The determination of hydrogen positions in superhydrous phase B

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ABSTRACT

Nominally hydrous high-pressure silicate phases such as the superhydrous phase B are of considerable importance for the understanding of the water-cycle between the surface and the interior of the Earth. This study tackles the controversial issue of hydrogen positions in superhydrous phase B, a phase believed to be potentially stable in cold subducting ultramafic slabs. To investigate the nature of hydrogen incorporation into the structure of superhydrous phase B, neutron powder diffraction experiments have been performed. A structural model based on Pnn2 symmetry has been used for the analysis of the data, which is consistent with earlier spectroscopic studies. Application of Fourier synthesis with subsequent analyses of difference nuclear density maps and Rietveld fits reveal two distinct positions for deuterium, at 4c (0.194, 0.052, 0.596) and at 4c (0.186, 0.119, 0.388). This unambiguously shows that deuterium lies within large channels, which are formed between the edge-shared octahedra and vertex-linked tetrahedra along the b-axis of the structure. These results contrast with recent polarized single-crystal infrared spectroscopy studies where the position of one of two H atoms was estimated to lie close to the octahedral edge of an MgO octahedron, thereby leaving the large structural channel empty.

Keywords: Hydrous magnesium silicates, neutron diffraction, superhydrous phase B, crystal structure, hydrous minerals, determination of hydrogen positions

INTRODUCTION

Water exists in the Earth’s mantle in several different forms. It may exist as a free fluid phase; it may be dissolved in silicate melts or incorporated into nominally anhydrous minerals, such as the polymorphs of Mg2SiO4 (forsterite, wadsleyite, and ringwoodite). It may also be incorporated into nominally hydrous high-pressure silicate phases, such as dense hydrous magnesium silicate (DHMS) phases, which have to date mainly been characterized in the in MgO-SiO2-H2O ternary system. The DHMS phases, referred to as A, E, B, and superhydrous phase B (SHyB), might be stable at the pressure and temperature conditions compatible with cold portions of subducting slabs and they may form a network of phases with overlapping stability fields that transport water into the lower mantle. Although, the existence of DHMS in nature is still under debate, SHyB might be stable within ultramafic compositions coexisting with ringwoodite at conditions compatible with subducting slabs in the lower part of the transition zone (Angel et al. 2001). The formation of hydrous minerals such as SHyB may influence the mechanical and rheological properties of slabs, and the ultimate dehydration might potentially be related to the processes causing deep-focus earthquakes. Any attempt to understand the stability or transport properties of such hydrous phases, however, would benefit from an understanding of the crystal structure, including an appreciation of the hydrogen sites.

SHyB has an ideal chemical composition of Mg10Si3O14(OH)4, with a Mg/Si ratio of 3.3 and 5.8 wt% of stoichiometrically incorporated water and lies along the brucite–anhydrous phase B join of the MgO-SiO2-Mg(OH)2 ternary system. SHyB was first identified and characterized by Gasparik (1993). The current picture of the hydroxyl substitution mechanisms in Mg10Si3O14(OH)4 is based on results of X-ray diffraction studies (Pacalo and Parise 1992; Kudoh et al. 1994; Koch-Müller et al. 2005), nuclear magnetic resonance (NMR) studies (Xue et al. 2008), and infrared (Cynn et al. 1996; Koch-Müller et al. 2005) and Raman spectroscopy studies (Cynn et al. 1996; Frost and Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005).

