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 (β-Mg_2SiO_4) 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 ~10 000 ppm H_2O 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_2O. An empirical relation between the b/a axial ratio against estimated wt ppm concentrations of H_2O in wadsleyite (C_{H_2O}) was determined: $(b/a) = 2.008(1) + 1.25(3) \times 10^{-6} \cdot C_{H_2O}$

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^{-1} to a bent hydrogen bond O1···O1 (2.887 Å) along the M3 edge in the a-c plane. The band at 3581 cm^{-1} 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^{-1} 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^{-1} is unambiguously assigned to the O4···O4 (2.720 Å) tetrahedral edge of the Si_2O_7 group pointing along the [100] vector. On hydration to ~1 wt% H_2O, 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.

INTRODUCTION

Wadsleyite (β-Mg_2SiO_4) and ringwoodite (γ-Mg_2SiO_4) together have the potential to store more water as hydroxyl (OH)$^-$ in Earth's mantle transition zone (TZ) at 410–660 km depth than is currently present in the liquid oceans. Just 0.1 wt% H_2O (1000 wt ppm) throughout the TZ is equivalent to about one kilometer of liquid water across Earth's surface. Wadsleyite has an extraordinary affinity for hydrogen due to an unusual non-silicate oxygen atom (O1) in its structure (Smyth 1994). The atom at O1 is coordinated to only five $^{VI}Mg^{2+}$ atoms and has a Pauling bond strength of 1.67, thus having about one-thirds hydroxyl (1.0) and two-thirds oxygen (2.0) character.

Smyth (1987) predicted that wadsleyite should contain variable amounts of hydrogen at O1 based on its anomalously shallow electrostatic potential. Full hydration of O1 corresponds to 33 000 wt ppm (3.3 wt%) H_2O. The presence of H in synthetic wadsleyite was confirmed spectroscopically by McMillan et al. (1991) and Young et al. (1993). Inoue et al. (1995) synthesized pure-Mg (Fo$_{100}$) hydrous wadsleyite containing up to 31 000 wt

ppm (3.1 wt%) H_2O, measured by secondary ion mass spectrometry (SIMS). Kohlstedt et al. (1996) reported up to 24 000 wt ppm (2.4 wt%) H_2O in Fo$_{90}$ wadsleyite, estimated from unpolarized infrared spectroscopy using the calibration of Paterson (1982). Hydrous wadsleyite purported to contain 3.3 wt% H_2O (i.e., $Mg_{1.75}SiH_{0.5}O_4$) from the studies of Kudoh et al. (1996) and Kudoh and Inoue (1999) probably contains closer to ~2.5 wt% H_2O, as measured by SIMS (sample B of Inoue et al. 1995).

The O1 site is ideal for H based on electrostatic and crystal-chemical arguments, but there are several different ways to protonate O1, as well as up to 13 other possible O-H···O environments involving O2, O3, and O4. To date, a diverse arsenal of methods have been used to study the OH environments in wadsleyite, including calculated or experimental electrostatic potentials (Smyth 1987; Downs 1989), difference-Fourier analysis of the charge density from single-crystal X-ray diffraction data (Smyth et al. 1997; Kudoh and Inoue 1999), unpolarized infrared spectroscopy (Kohlstedt et al. 1996; Bolfan-Casanova et al. 2000; Kohn et al. 2002), analysis of triple-points in the Laplacian $\nabla^2\rho(\mathbf{r})$ of the electron density distribution (Ross et al. 2003), as well as ^{1}H (Kohn et al. 2002) and ^{17}O NMR (Ashbrook et al. 2003). The most direct way to locate H in wadsleyite,

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single-crystal neutron diffraction, should be possible in the near future as the increase in available neutron fluxes and recovered crystal sizes merge.

While O1 remains the favored protonation site in wadsleyite (Smyth 1987; Kudoh and Inoue 1999; Kohn et al. 2002; Ross et al. 2003), the sorosilicate-group bridging oxygen atom (O2) is also favored by Downs (1989), Kohn et al. (2002), and Ross et al. (2003), despite the fact that the oxygen atom at O2 has a Pauling bond strength greater than 2.0, and protonation of a bridging oxygen is unknown among the stoichiometric silicate structures. Kohn et al. (2002) showed that at least 14 of the 17 possible hydrogen bond sites were occupied in a highly disordered hydrous wadsleyite. Here, we offer a simplified interpretation of the six main IR bands related to O-H stretching based on polarized measurements from oriented single crystals and by systematically tracking variations in the O···O interatomic distances with increasing hydrogen-contents from new structure refinements. Polarized IR spectra obtained from the planes perpendicular to the major axes of the optical indicatrix are used to place constraints on the orientation of the major absorbers in the structure.

We have undertaken a systematic study of OH in pure-Mg hydrous wadsleyite using polarized FTIR spectroscopy and X-ray diffraction on oriented single-crystal samples. We have chosen to concentrate on hydrous wadsleyite with water contents ranging from a few tens of weight per parts million H_2O up to about 10 000 (1 wt% H_2O) because this range seems most pertinent to Earth's potentially hydrous mantle TZ. An empirical relation between the unit-cell parameters and the estimated water contents in wadsleyite is constructed using the (b/a) axial ratio. We report structure refinements and polarized FTIR spectra for the pure-Mg wadsleyite crystals containing ~150, 3200, and 9600 wt ppm H_2O. The infrared absorption spectra provide new insight into the OH environments in wadsleyite because the light is polarized and they were obtained from the three sections perpendicular to the major axes of the optical indicatrix ellipsoid. The strongly pleochroic nature of the O-H absorption bands in wadsleyite is used to place some constraints on the orientation of the four main O-H absorbers in the structure (Libowitzky and Rossman 1996). Structure refinements of the hydrous wadsleyite crystal show that many of the O···O environments systematically shorten with increasing H-content, leading us to conclude that protonation of these oxygen sites reduces the otherwise increasing O-O repulsive forces due to Mg^{2+} cation vacancies.

EXPERIMENTAL METHODS

Synthesis and characterization

Magnesium end-member hydrous wadsleyite crystals (β-$Mg_{1-x}SiH_{2x}O_4$) were synthesized under various *P-T* conditions ranging from about 16 to 18 GPa and quenched from 1200 to 2100 °C in one of three different multi-anvil presses at Bayerisches Geoinstitut (Table 1). Sample nomenclature refers to experiment numbers, preceded by WS for synthesis in the 1200 ton Sumitomo press, WH for the 1200 ton Hymag press, and WZ for the 5000 ton Zwick press. Our aim was to produce as large a single-crystal of hydrous wadsleyite as possible by treating the H_2O component as a flux (Dobson and Jacobsen 2004) and employing large-volume assemblies to maximize the capsule size. In the 5000-ton press we used either the 25/15 assembly (octahedral edge-length/anvil anvil truncation edge-length in millimeters) with a capsule of 4 mm in height and 3 mm in diameter, or the 18/11 assembly with a capsule size of 3.5 mm in height and 2 mm in diameter (Frost

et al. 2004). In the Hymag, we used a 14/8 assembly, but modified the furnace to increase the capsule size to 3 mm in height and 3 mm in diameter. This box-like geometry increases the temperature gradient across the sample, and appears to enhance large grain-growth in the cold zone. With the 14/8 box-furnace assembly, we have synthesized gem-quality single-crystals of hydrous wadsleyite measuring up to 1 mm in size.

