1   **Revision 1:** The determination of hydrogen positions in superhydrous phase B

2   Dmytro M. Trots,[1,*] Alexander Kurnosov,[1] M. A. Geeth M. Manthilake,[1] Sergei V.

3   Ovsyannikov,[1] Lev G. Akselrud,[2] Thomas Hansen,[3] Joseph R. Smyth,[4] and Daniel J.

4   Frost[1]

5   [1] Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

6   [2] Lvov Ivan Franko State University, Institute of Inorganic Chemistry, UA-79005 Lvov,

7   Ukraine

8   [3] Institut Max von Laue–Paul Langevin, 38042 Grenoble Cedex 9, France

9   [4] Department of Geological Sciences, University of Colorado, Boulder, Colorado, USA.

10   * – d_trots@yahoo.com

11   **Abstract**

12   In order to investigate the nature of hydrogen incorporation into the structure of

13   superhydrous phase B, neutron powder diffraction experiments have been performed. A

14   structural model based on *Pnn*2 symmetry has been used for the analysis of the data,

15   which is consistent with earlier spectroscopic studies. Application of Fourier synthesis

16   with subsequent analyses of difference nuclear density maps and Rietveld fits reveal two

17   distinct positions for deuterium, at 4c (0.194, 0.052, 0.596) and at 4c (0.186, 0.119,

18   0.388). This unambiguously ***shows*** that deuterium lies within large channels, which are

19   formed between the edge–shared octahedra and vertex–linked tetrahedra along the *b*–axis

20   of the structure. These results contrast with recent polarized single crystal infrared

21   spectroscopy studies where the position of one of two hydrogens was estimated to lie

22   close to the octahedral edge of an MgO_6 octahedron, thereby leaving the large structural

23   channel empty.

24   **Keywords:** hydrous magnesium silicates, neutron diffraction, superhydrous phase B,

25   crystal structure, hydrous minerals, determination of hydrogen positions.

26   **Introduction**

27   Water exists in the Earth's mantle in a number of different forms. It may exist as a

28   free fluid phase; it may be dissolved in silicate melts or incorporated into nominally

29   anhydrous minerals, such as the polymorphs of Mg_2SiO_4 (forsterite, wadsleyite and

30   ringwoodite). It may also be incorporated into nominally hydrous high-pressure silicate

31   phases, such as dense hydrous magnesium silicate (DHMS) phases, which have to date

32   mainly been characterized in the in $MgO–SiO_2–H_2O$ ternary system. The DHMS phases,

33   referred to as A, E, B and superhydrous phase B (SHyB), might be stable at the pressure

34   and temperature conditions compatible with cold portions of subducting slabs and they

35   may form a network of phases with overlapping stability fields that transport water into

36   the lower mantle. Although, the existence of DHMS in nature is still under debate, SHyB

37   *might* be stable within ultramafic compositions coexisting with ringwoodite at conditions

38   compatible with subducting slabs in the lower part of the transition zone (Angel et al.

39   2001). The formation of hydrous minerals such as SHyB may influence the mechanical

40   and rheological properties of slabs, and the ultimate dehydration might potentially be

41   related to the processes causing deep-focus earthquakes. Any attempt to understand the

42   stability or transport properties of such hydrous phases, however, ***would benefit*** from an

43   understanding of the crystal structure**,** including an appreciation of the hydrogen sites.

44   SHyB has an ideal chemical composition of $Mg_{10}Si_3O_{14}(OH)_4$, with a Mg/Si ratio

45   of 3.2 and 5.8 wt% of stoichiometrically incorporated water and lies along the brucite–

46   anhydrous phase B join of the $MgO–SiO_2–Mg(OH)_2$ ternary system. SHyB was first

2

47 identified and characterized by Gasparik (1993). The current picture of the hydroxyl

48 substitution mechanisms in $Mg_{10}Si_3O_{14}(OH)_4$ is based on results of X–ray diffraction

49 studies (Pacalo and Parise 1992; Kudoh et al. 1994; Koch-Müller et al. 2005), nuclear

50 magnetic resonance (NMR) studies (Xue et al. 2008), and infrared (Cynn et al. 1996;

51 Koch-Müller et al. 2005) and Raman spectroscopy studies (Cynn et al. 1996; Frost and

52 Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005).