The first model of the crystal structure of SHyB was established from X-ray diffraction studies by Pacalo and Parise (1992) who determined its orthorhombic Pnma symmetry with Z = 2. However, in this study the positions of the hydrogen atoms were determined only approximately from difference Fourier maps (Pacalo and Parise 1992). Hydrogen was placed into a general position 8h at (–0.0769, 0.3026, 0.1085) with multiplicity 8, which corresponds to a site within the channels along the a-axis (b-axis in our crystallographic setting) (Pacalo and Parise 1992). Kudoh et al. (1994) and Koch-Müller et...
al. (2005) performed single-crystal X-ray diffraction studies on Mg₆Si₉O₁₄(OH)₄ and proposed two non-centrosymmetric space groups, P₂₁₃ and Pmnn₂, respectively. Although, the hydrogen sites were not determined in the former paper, the P₂₁₃ symmetry implies the existence of two distinct crystallographic sites for the hydrogen atoms. Koch-Müller et al. (2005) proposed approximate coordinates for two distinct positions for hydrogen atoms, at 4c with (0.3, 0.6, 0.1) and at 4c (0.27, 0.18, 0.45). The first position was inferred from electron density Fourier difference maps obtained by means of X-ray diffraction studies, consistent with the polarized IR spectra, whereas the second position came from polarized single-crystal infrared spectroscopic studies only. The infrared and Raman spectroscopic studies (Cynn et al. 1996; Frost and Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005) do not corroborate the centrosymmetric Pmnn space group for SHyB suggested by Pacalo and Parise (1992). These spectra show two intense peaks in the infrared O–H stretching region that is clear evidence for the existence of two distinct crystallographic positions for hydrogen atoms (Cynn et al. 1996; Frost and Fei 1998; Liu et al. 2002; Koch-Müller et al. 2005). Furthermore, comprehensive 2D ¹H and ²Si NMR investigations have also shown the existence of dissimilar hydrogen (H1-H2) pairs in SHyB and found only one distinct tetrahedral Si site (Xue et al. 2008). These findings are consistent with the Pmn2 space group (Xue et al. 2008), which was proposed by Koch-Müller et al. (2005). Moreover, Xue et al. (2008) have also excluded Pmnn of Pacalo and Parise (1992) and P₂₁₃m of Kudoh et al. (1994). Xue et al. (2008) questioned the H positions and OH dipole directions found as proposed by Koch-Müller et al. (2005). In fact, while the H1 position at (0.3, 0.6, 0.1) is located inside a channel along the b-axis, the H2 position at (0.27, 0.18, 0.45) is close to the octahedral edge O3–O9 of the Mg3O₆ octahedron (Xue et al. 2008). The hydrogen bond of H2 belongs in this case to the same Mg3O₆ octahedron and hence the large structural channel remains unfilled. Furthermore, Koch-Müller et al. (2005) presented sufficient evidences to claim the existence of a high-temperature polymorph of Ni-doped SHyB. On the contrary, the existence of such a polymorph was questioned by Xue et al. (2008) based on an analysis of an undoped sample. Such discrepancies may suggest the existence of a phase transition between the “high-temperature polymorph of SHyB” and the “low-temperature polymorph of SHyB,” which is induced by changes in the Ni-content (Ni-SHyB and SHyB are substantially different compounds and this might lead to different crystallographic symmetries).

Thus, the available information from the literature concerning the predominant locations of hydrogen atoms in the structure of the SHyB is inconsistent. Therefore, a detailed investigation that could shed light on fine details of water incorporation in the structure of the SHyB is required for construction of realistic mineral physical models. Neutron diffraction is the most rigorous method for determination of deuterium site occupancies in crystalline phases because neutron scattering cross sections are not a function of atomic mass as for X-ray diffraction and are relatively large for deuterium. In this study the deuterium sites in the SHyB structure have been precisely determined by means of neutron powder diffraction.