Hydrous wadsleyite samples WH2082, WZ292, and WZ336 were synthesized from pre-fired mixed oxides with water added as brucite for Mg_2SiO_4 plus 3–5 wt% H_2O and 1–2 wt% excess silica. Platinum capsules were made of 0.5 mm thick foil and welded shut to prevent loss of the fluid phase. A typical *P-T* path involved compression to the target pressure (Table 1), and slow heating to the target temperature (Table 1) over the course of about 10–20 minutes. Target temperatures were held typically for 1–2 hours. Experiments WZ292 and WZ336 were carried out in the 25/15 assembly and were cooled in a cyclic fashion with several drops of 100–200 °C followed each time by reheating to the target temperature before rapid quenching. Recovered grain sizes from this method were 50 to 300 μm. The WH2082 experiment was carried out in the 14/8 box-furnace assembly and was allowed to anneal for several hours at a lower temperature (~1100 °C) before rapid quenching. Grain sizes from the box-furnace assembly reach 1 mm in size, appearing in the central (cold) part of the capsule, and are surrounded by fine-grained quench glass. The hourglass shape of the boundary between the wadsleyite and the glass suggests that grain growth was enhanced by the presence of a large temperature gradient across the capsule. Additional experimental products are listed in Table 1.

We made three attempts to synthesize anhydrous wadsleyite crystals, resulting in no less than ~50 ppm wt H_2O. In experiment WH833, a synthetic forsterite starting material was used in the box-furnace assembly and transformed to wadsleyite at about 15–16 GPa and 1100–1200 °C (held for four hours). This experiment produced large crystals measuring up to 500 μm and containing approximately 3200 ppm wt H_2O, which may have come from residual moisture on the starting material and assembly (humidity) and diffused into the wadsleyite during the long annealing period. The WH833 experiment demonstrates the difficulty of synthesizing anhydrous wadsleyite. In experiment WZ304, the 18/11 assembly was used in the 5000-ton press to transform synthetic forsterite at about 17 GPa and 1400 °C (held for one hour) before rapid quenching. FTIR indicates there is still ~150 wt ppm H_2O present in the wadsleyite (WZ304). In experiment WS3056, we heated the forsterite to ~2100 °C before rapid quenching in an attempt to partition any existing hydrogen into the melt, but the wadsleyite still contained no less than ~50 wt ppm H_2O. It appears that no matter how carefully the starting materials and assemblies are prepared (i.e., dried), synthetic wadsleyite samples still contain a minimum of 5–50 times the amount of H than is typical for natural olivines from spinel lherzolite (Bell and Rossman 1992).

The reported water contents listed in Table 1 for samples WS3056 and WH2082 were estimated from averaged unpolarized FTIR spectra using the calibration of Paterson (1982). For samples with fully resolved polarized spectra (WZ304 and WH833) we report the average obtained from unpolarized spectra (Paterson 1982) and that obtained from polarized spectra using the calibration of Libowitzky and Rossman (1997). Very thin slices ~15 μm thick were used to estimate the water contents of WZ292 and WZ336 from unpolarized spectra.

X-ray diffraction

The cell parameters of hydrous wadsleyite from this study, listed in Table 1, were determined from several crystals from each experiment by single-crystal X-ray diffraction using the high-precision method of eight-position centering on a four-circle diffractometer (King and Finger 1979). The quality of the crystals is demonstrated by the sharp diffraction peak profiles, typically about 0.06 degrees (FWHM) in the final omega scan. Only the most anhydrous wadsleyite crystals from WS3056 containing ~50 wt ppm H_2O showed evidence of twinning, with FWHM values about twice that of all the others (Table 1).

Three wadsleyite compositions spanning almost two orders of magnitude in water-content were chosen for single-crystal structure refinements and polarized FTIR spectroscopy; wadsleyite WZ304 (with ~150 wt ppm H_2O), wadsleyite WH833 (with ~3200 wt ppm H_2O), and WZ292 (with ~9600 wt ppm H_2O). Single-crystal X-ray diffraction intensity data were collected with a CAD4 diffractometer using a sealed-tube Mo X-ray source. A hemisphere of reciprocal space was visited to 70° 2θ, resulting in about 2500 total reflections. The structures of these hydrous wadsleyites were refined in *Imma* because the deviations from orthorhombic symmetry (with respect to atom positional parameters) did not warrant treatment in the monoclinic *I2/m* space group. Pertinent data collection and model parameters are listed in Table 1. Atom positions are given in Table 2, and thermal displacement parameters are given in Table 3. The systematic variation of M-site occupancies and

TABLE 1. Hydrous wadsleyite synthesis conditions, estimated water contents from FTIR, cell parameters, and data collection parameters

Experiment no.	WS3056	WZ304	WH833	WH2082	WZ292	WZ336
P-T Conditions	18 GPa, 2100 °C	17 GPa, 1400 °C	16 GPa, 1200 °C	16 GPa, 1300 °C	16 GPa, 1400 °C	16 GPa, 1400 °C
ppm wt. H$_2$O*	~50	~150	~3200	~6000	~9600	~10600
Products†	β + maj	β + AnB	β	β	β + E + cpx	β + E + cpx
Cell Parameters						
a (Å)	5.7002(2)	5.6998(2)	5.6941(2)	5.6881(3)	5.6890(4)	5.6900(2)
b (Å)	11.4385(2)	11.4383(3)	11.4597(3)	11.4868(3)	11.4830(4)	11.4778(3)
c (Å)	8.2587(2)	8.2573(2)	8.2556(2)	8.2508(2)	8.2527(4)	8.2529(3)
β (°)	90.004(2)	90.003(2)	90.002(3)	90.055(3)	90.085(4)	90.125(3)
V (Å^3)	538.46(2)	538.34(3)	538.70(3)	539.08(3)	539.13(4)	538.98(3)
<FWHM>† in ω	0.120°	0.08°	0.05°	0.06°	0.05°	0.08°
Intensity Data (Imma)						
(h ± 9, k ± 18, l + 13)						
°2θ max		70°	70°		70°	
No. refl.		2480	2490		2590	
No. unique refl.		662	665		666	
Unique with Fo > 4σ(Fo)		495	556		499	
R$_{int}$ (merging R)		0.046	0.042		0.041	
R(F)		0.018	0.017		0.021	
R(F^2) all data		0.043	0.043		0.051	

* Estimated from averaged unpolarized-FTIR spectra using the calibration of Paterson (1982).
† β = hydrous wadsleyite (β-Mg$_{2-x}$H$_{2x}$SiO$_4$); E = phase E (Mg$_{2.08}$Si$_{1.16}$H$_{3.2}$O$_6$); cpx = clinopyroxene (MgSiO$_3$); AnB = anhydrous phase B (Mg$_{14}$Si$_5$O$_{24}$); maj = majorite (MgSiO$_3$). All experiments contained fine-grained quench glass.
‡ Average full-width at half-maximum for the final omega scan.

interatomic distances as a function of water content is provided in Table 4.

