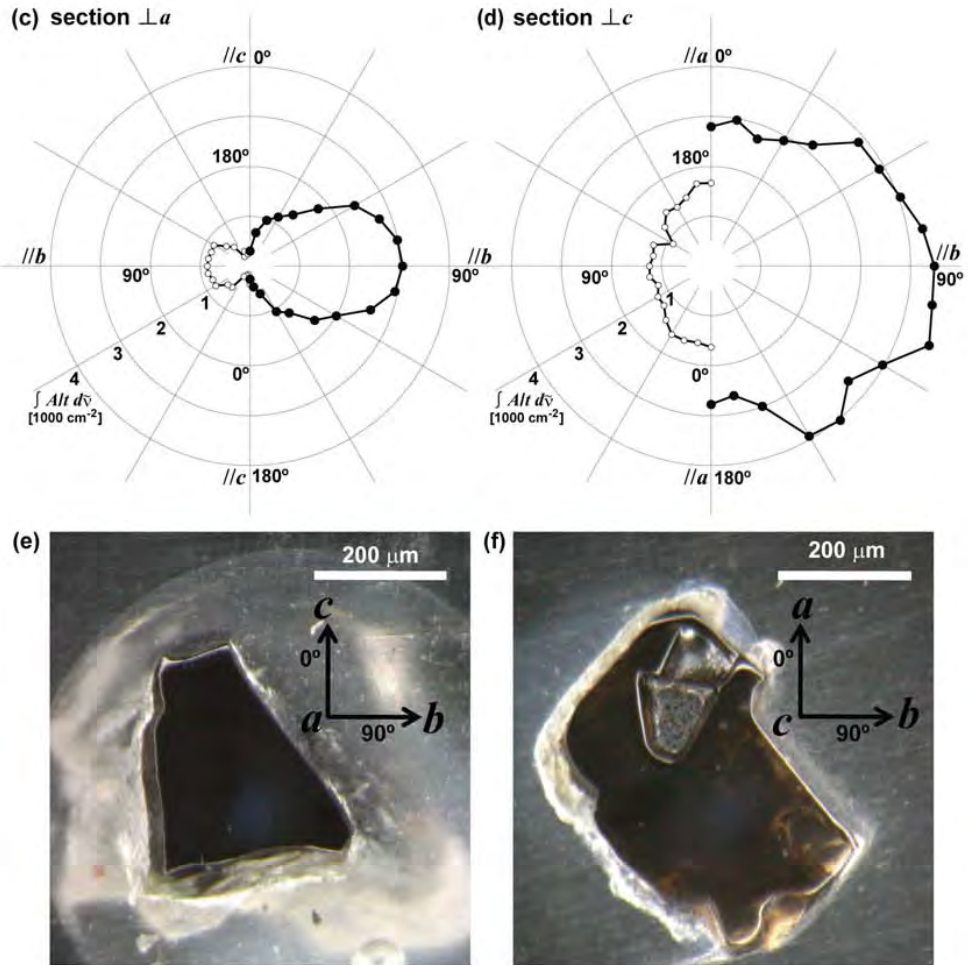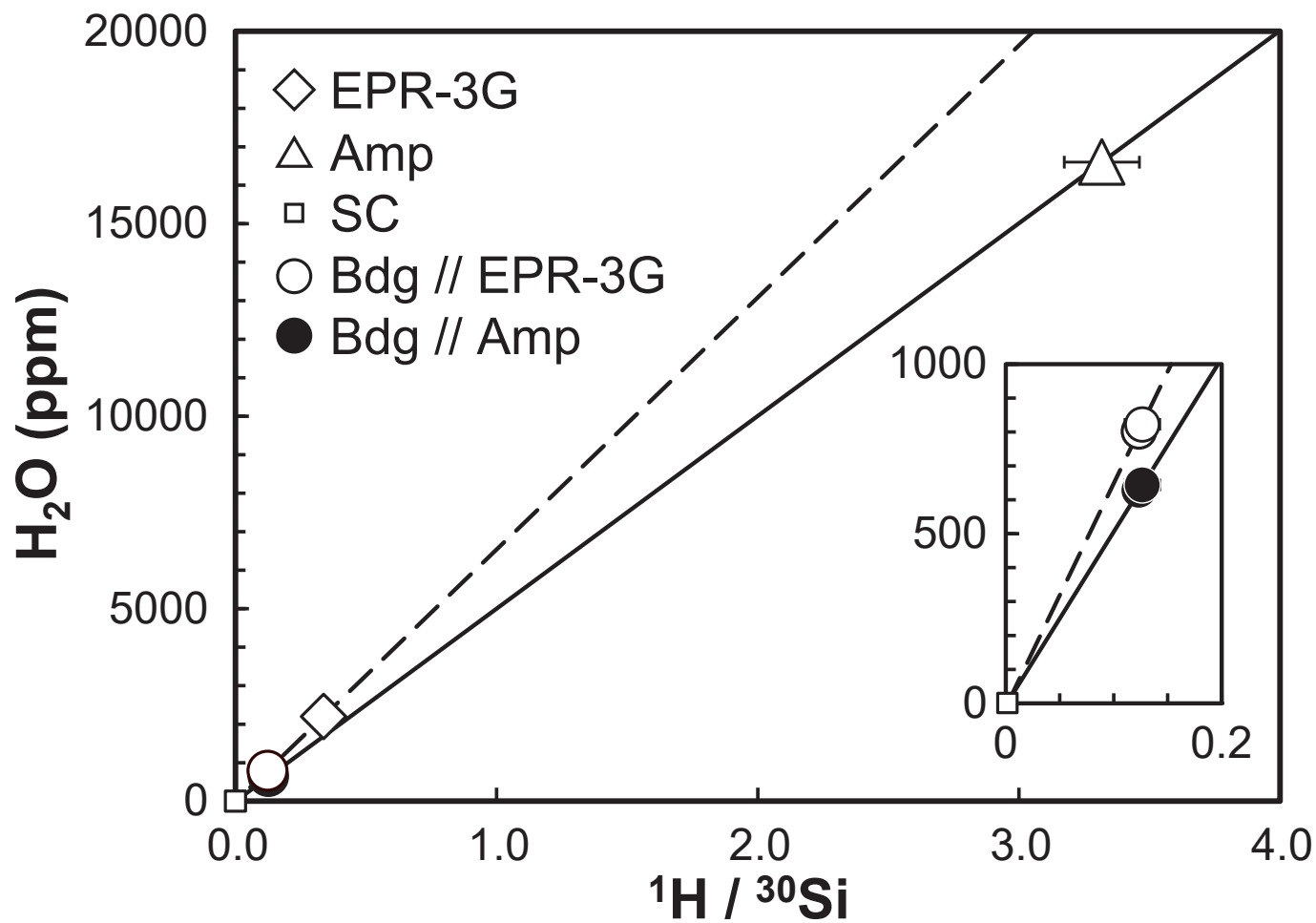
Figure 5

Figure 6

Figure 7