53   The first model of the crystal structure of SHyB was established from X–ray

54 diffraction studies by Pacalo and Parise (1992) who determined its orthorhombic *Pnnm*

55 symmetry with *Z*=2. However, in this study the positions of the hydrogen atoms were

56 determined only approximately from difference Fourier maps (Pacalo and Parise 1992).

57 Hydrogen was placed into a general position 8h at (-0.0769, 0.3026, 0.1085) with

58 multiplicity 8, which corresponds to a site within the channels along the *a*-axis (*b*-axis in

59 our crystallographic setting) (Pacalo and Parise 1992). Kudoh et al. (1994) and Koch-

60 Müller et al. (2005) performed single crystal X-ray diffraction studies on

61 $Mg_{10}Si_3O_{14}(OH)_4$ and proposed two non-centrosymmetric space groups, *P2₁nm* and *Pnn*2,

62 respectively. Although, the hydrogen sites were not determined in the former paper, the

63 *P2₁nm* symmetry implies the existence of two distinct crystallographic sites for the

64 hydrogen atoms. Koch-Müller et al. (2005) proposed approximate coordinates for two

65 distinct positions for hydrogen atoms, at 4*c* with (0.3, 0.6, 0.1) and at 4*c* (0.27, 0.18,

66 0.45). The first position was inferred from electron density Fourier difference maps

67 obtained by means of X–ray diffraction studies, ***consistent with the polarized IR spectra***,

68 whereas, the second position came from polarized single-crystal infrared spectroscopic

69 studies ***only***. The infrared and Raman spectroscopic studies (Cynn et al. 1996; Frost and

3

70   Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005) do not corroborate the

71   centrosymmetric *Pnnm* space group for SHyB suggested by Pacalo and Parise (1992).

72   These spectra show two intense peaks in the infrared O–H stretching region that is clear

73   evidence for the existence of two distinct crystallographic positions for hydrogen atoms

74   (Cynn et al. 1996; Frost and Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005).

75   Furthermore, comprehensive 2D ^{1}H and ^{29}Si NMR investigations have also shown the

76   existence of dissimilar hydrogen (H1-H2) pairs in SHyB and found only one distinct

77   tetrahedral Si site (Xue et al. 2008). These findings are consistent with the *Pnn*2 space

78   group (Xue et al. 2008)*, which was proposed by Koch-Müller et al (2005). Moreover,*

79   *Xue et al. (2008) have also excluded Pnnm of Pacalo and Parise (1992) and P2₁mn of*

80   *Kudoh et al. (1994). Xue et al. (2008)* questioned the H positions and OH dipole

81   directions found *as proposed by* Koch-Müller et al. (2005). In fact, while the H1 position

82   at (0.3, 0.6, 0.1) is located inside a channel along the *b*-axis, the H2 position at (0.27, 0.18,

83   0.45) is close to the octahedral edge O3–O9 of the Mg3O$_6$ octahedron (Xue et al. 2008).

84   The hydrogen bond of H2 belongs in this case to the same Mg3O$_6$ octahedron and hence

85   the large structural channel remains unfilled. *Furthermore, Koch-Müller et al. (2005)*

86   *presented sufficient evidences to claim the existence of a high-temperature polymorph*

87   *of Ni-doped SHyB. On the contrary, the existence of such polymorph was questioned*

88   *by Xue et al. (2008) based on analysis of undoped sample. Such discrepancies may*

89   *suggest the existence of a phase transition between the "high-temperature polymorph*

90   *of SHyB" and the "low-temperature polymorph of SHyB", which is induced by*

91   *changes in the Ni-content (Ni-SHyB and SHyB are substantially different compounds*

92   *and this might lead to different crystallographic symmetries).*

4

93   Thus, the available information from the literature concerning the predominant

94   locations of hydrogen atoms in the structure of the SHyB is inconsistent. Therefore, a

95   detailed investigation that could shed light on fine details of water incorporation in the

96   structure of the SHyB is required for construction of realistic mineral physical models.