### EXPERIMENTAL DETAILS

A sample of about 20 mg of SHyB was synthesized from Mg₂SiO₄ (forsterite) + D₂O in a 5000 tonne large-volume press (Frost et al. 2004). An 18 mm edge length CrO₃-doped octahedral pressure assembly was used with tungsten carbide cubes that had 8 mm edge length corner truncations. MgSiO₃ + D₂O were placed inside a welded platinum capsule of 3 mm diameter and approximately 4 mm length. The capsule was inserted into an MgO sleeve and placed into a cylindrical LaCrO₃ heater that was inserted into the octahedral assembly. The temperature during the experiment was monitored using a W3Re/W25Re thermocouple inserted within an alumina tube, with the junction in contact with the top of the Pt capsule. Other details were similar to those reported in previous studies (Frost et al. 2004). The synthesis was performed at 22 GPa, and a temperature of 1100 °C, with an annealed duration of 4 h. The recovered sample was milled into a powder and characterized by Raman spectroscopy and X-ray powder diffraction. Neutron powder diffraction measurements were performed at the D20 high-flux instrument installed at the neutron reactor at the Institut Laue-Langevin in Grenoble, France (Hansen et al. 2008). A vanadium sample holder of 4 mm in diameter was filled with a sample of the SHyB and was loaded inside a cryostat sample chamber. The measurements were carried out at ambient temperature and at 10 K. Reducing the temperature to 10 K permitted the deuterium positions to be determined more precisely since the atomic displacement parameters (a.d.p.) of atoms are strongly reduced at low temperatures. The wavelength of 2.415 Å was determined using a Na₂Ca₃Al₂F₁₄ reference material; a second wavelength of 2.419 Å was also recognized and included in the Rietveld fits. Despite the presence of the second wavelength, this experimental setup gave the maximum of intensity at the sample position and allowed us to perform high-quality neutron diffraction experiments on a relatively small sample of approximately 20 mg. After switching on the oscillation of the sample, a microstrip position sensitive detector was used for data collection in the range of 15–150° of 2θ. The collected diffraction patterns were analyzed by full-profile Rietveld refinements and difference Fourier analyses using the WinPLOTR package (Rodriguez-Carvajal 1993). The resolution function of the diffractometer and the peak profile shape were modeled using a pseudo-Voigt function, determined by fitting a Na₂Ca₃Al₂F₁₄ reference material. The background of the diffraction pattern was fitted using a linear interpolation between selected data points in non-overlapping regions. The scale factor, the lattice parameters, zero shift, and the Y profile shape parameter were varied during the fitting procedure. As the crystal structure of SHyB is complex with 18 distinct sites for Mg, Si, and O, the atomic coordinates of these atoms were fixed at those values determined by single-crystal synchrotron diffraction measurements (Koch-Müller et al. 2005), whereas the fractional coordinates and the occupancies of the deuterium atoms and a.d.p.’s parameters of all atoms were varied.

### RESULTS

The initial crystal model (except for the hydrogen positions) and the crystallographic setting used for the refinement of the SHyB structure were those proposed by Koch-Müller et al. (2005), i.e., with Pmn2 symmetry. The Pmn2 symmetry is also consistent with NMR results of Xue et al. (2008). Secondary minor phases of stishovite and ringwoodite were detected in the sample and included in the full-profile refinements. The fit residuals R_p = 3.37%, R_w = 4.62%, and χ² = 8.97 (Pmn2 space group) were achieved without deuterium positions in the structural model. We determined the initial positions of the deuterium atoms from analyses of the Fourier nuclear density difference maps (Fig. 1). These maps were calculated from the difference between observed neutron structure factors and structure factors that were inferred from the “deuterium-free” structural model based on structural parameters found in synchrotron single-crystal diffraction studies (Koch-Müller et al. 2005). Figure 1 demonstrates the difference nuclear density at a level in the structure of x ≈ 0.19 with two pronounced maxima around y = 0.05, z = 0.62 and y = 0.05, z = 0.4. Therefore, it was possible to establish the initial positions of the deuterium atoms, D1 and D2 as (0.19, 0.05, 0.62) and (0.19, 0.05, 0.4), respec-
Rietveld refinement of the structural model by varying only the coordinates of the D1 and D2 atoms, a.d.p. values and occupancies resulted in excellent convergence with residuals $R_p = 2.27\%$, $R_{wp} = 3.13\%$, and $\chi^2 = 4.15$, i.e., the residuals were considerably improved with respect to the “deuterium-free” model. The detailed crystallographic data obtained from the Rietveld refinements of the structural models at 300 and 10 K are given in the supplementary information in the form of standard crystallographic information files (CIFs). We show the observed and calculated neutron diffraction profiles for SHyB in Figure 2.