Oriented plates perpendicular to the major axes of the WZ304, WH833, and WZ292 samples were prepared using a four-circle diffractometer and the micro-mounting method described by Jacobsen et al. (2004) for the preparation of oriented ultrasonic samples. At least three different crystals of each composition were oriented with X-rays on a four-circle diffractometer. Once the orientation matrix was obtained, the crystal was driven to the machine angles necessary to bring the desired (hkl) vector into a vertical orientation. A glass slide mounted parallel to the goniometer table was brought close to the sample, and finally the z-translation of the sample goniometer was adjusted so as to place the crystal into a drop of Loctite349 (Impruv) UV-curing epoxy. A high-intensity fiber-optic UV light source was used to rapidly cure the epoxy. The initial face of the oriented crystal was then polished. In this way, three different sections perpendicular to **a**, **b**, and **c**, were doubly polished to about 50 micrometers thickness for WZ304 and WH833 and to about 15 micrometers thickness for WZ292 and WZ336.

Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed using a Bruker IFS 120 HR high-resolution FTIR spectrometer. The instrument contains Casse-granian optics and is equipped with a metal-strip polarizer on a KRS-5 substrate. Spectra acquisitions were carried out in the wavenumber range from 1500 to 4800 cm^{-1} using a CaF$_2$ or KBr beam splitter with a tungsten or Glowbar light source, respectively, and a high-sensitivity narrow-band MCT (mercury-cadmium-telluride) detector cooled by liquid nitrogen. Analyses were made at room temperature and pressure, using a stream of H$_2$O- and CO$_2$-free purified air. About two hundred scans were accumulated for each spectrum at a resolution of 1 or 4 cm^{-1}.

The infrared beam was focused in the middle of the sample using apertures with different diameters: 1.35 (sample WH833), 1.2 (sample WZ304), or 0.75 mm (sample WZ292), which generate spot sizes of 90, 80, or 50 μm, respectively (in the focal plane). The samples were placed on a CaF$_2$ plate and submersed in poly-trichlorofluorethylene oil.

Each sample was initially characterized from several unpolarized IR spectra, from which an average spectrum was used to estimate the global water contents (Table 5). Polarized absorption spectra were taken with the electric vector (**E**) parallel to each crystallographic axis to study the pleochroism of the IR bands. The orientation of the samples in the direction of polarization was checked using transmitted light and crossed-Nichols on the FTIR microscope. After background and baseline corrections, the spectra were normalized to 1 cm thickness, and the water contents were determined for each spectrum using the calibration of Paterson (1982):

$$C_{OH} = \frac{X_i}{150\xi} \int \frac{k(\overline{v})}{(3780 - \overline{v})} \, d\overline{v}$$

with

$$\xi = 1/3 \text{ or } \xi = 1$$

TABLE 2. Crystal structures of hydrous wadsleyite (β-Mg2SiO4 in Imma) containing ~150 wt ppm H$_2$O (WZ304; first line), 3200 wt ppm (H833; second line), and 9600 wt ppm (WZ292; third line) from single-crystal X-ray diffraction data

Atom	x	y	z
Mg1	0	0	0
	0	0	0
	0	0	0
Mg2	0	0.25	0.97029(9)
	0	0.25	0.97035(7)
	0	0.25	0.97013(10)
Mg3	0.25	0.12748(5)	0.25
	0.25	0.12650(3)	0.25
	0.25	0.12516(6)	0.25
Si	0	0.11978(3)	0.61685(4)
	0	0.12011(2)	0.61651(3)
	0	0.12033(3)	0.61619(4)
O1	0	0.25	0.21689(17)
	0	0.25	0.21848(14)
	0	0.25	0.21995(19)
O2	0	0.25	0.71691(17)
	0	0.25	0.71663(13)
	0	0.25	0.71649(17)
O3	0	0.98983(9)	0.25540(12)
	0	0.98934(7)	0.25571(9)
	0	0.98863(10)	0.25578(12)
O4	0.26133(13)	0.12261(6)	0.99250(8)
	0.26098(11)	0.12288(4)	0.99297(6)
	0.26092(14)	0.12317(7)	0.99359(8)

where $k(v)$ is the absorption coefficient at wavenumber v, X_i is the extinction coefficient equal to 4.050×10^4 H/10^{6}Si (2590 wt ppm) for Mg-wadsleyite (Bol-fan-Casanova et al. 2000), and ξ is the orientation factor, which is equal to 1/3 for unpolarized spectra and 1 for polarized spectra (Paterson 1982).

In addition, we estimated water contents from the polarized IR data using the more recent calibration of Libowitzky and Rossman (1997):

$$C_{(wt\% H_2O)} = A_i \frac{1.8}{D \, \varepsilon_i} \text{ with } \varepsilon_i = 246.6(3753 - v_m)$$

where ε_i is the integrated molar absorption coefficient in cm^{-2}, v_m is the mean wavenumber of the stretching band in cm^{-1}, A_i is the integrated absorbance normalized to 1 cm thickness, and D is the density in g/cm^3, here equal to 3.47 g/cm^3

TABLE 3. Anisotropic displacement parameters for hydrous wadsleyite (β-Mg_2SiO_4 in *Imma*) containing ~150 wt ppm H_2O (WZ304; first line), 3200 wt ppm (H833; second line), and 9600 wt ppm (WZ292; third line) from single-crystal X-ray diffraction data

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Mg1	0.0047(5)	0.0036(3)	0.0049(3)	0	0	−0.00038(19)	0.00440(18)
	0.0068(3)	0.0049(2)	0.0077(2)	0	0	0.00015(15)	0.00647(14)
	0.0093(5)	0.0049(3)	0.0099(3)	0	0	0.0009(2)	0.00804(19)
Mg2	0.0052(4)	0.0040(3)	0.0039(3)	0	0	0	0.00437(14)
	0.0064(3)	0.0048(2)	0.0052(2)	0	0	0	0.00547(13)
	0.0073(4)	0.0048(3)	0.0054(3)	0	0	0	0.00584(15)
Mg3	0.0042(3)	0.0044(2)	0.0056(2)	0	−0.00087(14)	0	0.00470(11)
	0.0050(2)	0.0064(2)	0.0057(2)	0	−0.00072(11)	0	0.00571(13)
	0.0054(3)	0.0084(3)	0.0060(3)	0	−0.00077(16)	0	0.00660(17)
Si	0.00302(14)	0.00288(14)	0.00324(14)	0	0	0.00018(12)	0.00305(8)
	0.00348(14)	0.00373(13)	0.00379(13)	0	0	0.00003(8)	0.00367(9)
	0.00479(16)	0.00470(15)	0.00432(15)	0	0	−0.00017(12)	0.00460(10)
O1	0.0044(6)	0.0040(6)	0.0048(5)	0	0	0	0.00441(24)
	0.0048(5)	0.0064(4)	0.0068(4)	0	0	0	0.00600(20)
	0.0051(6)	0.0084(6)	0.0076(5)	0	0	0	0.00702(26)
O2	0.0066(7)	0.0032(5)	0.0043(5)	0	0	0	0.00473(25)
	0.0077(5)	0.0042(4)	0.0044(4)	0	0	0	0.00541(19)
	0.0085(7)	0.0061(6)	0.0040(5)	0	0	0	0.00622(26)
O3	0.0057(6)	0.0049(4)	0.0046(4)	0	0	0.0011(3)	0.00504(21)
	0.0068(4)	0.0055(3)	0.0050(3)	0	0	0.0011(2)	0.00579(16)
	0.0068(6)	0.0074(4)	0.0058(4)	0	0	0.0007(3)	0.00663(22)
O4	0.0045(4)	0.0049(3)	0.0048(3)	0.0000(4)	0.00080(19)	0.0001(2)	0.00473(14)
	0.0049(3)	0.0060(2)	0.0058(2)	0.0000(2)	0.00087(14)	0.0001(2)	0.00559(13)
	0.0056(3)	0.0067(3)	0.0062(3)	0.0003(3)	0.00071(19)	0.0003(2)	0.00615(14)

