

## **A systematic study of OH in hydrous wadsleyite from polarized FTIR spectroscopy and single-crystal X-ray diffraction: Oxygen sites for hydrogen storage in Earth's interior**

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### **ABSTRACT**

The incorporation of hydrogen into wadsleyite ( $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>) was investigated using polarized FTIR spectroscopy and X-ray diffraction on oriented single crystals. The experiments were carried out with a new suite of samples containing between ~100 and ~10000 ppm H<sub>2</sub>O by weight (wt ppm), encompassing the H-contents most relevant to Earth's potentially hydrous mantle transition zone. Attempts to synthesize anhydrous wadsleyite resulted in water contents of no less than ~50 wt ppm H<sub>2</sub>O. An empirical relation between the *b/a* axial ratio against estimated wt ppm concentrations of H<sub>2</sub>O in wadsleyite (*C*<sub>H<sub>2</sub>O</sub>) was determined:  $(b/a) = 2.008(1) + 1.25(3) \times 10^{-6} \cdot C_{\text{H}_2\text{O}}$

Polarized infrared absorption spectra were measured in the three orthogonal sections perpendicular to the major axes of the optical indicatrix ellipsoid and are used in concert with results from new structure refinements to place constraints on the main absorbers in the structure. All of the main bands in the O-H stretching region of the FTIR can be explained by protonation of O1, the anomalous non-silicate oxygen site. We assign the band at 3614 cm<sup>-1</sup> to a bent hydrogen bond O1...O1 (2.887 Å) along the M3 edge in the a-c plane. The band at 3581 cm<sup>-1</sup> is assigned to a bent hydrogen bond on O1...O3 (3.016 Å) of the M3 edge in the b-c plane. The absorption bands at 3360, 3326, and 3317 cm<sup>-1</sup> are best explained by hydrogen bonds on O1...O4 (3.092 Å) and O1...O4 (2.795 Å) along the M3 and M2 edges with possible splitting of one band due to vacancy ordering, but we cannot rule out contributions from three other (O1...O3) edges. The broad absorption feature at 3000 cm<sup>-1</sup> is unambiguously assigned to the O4...O4 (2.720 Å) tetrahedral edge of the Si<sub>2</sub>O<sub>7</sub> group pointing along the [100] vector. On hydration to ~1 wt% H<sub>2</sub>O, M-site vacancies are observed exclusively at M3. A systematic shortening of several (interpreted) hydrogen bonded O...O M-site edges is attributed to reduced O-O repulsive forces on protonation in the vicinity of an M-site vacancy.