97   Neutron diffraction is the most rigorous method for determination of deuterium site

98   occupancies in crystalline phases because neutron scattering cross sections are not a

99   function of atomic mass as for X-ray diffraction and are relatively large for deuterium. In

100   this study the deuterium sites in the SHyB structure have been precisely determined by

101   means of neutron powder diffraction.

102   **Experimental details**

103   A sample of the SHyB of about 20 mg was synthesised from Mg_2SiO_4 (forsterite)

104   + D_2O in a 5000 tonne large-volume press (Frost et al. 2004). An 18 mm edge length

105   Cr_2O_3 doped octahedral pressure assembly was used with tungsten carbide cubes that had

106   8 mm edge length corner truncations. Mg_2SiO_4 + D_2O were placed inside a welded

107   platinum capsule of 3 mm diameter and approximately of 4 mm length. The capsule was

108   inserted into an MgO sleeve and placed into a cylindrical $LaCrO_3$ heater that was inserted

109   into the octahedral assembly. The temperature during the experiment was monitored

110   using a W3Re/W25Re thermocouple inserted within an alumina tube, with the junction in

111   contact with the top of the Pt capsule. Other details were similar to those reported in

112   previous studies (Frost et al. 2004). The synthesis was performed at 22 GPa, and a

113   temperature of 1100 C^o, with an annealed duration of 4 hours. The recovered sample was

114   milled into a powder and characterized by Raman spectroscopy and X–ray powder

115   diffraction.

116   Neutron powder diffraction measurements were performed at the D20 high–flux

117 instrument installed at the neutron reactor at the Institut Laue-Langevin in Grenoble,

118 France (Hansen et al. 2008). A vanadium sample holder of 4 mm in diameter was filled

119 with a sample of the SHyB and was loaded inside a cryostat sample chamber. The

120 measurements were carried out at ambient temperature and at 10 K. Reducing the

121 temperature to 10 K permitted the deuterium positions to be determined more precisely

122 since the atomic displacement parameters (a.d.p.) of atoms are strongly reduced at low

123 temperatures. The wavelength of 2.415 Å was determined using a $Na_2Ca_3Al_2F_{14}$

124 reference material; a second wavelength of 2.419 Å was also recognized and included in

125 the Rietveld fits. Despite the presence of the second wavelength, this experimental setup

126 gave the maximum of intensity at the sample position and allowed us to perform high-

127 quality neutron diffraction experiments on a relatively small sample of approximately 20

128 mg. After switching on the oscillation of the sample, a microstrip position sensitive

129 detector was used for data collection in the range of 15–150 degrees of 2θ. The collected

130 diffraction patterns were analyzed by ***full-profile Rietveld refinements and difference***

131 ***Fourier analyses*** using the WinPLOTR package (Rodriguez–Carvajal 1993). The

132 resolution function of the diffractometer and the peak profile shape were modeled using a

133 pseudo-Voigt function, determined by fitting a $Na_2Ca_3Al_2F_{14}$ reference material. The

134 background of the diffraction pattern was fitted using a linear interpolation between

135 selected data points in non-overlapping regions. The scale factor, the lattice parameters,

136 zero shift and the Y profile shape parameter were varied during the fitting procedure. As

137 the crystal structure of SHyB is complex with 18 distinct sites for Mg, Si and O, the

138 atomic coordinates of these atoms were fixed at those values determined by single-crystal

139   synchrotron diffraction measurements (Koch-Müller et al. 2005), whereas, the fractional

140   coordinates and the occupancies of the deuterium atoms and a.d.p.'s parameters of all

141   atoms were varied.