for iron-free wadsleyite (Finger et al. 1993). For both methods, integration was performed in the wavenumber range 3700–2800 cm^{-1} and the total water content is equal to the sum of the water contents obtained for each crystallographic axis (Table 5). The contribution to the total water content from three different frequency ranges is listed in Table 6.

RESULTS AND DISCUSSION

Structural systematics

The cell parameters of wadsleyite as a function of water content from this and other single-crystal X-ray diffraction studies are plotted in Figure 1. The water contents were estimated from infrared spectroscopy (this study, and Kohn et al. 2002), or from SIMS data (Kudoh and Inoue 1999). Whereas the *a* and *c* dimensions decrease slightly with increasing water content, the *b* dimension increases by almost 0.5% (or ~100σ) on hydration to ~1 wt% H_2O. The total volume of hydration for wadsleyite is about 0.8 Å^3, or 0.15% on hydration to ~1 wt% H_2O.

Given the relative availability of X-ray diffraction instruments compared to polarized infrared and especially SIMS, a secondary calibration for the estimated H-content in wadsleyite was derived from the data shown in Figure 1. There is relatively large scatter in the available data, due perhaps in part to real variations in the hydration-substitution mechanisms and stoichiometry, but also probably due to experimental factors influencing the absolute value of the cell constants in the single-crystal experiments (such as variation in the effective radiation wavelength due to monochromation). Therefore, we propose an empirical calibration for estimating H-contents in wadsleyite based not on the absolute dimensions or cell volume, but on the *b*/*a* axial ratio (Figure 1d):

$$(b/a) = 2.008(1) + 1.25(3) \times 10^{-6} \cdot C_{H_2O}$$

where C_{H_2O} is the concentration of water in ppm H_2O by weight. This ratio was chosen because the *a* parameter exhibits the largest relative decrease while the *b* parameter increases on hydration, but also because the *b*/*a* ratio is independent of instrument or method (single-crystal or powder X-ray, or neutron).

Smyth et al. (1997) reported deviations from orthorhombic symmetry in Fo$_{90}$ hydrous wadsleyite (by about 30σ) containing ~2 wt% (20 000 wt ppm) H_2O, with a monoclinic β angle of 90.40(1)°. The monoclinic hydrous wadsleyite structure was confirmed by Kudoh and Inoue (1999), who proposed that variation of the stacking arrangement of Mg-vacant structural modules violates the mirror symmetry perpendicular to **a**. For this suite of hydrous wadsleyite samples, we detected monoclinic symmetry only for those containing more than about 0.5 wt% (5000 wt ppm) H_2O. The samples with about 50, 150, and 3200 wt ppm H_2O are statistically orthorhombic, but WH2081 (with ~6000 wt ppm), WZ292 (with ~9600 wt ppm), and WZ336 (with ~10 600 wt ppm) have systematically increasing β-angles of 90.055(3)°, 90.085(4)°, and 90.125(3)°, respectively.

To track changes in the O···O environments with increasing water contents, single-crystal X-ray structure refinements were carried out on the same samples as were used in the FTIR study: WZ304, WH833, and WZ292. Since incorporation of H as hydroxyl into wadsleyite (in the pure-Mg system) is expected to result in M-site (divalent cation) vacancies, details of the M-site occupancies and interatomic distances are reported in Table 4. The M1 and M2 sites show approximately full occupancy for all three compositions, but the occupancy of M3 (coordinated

TABLE 4. Variation of the M-site occupancies and interatomic distances R(M-O) and R(O-O) with water content in hydrous wadsleyite*

	WZ304 ~150	H833 ~3200	WZ292 ~9600	
ppm wt H_2O				
M1				
Occupancy	1.020(4)	1.020(4)	1.028(4)	
Mg1-O3 (2×)	2.112 Å	2.115 Å	2.115 Å	
Mg1-O4 (4×)	2.047	2.048	2.051	
Average Mg1-O	2.069	2.070	2.072	
				ΔR(O-O) Å
O3-O4a (4×)	2.840	2.842	2.844	0.004 longer
O3-O4b (4×)	3.039	3.042	3.045	0.006 longer
O4-O4a (2×)	2.979	2.972	2.969	0.010 shorter
O4-O4b (2×)	2.808	2.819	2.831	0.023 longer
Average O-O	2.924	2.927	2.930	0.006 longer
Polyhedral vol.	11.72 Å³	11.75 Å³	11.79 Å³	
M2				
Occupancy	1.016(4)	1.020(4)	1.024(4)	
Mg2-O1 (1×)	2.036 Å	2.049 Å	2.062	
Mg2-O2 (1×)	2.092	2.095	2.093	
Mg2-O4 (4×)	2.092	2.089	2.089	
Average Mg2-O	2.083	2.083	2.085	
				ΔR(O-O) Å
O1-O4 (4×)	2.788	2.792	2.795	0.007 longer
O2-O4 (4×)	3.086	3.088	3.091	0.004 longer
O4-O4a (2×)	2.979	2.972	2.969	0.010 shorter
O4-O4b (2×)	2.914	2.914	2.913	unchanged
Average O-O	2.940	2.941	2.942	unchanged
Polyhedral vol.	11.95 Å³	11.96	11.98	
M3				
Occupancy	1.000(4)	0.956(4)	0.928(4)	
Mg1-O1 (2×)	2.017 Å	2.024	2.035	
Mg1-O3 (2×)	2.124	2.121	2.117	
Mg1-O4 (2×)	2.128	2.123	2.117	
Average Mg3-O	2.0897	2.0895	2.0896	
				ΔR(O-O) Å
O1-O1 (1×)	2.902 Å	2.894	2.887	0.015 shorter
O3-O3 (1×)	2.851	2.849	2.846	0.005 shorter
O1-O3 (2×)	2.993	3.003	3.016	0.023 longer
O1-O4a (2×)	2.788	2.792	2.795	0.007 longer
O1-O4b (2×)	3.120	3.106	3.092	0.028 shorter
O3-O4a (2×)	3.039	3.042	3.045	0.006 longer
O3-O4b (2×)	2.914	2.915	2.918	0.004 longer
Average O-O	2.9551	2.9550	2.9555	
Polyhedral vol.	12.05 Å³	12.06	12.07	

* One standard deviation is 0.001 Å for R(M-O) and 0.002 Å for R(O-O) and ΔR(O-O).

to O1) systematically decreases from 0.99 to 0.96 and 0.92 for the samples containing 150, 3200, and 9600 wt ppm H_2O, respectively. The relatively large amount of M3 vacancy confirms that the dominant hydration mechanism is protonation of O1, the non-silicate oxygen site (Smyth 1987; Kudoh et al. 1996; Smyth et al. 1997; Kohn et al. 2002; Ross et al. 2003).