Variation of the occupation factors of the deuterium sites slightly improved the quality of the Rietveld refinement. The refined deuterium content was lower than expected from the SHyB stoichiometry, Mg$_{10}$Si$_3$O$_{18}$D$_4$. This suggests that some hydrogen contamination of the deuterated sample may have occurred during the sample synthesis. This fact is also supported by Raman spectroscopy, which shows pronounced peaks in the 0–H stretching region at frequencies near 3400 cm$^{-1}$. However, accounting for the presence of hydrogen in the structural model does not result in any further improvement to the residual and was therefore neglected.

**DISCUSSION**

Figure 3 shows the crystal structure of the SHyB together with the hydrogen positions determined from the neutron diffraction experiments. The structure is closely related to anhydrous phase B and phase B (Finger et al. 1991; Pacalo and Parise 1992). It can be considered as an ordered alternation of two structural motives along the $a$-axis: the first motive is composed of double octahedral-tetrahedral OT layers consisting of the edge-shared MgO$_6$ octahedra and vertex-linked SiO$_4$ tetrahedra, whereas the second motive is built up of octahedral O layers containing edge-shared MgO$_6$ and SiO$_6$ octahedra. These layers interchange as …–O–OT–OT–O–OT–OT–O… sequence. Large channels occur in the structure along the $b$-axis inside the OT layers, formed between the edge-shared octahedra and the vertex-linked tetrahedra. These channels are responsible for the high water capacity of the structure and would very likely lead to fast water diffusion through the SHyB structure.

In accordance with our structural model, the deuterium atoms are accommodated in the SHyB structure inside these channels.

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**FIGURE 1.** Difference nuclear density at a level of $x = 0.19$ in $Y-Z$ cross section at 300 K as an example, two pronounced maxima around $y = 0.05$, $z = 0.6$ and $y = 0.05$, $z = 0.4$ are clearly visible; the difference nuclear density is measured in fm/Å$^3$ units.

**FIGURE 2.** Results of the Rietveld refinements of SHyB diffraction patterns at 300 and 10 K. A small peak at $\theta = 70^\circ$ was also present in a reference sample pattern collected under the same conditions and apparently arises from the sample environment. The broad feature in background at $\sim$50–75$^\circ$ of 2$\theta$ may be a signature from amorphous silicate melt in the sample.
The geometry of the hydrogen bonding configuration.

The bond length of the O4–D1 hydroxyl group is 0.89(4) Å, whereas a slightly longer bond of 1.08(4) Å was found for the O3–O9 edge of the Mg3O6 octahedron and forms an O3–H2–O9 angle of 138°. The O3–H2 and O9–H2 distances were found to be 1.25 and 1.78 Å, respectively, whereas the O3–O9 distance (the length of the hypothetical O3–H2–O9 hydrogen bond), was 2.84 Å. The H1–H2 distance is almost equal to 1.8 Å, and hence, the geometrical configuration parameters of the hypothetical O3–H2–O9 hydrogen bond are very close to those determined in this study. This last point likely explains why the H2 position was spectroscopically assigned at (0.27, 0.18, 0.45) (Koch-Müller et al. 2005). Xue et al. (2008) reported that Koch-Müller et al. (2005) have estimated the H2 position from the polarization direction of the band near 3347 cm⁻¹ in single-crystal infrared spectra by using several assumptions (H2 position is shown as large black sphere in Fig. 3). According to Xue et al. (2008), it is very unlikely that the H2 site is close to the O3–O9 octahedral edge with H2 bonded to O9 acceptor inside the same octahedron Mg3O6. From a crystal structure point of view, the cationic H2–Mg3 distance of 1.58 Å, which follows from the model of Koch-Müller et al. (2005), seems to be slightly shorter than typical H–Mg distances. It seems also quiet strange if hydrogen atoms would in fact reside at the H2 positions, close to the O3–O9 edge, and would not go into the large empty cavities inside the OT layers, whereas the centers of these empty channels are only about 1.3 Å away from the H2 position. Note, that deuterium atoms cannot reside simultaneously at both D2 and H2 positions as this would lead to too short and nonphysical cationic D2–H2 distance of 1.31 Å. Thus, if we fix our D2 position at the coordinates of the H2 position (0.27, 0.18, 0.45) from reference of Koch-Müller et al. 2005, we cannot achieve a satisfactory Rietveld refinement of the pattern. On the other hand, varying the coordinates of the D2 position we can achieve good Rietveld refinement where the resulting coordinates are (0.19, 0.05, 0.4), i.e., identical to those derived from the difference nuclear density Fourier maps. We should mention that we have also performed a difference Fourier analysis with subsequent Rietveld refinements based on both Pnmn (Pacalo and Parise 1992) and P2₁nm (Kudoh et al. 1994) symmetries. Reasonable residuals were achieved only for deuterium located inside the above cavities in the OT layers. However, our preferred structural model is based on the Pnmn2 symmetry in agreement with spectroscopic investigations (Koch-Müller et al. 2005; Xue et al. 2008). Therefore, our results, supported also by the recent NMR study by Xue et al. (2008), indicate two distinct positions of hydrogen accommodated in channels along the b-axis within the OT layers of SHyB.