142   **Results**

143   The initial crystal model and the crystallographic setting used for the refinement of

144   the SHyB structure were those proposed by Koch-Müller et al. (2005), i.e., with *Pnn*2

145   symmetry. Hydrogen positions proposed in this paper were not introduced into the

146   refinements. The *Pnn*2 symmetry is also consistent with NMR results of Xue et al. (2008).

147   In the sample secondary minor phases of stishovite and ringwoodite could be detected

148   which were included in the full-profile refinements. The fit residuals R_p =3.37%,

149   R_{wp}=4.62% and χ^2=8.97 (*Pnn*2 space group) were achieved when deuterium positions

150   were not introduced into the structural model. Thereafter, we determined the initial

151   positions of the deuterium atoms from analyses of the Fourier nuclear density difference

152   maps (Fig. 1). These maps were calculated from the difference between observed neutron

153   structure factors and structure factors that were inferred from the 'deuterium–free'

154   structural model based on structural parameters found in synchrotron single-crystal

155   diffraction studies (Koch-Müller et al. 2005). Figure 1 demonstrates the difference

156   nuclear density at a level in the structure of $x{\approx}0.19$ with two pronounced maxima around

157    $y{\approx}0.05$, $z{\approx}0.62$ and $y{\approx}0.05$, $z{\approx}0.4$. Therefore, it was possible to establish the initial

158   positions of the deuterium atoms, D1 and D2 as (0.19, 0.05, 0.62) and (0.19, 0.05, 0.4),

159   respectively. Rietveld refinement of the pattern by then varying the coordinates of the D1

160   and D2 atoms, a.d.p.'s and occupancies resulted in excellent convergence with residuals

161   R_p=2.27%, R_{wp}=3.13% and χ^2=4.15, i.e., the residuals are considerably improved with

7

162   respect to the "deuterium-free" model. The detailed crystallographic data obtained from

163   the Rietveld refinements of the structural models at 300 and 10 K are given in the

164   supplementary information in the form of standard crystallographic information files (cif-

165   files). We show the observed and calculated neutron diffraction profiles for SHyB in

166   Figure 2.

167   Variation the occupation factors of the deuterium sites slightly improved the quality

168   of the Rietveld refinement. The refined deuterium content was lower than expected from

169   the SHyB stoichiometry, $Mg_{10}Si_3O_{18}D_4$. This suggests that some hydrogen contamination

170   of the deuterated sample may have occurred during the sample synthesis. This fact is also

171   supported by Raman spectroscopy which shows pronounced peaks in the O–H stretching

172   region at frequencies near 3400 cm^{-1}. However, accounting for the presence of hydrogen

173   in the structural model does not result in any further improvement to the residual and this

174   was therefore neglected.

175   **Discussion**

176   Figure 3 shows the crystal structure of the SHyB together with the hydrogen positions

177   determined from the neutron diffraction experiments. The structure is closely related to

178   anhydrous phase B and phase B (***Finger et al. 1991***, Pacalo and Parise 1992). Its can be

179   considered as an ordered alternation of two structural motives along the *a*–axis: the first

180   motive is composed of double octahedral-tetrahedral OT layers consisting of the edge–

181   shared MgO_6 octahedra and vertex-linked SiO_4 tetrahedra, whereas the second motive is

182   built up of octahedral O layers containing edge–shared MgO_6 and SiO_6 octahedra. These

183   layers interchange as …–O–OT–OT–O–OT–OT–O–… sequence. Large channels occur

184   in the structure along the *b*–axis inside the OT layers, formed between the edge–shared

8

185 octahedra and the vertex–linked tetrahedra. These channels are responsible for the high

186 water capacity of the structure and would very likely lead to fast water diffusion through

187 the SHyB structure.