M-site polyhedral volumes do not change significantly on hydration to 1 wt% (10 000 wt ppm) H_2O, but a systematic change in the M-site edge lengths may reveal which O···O environments become hydrogen bonds. Whereas almost all the R(O-O) interatomic distances increase with hydration (Table 4), four O···O distances decrease with increasing global H-content. Locally, the strong O-O repulsion on each edge of an M-site will increase when the adjacent M-site cation is missing, resulting in increased O-O interatomic distances and polyhedral volumes. However, if the strong O-O repulsive forces are relaxed by the introduction of a hydrogen bond along the M-site edge, the O-O distance may shorten. We observed a systematic shortening along the O1···O1, O1···O4, and O3···O3 edges of M3, and along the O4···O4 edges of M1 and M2 (Table 4).

Spectroscopic systematics and OH concentrations

Polarized infrared spectra were obtained from the same samples studied by single-crystal X-ray diffraction (WZ304, WH833, and WZ292). The averaged unpolarized spectra are scaled equally and shown together in Figure 2a. Polarized FTIR spectra taken with **E** parallel to the major axes of the optical indicatrix are shown for all three compositions in Figures 2b–d. In agreement with Kohn et al. (2002), we observed an increase in the number of absorption bands with increasing water content, in particular between WZ304 with ~150 wt ppm and WH833 with ~3200 wt ppm. Also, the main bands in the spectra from WZ304 (3619, 3471, and 3324 cm⁻¹) do not correspond exactly to the main bands at higher water contents, indicating that different hydration mechanisms become important at higher H concentrations or that distortions due to M-site vacancies, vacancy ordering, and possibly also different R(O-O) interatomic distances cause the positions of the bands to shift at higher water contents (Kohn et al. 2002). The spectra for higher water contents (WH833 and WZ292) are characterized by three main groups: a pleochroic doublet at 3614 and 3581 cm⁻¹, a less pleochroic but very strong absorption triplet at 3360, 3326, and 3317 cm⁻¹, and a very broad and pleochroic band centered around 3000 cm⁻¹. The spectra are similar to those from Kohn et al. (2002) with the major exception being that we do not observe the band at 3657 cm⁻¹.

There is no absolute calibration for OH in wadsleyite as there is for olivine (Bell et al. 2003). Therefore, we can only estimate the concentration of OH using at best empirical scales made from other minerals and at generally lower concentrations. The aim of this study is to compare order of magnitude differences, so we will not dwell on whether or not a particular OH concentration is known to within a few weight per parts million, but will instead consider the uncertainties to be on the order of 10%. For comparison to previous results, we have chosen to use the calibrations of Paterson (1982) for unpolarized spectra (the values given in Table 1) and the OH concentrations obtained using the newer Libowitzky and Rossman (1997) calibration for polarized spectra (Table 5). For samples WZ304 and WH833 where the spectra are completely resolved, we used the average of both methods (Table 1). The estimated bulk concentration of H in wadsleyite as a function of crystal orientation is given in Table 5, and contributions from different frequency ranges are given in Table 6.

Assignment of peaks in the FTIR spectra

In this section we attempt to assign the main bands at 3614, 3581, 3360, 3326, 3317, and 3000 cm⁻¹ to specific O-H···O environments. These bands correspond to those at 3611, 3585, 3359, 3343, 3331, and 3000 cm⁻¹, respectively, in the spectra of Kohn et al. (2002), although we did not observe the band at 3657 cm⁻¹. Assignment of the main bands must account for the two most robust observations which are (1) pleochroism in the polarized spectra and (2) significant M-site vacancy at M3. To a lesser extent, we will consider (3) the frequency-distance correlations (e.g., Libowitzky 1999), although we place less weight on this than Kohn et al. (2002) because some of the hydrogen bonds in wadsleyite appear to be highly non-linear; (4) electrostatic arguments that silicate-oxygen atoms are less likely to be protonated than non-silicate oxygen atoms; and (5) systematically shortened

TABLE 5.   Estimated bulk concentration of H in wadsleyite (in wt ppm H₂O) and as a function of the crystal orientation

Sample	Water content* 3670-3130 cm⁻¹ wt ppm H₂O	Water content† **E** // [100] wt ppm H₂O	Water content† **E** // [010] wt ppm H₂O	Water content† **E** // [001] wt ppm H₂O	Total water content‡ wt ppm H₂O
		Using the calibration of Paterson (1982)			
WZ304	136 ± 34	27 ± 10	32 ±13	64 ± 22	123 ± 45
WH833	2235 ± 245	500 ± 86	846 ± 121	1450 ± 52	2796 ± 259
WZ292§	> 4624 ± 2000	> 874 ± 449	> 1733 ± 230	> 2400 ± 887	> 5007 ± 1566
		Using the calibration of Libowitzky and Rossman (1997)			
WZ304	–	59 ± 27	50 ± 5	71 ± 3	179 ± 57
WH833	–	757 ± 65	1410 ± 45	1579 ± 26	3747 ± 137
WZ292§	–	> 1367 ± 290	> 2674 ± 79	> 4333 ± 650	> 8373 ± 1019