The possibility of incorrect assignment of the H2 position that was proposed by Koch-Müller et al. (2005) deserves some consideration. This could potentially be due to a mixing up of the a- and c-axes. According to the Koch-Müller et al. (2005), the lowest intensity for their OH2 band with E parallel to the a-axis and the most intense band with E parallel to c-axis, were observed in the (010) plane. This served as a basis for the assignment of the H2 position. In fact, a hypothetical O3–H2
hydroxyl group is oriented nearly parallel to the e-axis (Fig. 3), which corresponds to the maximum absorbance intensity with E parallel to the e-axis, and to the minimum absorbance intensity with E perpendicular to the e-axis [see Fig. 10b in Koch-Müller et al. (2005)]. Let us assume that Koch-Müller et al. (2005) have interchanged the directions of the a- and e-axes in the (010) oriented plate, i.e., the lowest intensity for their OH2 band with E parallel to the e-axis and the strongest intensity for their OH2 with E parallel to the a-axis have to be observed in the (010) plane. This means that such a hydroxyl group must be oriented nearly parallel to the a-axis, as is the case for our O3–D2 group (Fig. 3). This corresponds to the maximum absorbance intensity with E parallel to the a-axis and to the minimum absorbance intensity with E perpendicular to the a-axis [see Fig. 10b of Koch-Müller et al. (2005)]. Hence, if mixing up of a- and e-axes would be true, our assignment of D2 position would agree perfectly with the polarization behavior from reference by Koch-Müller et al. (2005).

In summary, we have performed the first direct determination of deuterium locations in the SHyB structure by means of neutron diffraction. This information is important for understanding the mechanisms of water incorporation and hydrogen transportation through mantle silicates and, therefore, for the construction of models of geological processes in the deep mantle. Knowledge of the hydrogen sites is required for local studies, aimed at the identification of possible hydrogen pathways responsible for macroscopic water transportation though the SHyB structure. The findings of our work, in particular, the orientation, strength, and H–H distance of the O–H bond will assist in the understanding of the infrared hydroxyl stretching bands, which are commonly used to quantify the water content in mantle minerals.

ACKNOWLEDGMENTS

We acknowledge the support of the ERC advanced grant no. 227893 “DEEP” funded via the EC 7th Framework Programme. The neutron diffraction measurements were carried at the Institute Laue-Langevin in Grenoble (France) and were supported by a beamtime Project 5-21-1066. The comments and suggestions by Monika Koch-Müller (GFZ Potsdam) and two anonymous reviewers helped to improve the manuscript.

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