188   In accordance with our structural model, the deuterium atoms are accommodated in

189 the SHyB structure inside these channels in the OT layers (Fig. 3). D atoms form

190 hydroxyl groups together with oxygens that coordinate only to magnesium. The bond

191 length of the O4–D1 hydroxyl group is 0.89(4) Å, whereas, a slightly longer bond of

192 1.08(4) Å was found for the O3–D2 hydroxyl group. The O4–D1···O1 and O3–D2···O1

193 hydrogen bond lengths are equal to 2.89(4) Å and 2.83(4) Å, respectively, i.e., both

194 bonds form weak hydrogen bonds and should yield typical stretching vibration

195 frequencies in the range 3200–3750 cm^{-1}. This is in good agreement with numerous

196 spectroscopic studies (Cynn et al. 1996; Frost and Fei 1998; Liu et al. 2002; Koch-Müller

197 et al. 2005). The internal angles of the O4–D1···O1 and O3–D2···O1 bonds were found to

198 be of 166 and 162 degrees. The O4–D1 and O3–D2 hydroxyl groups are bonded to the

199 same acceptor oxygen atom O1, and hence they form together a O4–D1···O1···D2–O3

200 configuration. ***Such a configuration is similar to that reported for the phase B (Finger***

201 ***et al. 1991) as well as with results of density functional calculations for SHyB (Poswal***

202 ***et al. 2010).*** The hydrogen repulsion could also influence the geometry of the hydrogen

203 bonding in solids, and hence, a precise determination of the D1–D2 distance of 1.90(5) Å

204 is also a crucial point for characterization of the geometry of the hydrogen bonding

205 configuration.

206   Koch-Müller at al. (2005) proposed the H1 position (0.3, 0.6, 0.1), which is also

207 inside the channel along the *b*-axis in the OT layer, and practically coincides with the D1

208   position determined in this study. The H2 position (0.27, 0.18, 0.45) spectroscopically

209   assigned by Koch-Müller at al. (2005), shown as a large black sphere in Figure 3, lies

210   close to the octahedral O3–O9 edge of the $Mg3O_6$ octahedron and forms an O3–H2–O9

211   angle of 138 degrees. The O3–H2 and O9–H2 distances were found to be 1.25 and 1.78

212   Å, respectively, whereas the O3–O9 distance (the length of the hypothetical O3–H2···O9

213   hydrogen bond), was 2.84 Å. The H1–H2 distance is almost equal to 1.8 Å, and hence,

214   the geometrical configuration parameters of the hypothetical O3–H2···O9 hydrogen bond

215   are very close to those determined in this study. This last point likely explains why the

216   H2 position was spectroscopically assigned at (0.27, 0.18, 0.45) (Koch-Müller et al.

217   2005). Xue et al. (2008) reported that Koch-Müller et al. (2005) have estimated the H2

218   position from the polarization direction of the band near 3347 cm^{-1} in single-crystal

219   infrared spectra by using a number of assumptions (H2 position is shown as large black

220   sphere in Fig. 3). According to Xue et al. (2008), it is very unlikely that the H2 site is

221   close to the O3–O9 octahedral edge with H2 bonded to O9 acceptor inside the same

222   octahedron $Mg3O_6$. From a crystal structure point of view, the cationic H2–Mg3 distance

223   of 1.58 Å, which follows from the model of Koch-Müller et al. (2005), seems to be

224   slightly shorter than typical H–Mg distances. It seems also quiet strange if hydrogen

225   atoms would in fact reside at the H2 positions, close to the O3–O9 edge, and would not

226   go into the large empty cavities inside the OT layers, whereas the centers of these empty

227   channels are only about 1.3 Å away from the H2 position. Note, that deuterium atoms

228   cannot reside simultaneously at both D2 and H2 positions as this would lead to too short

229   and nonphysical cationic D2–H2 distance of 1.31 Å. Thus, if we fix our D2 position at

230   the coordinates of the H2 position (0.27, 0.18, 0.45) from reference of Koch-Müller et al.

10

231   2005, we cannot achieve a satisfactory Rietveld refinement of the pattern. On the other

232   hand, varying the coordinates of the D2 position we can achieve good Rietveld

233   refinement where the resulting coordinates are (0.19, 0.05, 0.4), i.e., identical to those

234   derived from the difference nuclear density Fourier maps. We should mention that we

235   have also performed a difference Fourier analysis with subsequent Rietveld refinements

236   based on both *Pnnm* (Pacalo and Parise 1992) and *P2$_1$nm* (Kudoh et al. 1994) symmetries.