* Obtained from the calibration of Paterson (1982) for unpolarized IR radiation using the average of several spectra taken from each crystal.
† Obtained from polarized IR using the average spectra of several taken from each direction.
‡ Sum of the water content from each crystallographic direction.
§ Maximum absorbance could not be resolved so the (>) symbol is used to indicate that these are minimum wt ppm values.
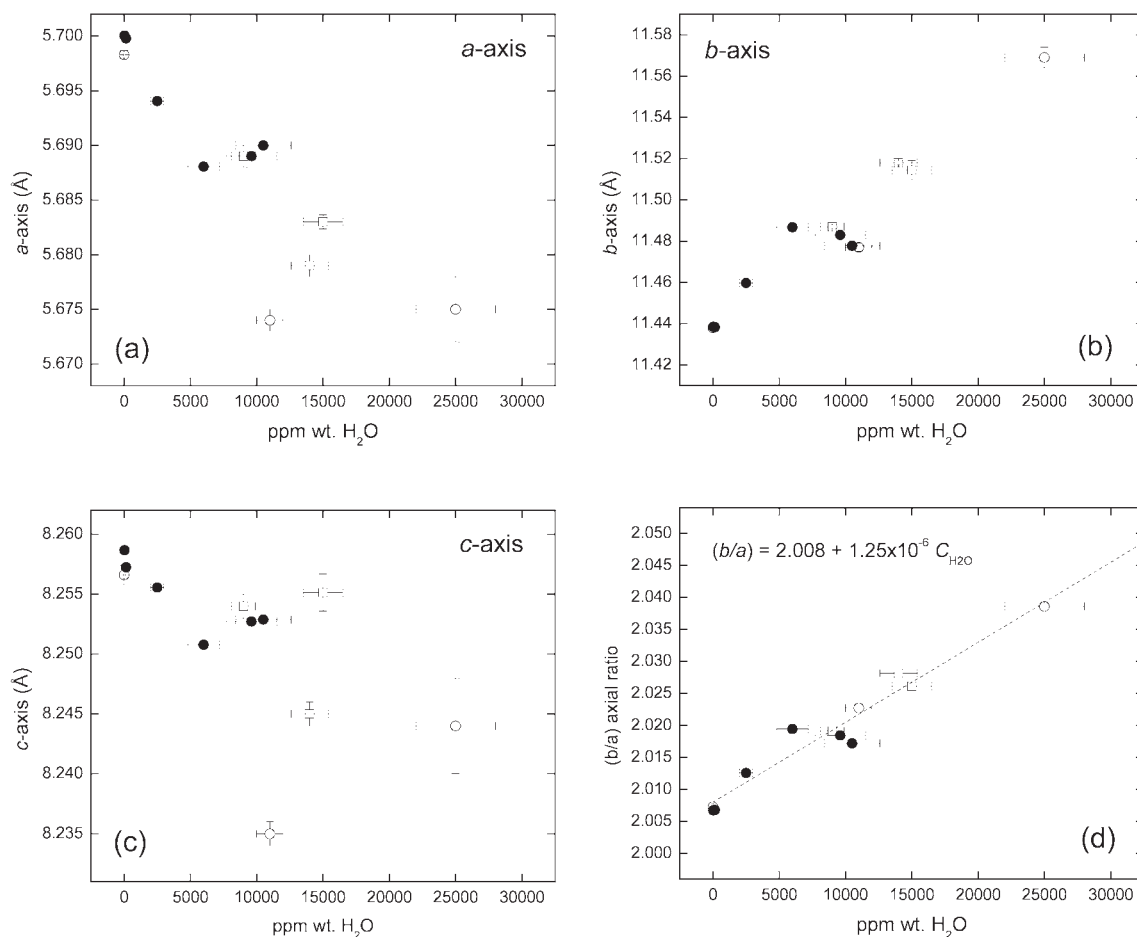

FIGURE 1. (a–c) Variation of the wadsleyite unit-cell parameters with water content from single-crystal studies; the current study (filled circles), Kudoh and Inoue (1999) (open circles), and Kohn et al. (2002) (open squares). **(d)** A wavelength-independent calibration for water in wadsleyite made using the (*b/a*) axial ratio.

O···O distances may indicate reduced O-O repulsive forces in the vicinity of a vacancy. For many of the O···O groups (e.g., O4···O4), there are several crystallographically distinct choices, so we refer to each by their *R*(O-O) interatomic distance from the most hydrous structure (WZ292) provided in Table 4. We will refer to the polarized spectra in Figure 3 for sample WH833 because all the bands are well resolved and their frequencies are the same as for WZ292.

3614 cm⁻¹

The band at 3614 cm⁻¹ corresponds to an absorber lying nearly in the **a-c** plane because there is almost no absorption for **E**//**b** (Figs. 3a–c). The absorber has almost equal component vectors of **a** and **c** because there is almost no variation in absorption in the **a-c** plane (Fig. 3b). There are five possible candidates: O1···O1 (2.887 Å), O2···O2 (2.898 Å), O3···O3 (2.846 Å), O4···O4 (2.969 Å), and O4···O4 (2.720 Å). We can eliminate the shorter O4···O4
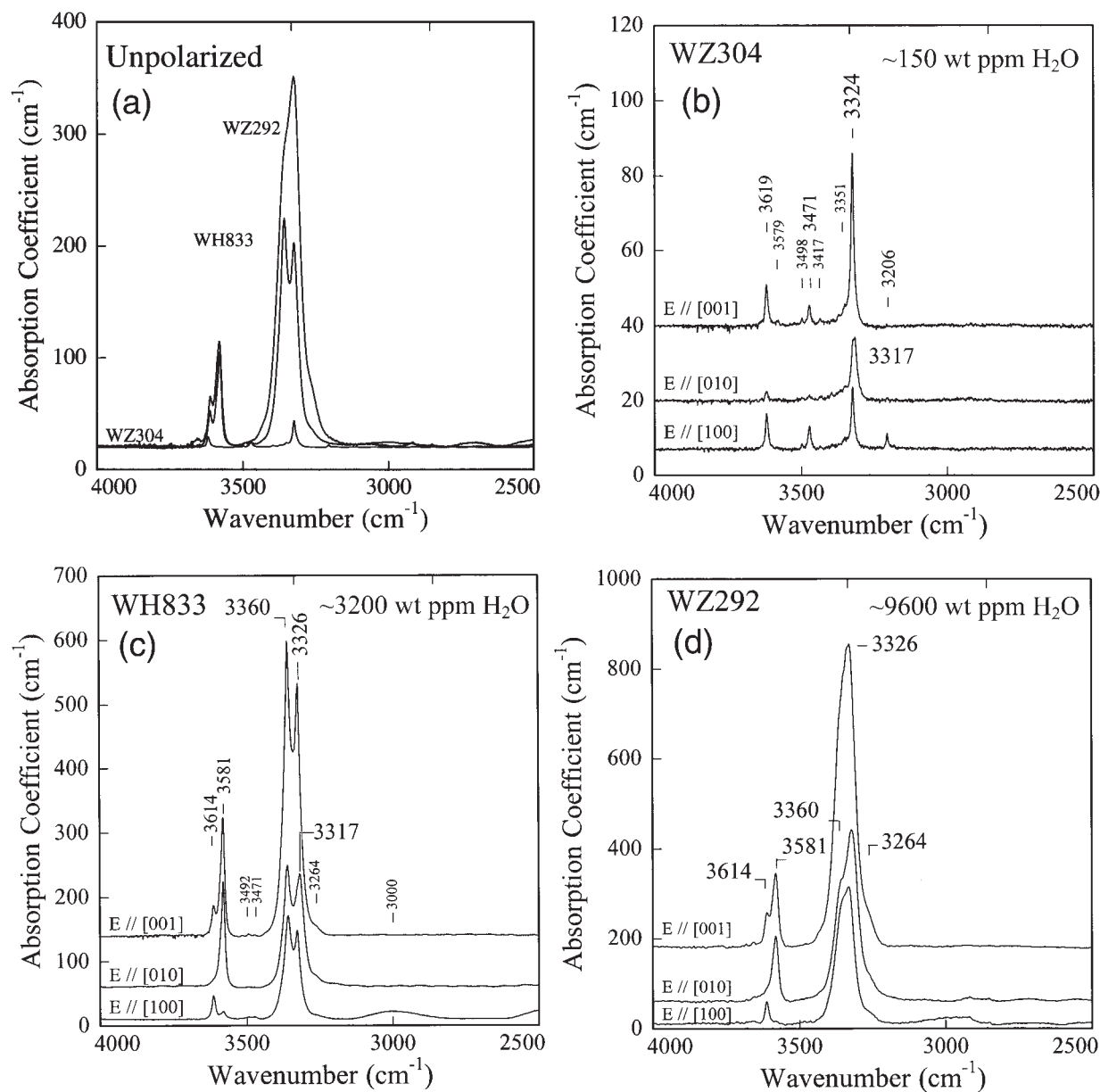
FIGURE 2. FTIR spectra of hydrous wadsleyite containing water contents that span two orders of magnitude. (**a**) Unpolarized spectra from WZ304 with about 150 wt ppm H_2O, WH833 with about 3200 wt ppm H_2O, and WZ292 with about 9600 wt ppm H_2O. (**b-d**) Polarized spectra with **E** parallel to each of the major crystallographic axes. The spectra for WZ292 do not reach full intensity for the main bands due to complete absorption.

