Location and quantification of hydroxyl in wadsleyite: New insights

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Abstract

Anhydrous and hydrous wadsleyite were synthesized at 13.3–13.5 GPa and 1150–1200 °C in a multianvil press and investigated by Fourier transform infrared (FTIR) spectroscopy, single-crystal X-ray refinement (SC-XRD), and electron microprobe analyses (EMPA). The FTIR spectra agree with previous data, i.e., the spectra are dominated by a broad band around 3380 cm⁻¹, resolvable in three bands 3326 (ν2), 3382 (ν3), and 3546 (ν4) cm⁻¹ besides some weaker OH-bands around 3600 cm⁻¹. We confirm that wadsleyite incorporates water in the wt% range and that the concentration strongly increases with decreasing temperature when using secondary ion mass spectrometry (SIMS) and Raman spectroscopy. The quantifications combined with FTIR spectra led us to develop the first IR calibration for water in wadsleyite, i.e., calculating an εH₂O of 73 000 ± 7000 (L mol⁻¹ cm⁻²). A SC-XRD determination of hydrous wadsleyite FD0718, bearing 8000 ± 1000 wt ppm H₂O, certifies the presence of Mg vacancies at the M3 sites as previously suggested. Furthermore, we found maxima in the electron density map close to the O atoms O1 and O3 of an M3 octahedron assuming the anhydrous structure. Based on our new data we suggest that the main protonation in wadsleyite occurs along the O1···O4 (3.1 Å) and O3···O4 (3.05 Å) edges of a vacant M3 octahedron. H-incorporation seems to be random leading to protonation of either two O1, two O3, or one O1 and one O3 of the vacant M3 octahedra. With this assignment, the observed ambient and high-pressure IR pattern can now be explained.

Keywords: Wadsleyite, FTIR spectroscopy, Raman spectroscopy, protonation, SIMS, absorption coefficient for water

Introduction

In previous decades, the petrologic importance of the so-called nominally anhydrous minerals (NAMs) as storage containers for water (OH content in the structure expressed as water) in the Earth’s mantle has grown. Several studies have shown that these minerals may incorporate considerable amounts of water as structurally bonded OH via point defects (Wilkins and Sabine 1973; Bell and Rossman 1992; Miller et al. 1987; Ingrin and Skogby 2000; Smyth and Jacobsen 2006; Koch-Müller et al. 2006; Mosenfelder et al. 2006). Wadsleyite (β-Mg₂SiO₄), the high-P polymorph of olivine (α-Mg₂SiO₄), belongs to this category. It is a major constituent of the transition zone of the Earth upper mantle, thus being a very suitable candidate as a hydrogen reservoir. Smyth (1987) predicted the maximum water content of wadsleyite as 3.3 wt% (where the OH content in the structure is reported as water). However, the storage capacity strongly depends on the experimental constraints such as P, T, and phase assembly.

Kohlstedt et al. (1996) studied the water solubility of the (Mg, Fe)₂SiO₄ polymorphs experimentally by using unpolarized FTIR spectra in combination with the calibration of Paterson (1982) and found that wadsleyite synthesized at 1100 °C and 14–15 GPa incorporates up to 2.4 wt% H₂O. Demouchy et al. (2005) used secondary ion mass spectrometry (SIMS) and observed that the water solubility of wadsleyite in the system MgO-SiO₂-H₂O decreases with increasing T, and attributed this to increased fractionation of water into coexisting melt with increasing T: at 900 °C wadsleyite incorporates 2.2 wt% H₂O, whereas at 1400 °C the storage capacity decreases to 0.9 wt% H₂O. Other studies have confirmed the high but variable water content of wadsleyite (e.g., McMillan et al. 1991; Young et al. 1993; Inoue 1994; Inoue et al. 1995; Chen et al. 2002; Kohn et al. 2002).

In each of these studies, different methods were used to quantify water in wadsleyite such as SIMS, nuclear magnetic resonance (NMR) spectroscopy, and polarized and unpolarized IR spectroscopy using either the Paterson (1982) or the Libowitzky and Rossman (1997) calibration. Bell et al. (2003) showed that if the general IR calibration of Paterson (1982) is adopted, the water concentration of olivine would be underestimated by about 25%. Blanchard et al. (2009) obtained a very similar result for Fe-free ringwoodite and found that the absorptivity of water in ringwoodite was about 20% smaller than that inferred from a general calibration law established for hydrous minerals. More recently, Thomas et al. (2009) used a variety of analytical methods and found that ignoring mineral-specific IR-calibrations