237   Reasonable residuals were achieved only for deuterium located inside the above cavities

238   in the OT layers. However, our preferred structural model is based on the *Pnn2* symmetry

239   in agreement with spectroscopic investigations (Koch-Müller et al. 2005; Xue et al. 2008).

240   Therefore, our results, supported also by the recent NMR study by Xue et al. (Xue et al.

241   2008), indicate two distinct positions of hydrogen accommodated in channels along the

242   *b*–axis within the OT layers of SHyB.

243   *Further, we have to discuss a possibility of incorrect assignment of the H2 position*

244   *that was proposed by Koch-Müller et al. (2005). This could happen because of*

245   *confusing of the a- and c-axes. According to the last paper, the lowest intensity for*

246   *their OH2 band with E parallel to the a-axis and the most intense band with E parallel*

247   *to c-axis, were observed in the (010) plane. This served as a basis for the assignment of*

248   *the H2 position. In fact, hypothetical O3–H2 hydroxyl group is oriented nearly parallel*

249   *to the c-axis (figure 3) which corresponds to the maximum absorbance intensity with E*

250   *parallel to the c-axis and to the minimum absorbance intensity with E perpendicular to*

251   *the c-axis (see figure 10 b in Koch-Müller et al. (2005)). Now, lets us to assume that*

252   *Koch-Müller et al. (2005) have changed the directions of the a- and c-axes in the (010)*

253   *oriented plate, i.e. the lowest intensity for their OH2 band with E parallel to the c-axis*

11

254   *and the strongest intensity for their OH2 with E parallel to the a-axis have to be*

255   *observed in the (010) plane. This means that such hydroxyl group must be oriented*

256   *nearly parallel to the a-axis, as in the case of our O3–D2 group (figure 3). This*

257   *corresponds to the maximum absorbance intensity with E parallel to the a-axis and to*

258   *the minimum absorbance intensity with E perpendicular to the a-axis (see figure 10 b*

259   *of Koch-Müller et al. (2005)). Hence, if mixing up of a– and c–axes would be true, our*

260   *assignment of D2 position would agree perfectly with the polarization behavior from*

261   *reference by Koch-Müller et al. (2005).*

262   In summary, we have performed the first direct determination of deuterium locations

263   in the SHyB structure by means of neutron diffraction. This information is important for

264   understanding the mechanisms of water incorporation and hydrogen transportation

265   through mantle silicates and, therefore, for the construction of models of geological

266   processes in the deep mantle. Knowledge of the hydrogen sites is required, for instance,

267   for local structure studies, aimed at the identification of possible hydrogen pathways

268   responsible for macroscopic water transportation though the SHyB structure. The

269   findings of our work, in particular, the orientation, strength and H–H distance of the O-H

270   bond will assist in the understanding of the infrared hydroxyl stretching bands, which are

271   commonly used to quantify the water content in mantle minerals.

272   **Acknowledgements**

12

276   Project 5-21-1066. ***The comments and suggestions by Prof. Monika Koch-Müller (GFZ***

277   ***Potsdam) and two anonymous reviewers helped to improve the manuscript.***

278   **References cited**

279   Angel, R.J., Frost, D.J., Ross, N.L., and Hemley, R. (2001) Stabilities and equations of
280   state of dense hydrous magnesium silicates. Physics of the Earth and Planetary
281   Interiors, 127, 181-196.

282   Cynn, H., Hofmeister, A.M., Burnley, P.C., and Navrotsky, A. (1996) Thermodynamic
283   properties and hydrogen specification from vibrational spectra of dense hydrous
284   magnesium silicates. Physics and Chemistry of Minerals, 23, 361-376.

285   Finger, L.W., Hazen, R.M., and Prewitt, C.T. (1991) Crystal structures of
286          $Mg_{12}Si_4O_{19}(OH)_2$ (phase B) and $Mg_{14}Si_5O_{24}$ (phase AnhB). American
287   Mineralogist, 76, 1–7.