TABLE 6. Estimated concentration of H in wadsleyite as a function of crystal orientation and frequency

Sample	Orientation	Group 1 3670-3550 cm⁻¹ wt ppm H_2O	Group 2 3550-3130 cm⁻¹ wt ppm H_2O	Group 3 3130-2800 cm⁻¹ wt ppm H_2O
WZ304				
	E// [100]	18 ± 3	23 ± 4	–
	[010]	6 ± 1	25 ± 4	–
	[001]	20 ± 4	40 ± 4	–
WH833				
	E// [100]	76 ± 22	486 ± 59	39 ± 16
	[010]	320 ± 41	586 ± 81	–
	[001]	405 ± 53	1066 ± 95	–
WZ292				
	E// [100]	98 ± 21	588 ± 79	58 ± 26
	[010]	460 ± 55	1294 ± 205	–
	[001]	509 ± 75	2607 ± 425	–

(2.720 Å) choice because it is a tetrahedral edge and would be expected to show absorption below ~3200 cm⁻¹. We also find O2···O2 (2.898 Å) an unlikely candidate because it involves two bridging oxygen atoms and would therefore require an Si vacancy for which there is no evidence from the structure refinements. Of the remaining three choices, O4···O4 (2.969 Å), O1···O1 (2.887 Å), and O3···O3 (2.846 Å), only the longest (O4···O4) falls within the envelope of the distance-frequency correlation (Libowitzky 1999; Kohn et al. 2002), but since there is no evidence for M1 and M2 vacancies for that edge, we prefer an assignment to O1···O1 (2.887 Å) along the shared M3/M3 edge because it shortens the most (Table 4), is consistent with M3 vacancies, and involves the non-silicate oxygen atom (O1). The fact that
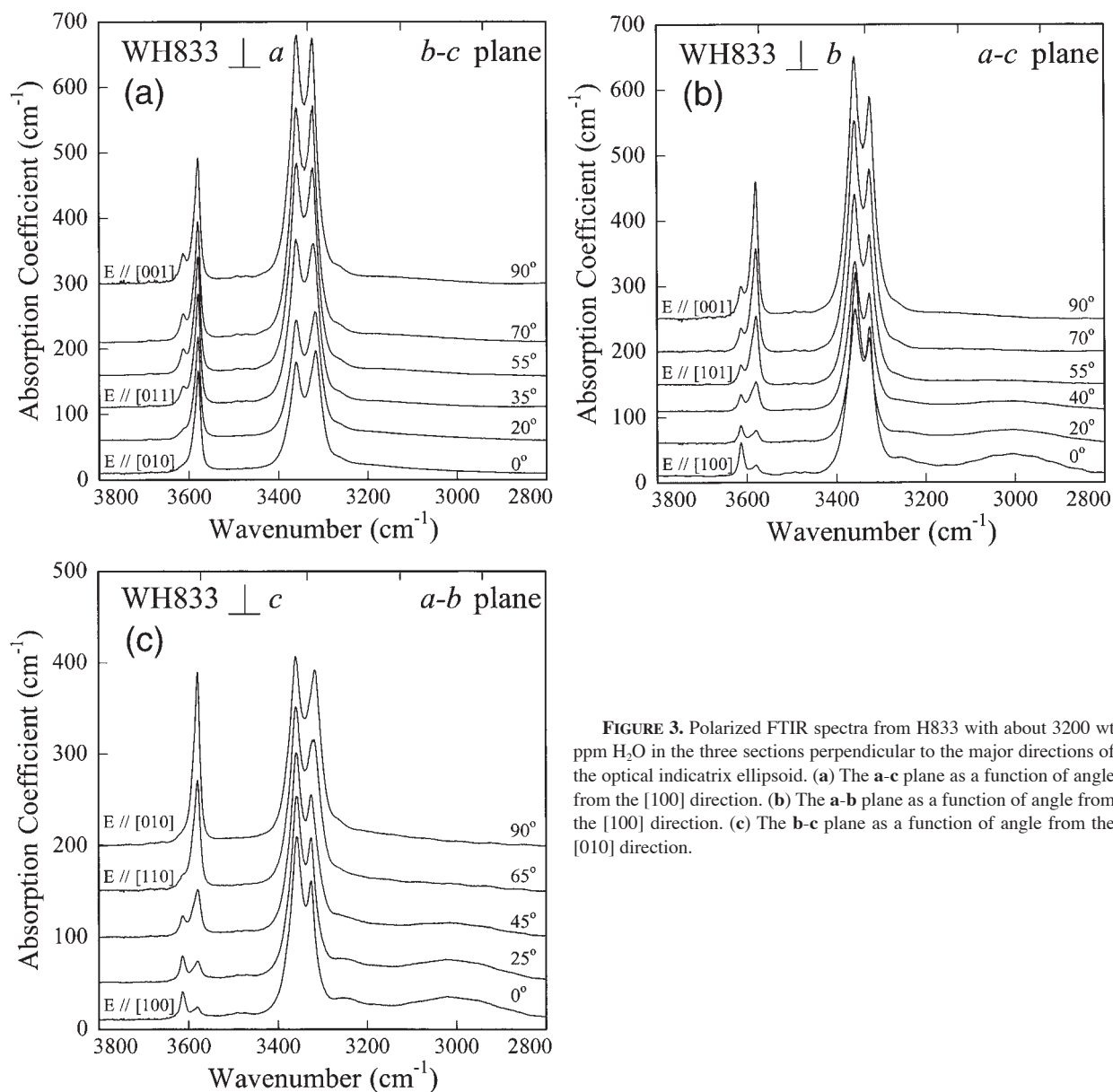
FIGURE 3. Polarized FTIR spectra from H833 with about 3200 wt ppm H_2O in the three sections perpendicular to the major directions of the optical indicatrix ellipsoid. (**a**) The **a**-**c** plane as a function of angle from the [100] direction. (**b**) The **a**-**b** plane as a function of angle from the [100] direction. (**c**) The **b**-**c** plane as a function of angle from the [010] direction.