288   Frost, D.J. and Fei, Y. (1998) Stability of phase D at high pressure and high temperature.
289   Journal of Geophysical Research: Solid Earth, 103, 7463-7474.

290   Frost, D.J., Poe, B.T., Trønnes, R.G., Liebske, C., Duba, A., and Rubie, D.C. (2004) A
291   new large-volume multianvil system. Physics of the Earth and Planetary Interiors,
292   143-144, 507-514.

293   Gasparik, T. (1993) The role of volatiles in the transition zone. Journal of Geophysical
294   Research: Solid Earth, 98, 4287-4299.

295   Hansen, T.C., Henry, P.F., Fischer, H.E., Torregrossa, J., and Convert P. (2008) The D20
296   instrument at the ILL: a versatile high-intensity two-axis neutron diffractometer.
297   Measurement Science and Technology, 19, 034001.

13

298   Koch-Müller, M., Dera, P., Fei, Y., Hellwig, H., Liu, Z., van Orman, J., and Wirth, R.

299   (2005) Polymorphic phase transition in Superhydrous Phase B. Physics and

300   Chemistry of Minerals, 32, 349-361.

301   Kudoh, Y., Nagase, T., Ohta, S., Sasaki, S., Kanzaki, M., and Tanaka, M. (1994) Crystal

302   structure and compressibility of superhydrous phase B, $Mg_{20}Si_6H_8O_{36}$. AIP

303   Conference Proceedings, 309, 469-472 (as quoted in the card number 80073 of

304   Inorganic Crystal Structure Data Base ICSD).

305   Liu, L.-G., Lin, C.-C., Mernagh, T.P., and Inoue, T. (2002) Raman spectra of phase C

306   (superhydrous phase B) at various pressures and temperatures. European Journal

307   of Mineralogy, 14, 15-23.

308   Pacalo, R.E.G. and Parise, J.B. (1992) Crystal structure of superhydrous B, a hydrous

309   magnesium silicate synthesized at 1400 $^{\circ}$C and 20 GPa. American Mineralogist,

310   77, 681-684.

311   ***Poswal, H. K., Sharma, S. M., and Sikka, S.K. (2010) Investigation of structure and***

312   ***hydrogen bonding of superhydrous phase B (HT) under pressure using first-***

313   ***principles density functional calculations. High Pressure Research, 30(1), 198-***

314   ***206.***

315   Rodriguez-Carvajal, J. (1993) Recent advances in magnetic structure determination by

316   neutron powder diffraction. Physica B, 192, 55-69.

317   Xue, X., Kanzaki, M., and Shatskiy, A. (2008) Dense hydrous magnesium silicates, phase

318   D, and superhydrous B: New structural constraints from one- and two-

319   dimensional ^{29}Si and ^{1}H NMR. American Mineralogist, 93, 1099-1111.

320   **List of figure captions**

14

321   Figure 1. Difference nuclear density at a level of $x\approx0.19$ in *Y-Z* cross-section at 300 K as

322   an example, two pronounced maxima around $y\approx0.05$, $z\approx0.6$ and $y\approx0.05$, $z\approx0.4$ are clear;

323   the difference nuclear density is measured in fm/Å^3 units.

324   Figure 2. Results of the Rietveld refinements of SHyB diffraction patterns at 300 and 10

325   K. A small peak at $\sim 2\theta=70°$ was also present in a reference sample pattern collected

326   under the same conditions and apparently arises from the sample environment. The broad

327   feature in background at $\sim$ 50–75 degrees of 2θ may be a signature from amorphous

328   silicate melt in the sample.

329   Figure 3. A polyhedral representation of the SHyB crystal structure along the *b*–axis and

330   stacking within OT layers with hydrogens along *a*–axis.

O   OT   OT   O   OT   OT   O

D1   O4
O1   O9
      H2
D2   Mg3
      O3

c
a

SiO4   MgO6   SiO6

b
c