O1···O1 does not match well with the distance-frequency correlation can be explained by the fact that it is a non-linear hydrogen bond, indicated by relatively uniform absorption across the **a**-**c** plane (Fig. 3b).

3581 cm⁻¹

The band at 3581 cm⁻¹ corresponds to an absorber lying nearly in the **b**-**c** plane because there is almost no absorption for **E**//**a** compared to **E**//**b** and **E**//**c** (Figs. 3b–c). The absorber has almost equal **b** and **c** component vectors because there is almost no variation in absorption as a function of angle in the **b**-**c** plane (Fig. 3a). There are four possible candidates: O1···O3 (3.016 Å), O4···O4 (2.913 Å), O4···O4 (2.831 Å), and O2···O3 (2.750 Å). We eliminate O2···O3 (2.750 Å) because it is a tetrahedral edge and would be expected to show absorption below ~3200 cm⁻¹.

The remaining three possibilities all intersect within the envelope of the distance-frequency correlation of Libowitzky (1999) and shown by Kohn et al. (2002). None of the three remaining choices shows decreasing O···O distances on hydration (Table 4). Still, of the three, only one must be chosen because the O···O distances are probably too disparate to produce a single sharp peak, even if non-linear hydrogen bond angles are considered. Both O4···O4 environments involve the sorosilicate group, the longer being between two tetrahedra of the same Si_2O_7 group, and the shorter being between two adjacent Si_2O_7 groups. Still, protonation of O4 here would probably require some Si vacancy, for which there is no evidence. Thus, O1···O3 (3.016 Å) along the shared M3/M3 edge is the best choice because it involves O1 (the non-silicate oxygen atom) and would be accompanied by M3 vacancies which are observed in the structure refinements.

The O1-H···O3 hydrogen bond is also expected to be highly non-linear because it shows relatively constant absorption in the **b**-**c** plane (Fig. 3c).

3360, 3326, and 3317 cm⁻¹

The main band pair or triplet at 3360, 3326, and 3317 cm⁻¹ is perhaps the most difficult to assign because it is less pleochroic than the bands at 3614, 3581, and 3000 cm⁻¹. This means the corresponding O-H absorbers point in non-unique directions of the unit cell, and therefore have fairly equal components of **a**, **b**, and **c**. We can start by eliminating all O4···O4, and all O1···O3 choices because all these groups produce O-H vectors lying close to one of the three major planes of the indicatrix. We also choose to rule out O2···O2 and O2···O4 because they involve the bridging silicate oxygen atom of the Si_2O_7 group and, although it may be present in small quantities, protonation of O2 would be highly unlikely to produce the main band triplet considering that there are much better choices. The five remaining possibilities are: O3···O4 (2.844 Å) and O3···O4 (3.045 Å), both along the M1 edge, O3···O4 (2.918 Å), which is along the M3 edge, O1···O4 (3.092 Å) along the unshared M3 edge, and O1···O4 (2.795 Å) along the shared M2/M3 edge. Considering the distance-frequency correlation (Libowitzky 1999), only O1···O4 at 2.795 Å (along M2) and O3-O4 at 2.844 Å (along M1) fall within the envelope shown by Kohn et al. (2002). However, since both O3 and O4 are silicate oxygen atoms and there is no evidence for significant vacancies at M1, O1···O4 (2.795 Å) is a better choice. However, protonation of this edge doesn't fully account for the fact that there is no significant vacancy at M2 and that there are two or three distinct bands. The other prime choice is O1···O4 (3.092 Å) along the M3 edge, where most vacancies occur. This O1···O4 distance at 3.092 Å is also the one that shortens the most (0.028 ± 0.002 Å) on hydration, which might be explained by reduced O···O repulsive forces introduced by the M3 vacancy. Protonation on an M3 edge may result in splitting of the bands in the infrared if cation-vacancy ordering were to occur at M3, which is known for monoclinic hydrous Fe-bearing wadsleyite (Smyth et al. 1997). Vacancy ordering at M3 might therefore account for the apparent splitting of the 3324 cm⁻¹ band (at low concentrations) into at least two pleochroic bands (at 3326 and 3317 cm⁻¹) for higher water contents. In conclusion, one or both O1···O4 edges along M3 can account best for the three bands at 3360, 3326, and 3317 cm⁻¹, but there is no definitive way to rule out the three possible O3···O4 choices.

3000 cm⁻¹

The very broad and low-absorption band centered at around 3000 cm⁻¹ is perhaps the most straightforward to assign. By comparing ¹H NMR spectra between hydrous wadsleyite samples with normal H/D ratios to one that had been partially deuterated, Kohn et al. (2002) showed that this feature results from O-H absorption from a strong hydrogen bond in the structure rather than some other water-related overtone or combination of Si-OH bands, etc. Although the contribution of the 3000 cm⁻¹ band to the total water content is negligible (Table 6), it is interesting because it corresponds to very strong hydrogen bond that may have more relevance at high pressure, and is another demonstration of very strong hydrogen-bonding in an Si-OH group (e.g.,

Jacobsen et al. 2000). The band at 3000 cm⁻¹ is also strongly pleochroic, corresponding to an OH vector pointing nearly in the [100] direction because there is no absorption for **E**//**b** or **E**//**c** (Figs. 3a-c). There is only one O···O environment pointing in the **a**-direction with an appropriately short distance, so the 3000 cm⁻¹ band is almost unambiguously assigned to the short O4···O4 (2.720 Å) tetrahedral edge of the Si_2O_7 group.

Implications for hydrogen in the Earth's interior

Wadsleyite in the Earth's transition zone potentially holds one of the largest reservoirs of hydrogen in the planet. All of the main bands in the FTIR spectra of hydrous wadsleyite are explained by protonation of O1, the anomalous non-silicate oxygen atom. We assign the band at 3614 cm⁻¹ to a bent hydrogen bond O1···O1 along the M3 edge in the **a**-**c** plane. The band at 3581 cm⁻¹ can be explained by a bent hydrogen bond on O1···O3 along the M3 edge in the **b**-**c** plane. The less significant (in OH contribution) but no less interesting band at 3000 cm⁻¹ is almost unambiguously assigned to the very strong hydrogen bond formed along the O4···O4 tetrahedral edge of the Si_2O_7 group pointing nearly along the [100] vector. Finally, the three bands at 3360, 3326, and 3317 cm⁻¹ are best explained by hydrogen bonds pointing along the non-unique direction of the O1···O4 edges of M3 and M2. The results of this study provide strong experimental evidence in support of the theoretical prediction by Smyth (1987) that the non-silicate oxygen atom (O1) is the most important oxygen site for hydrogen storage in wadsleyite.

The actual concentration and distribution of hydrogen in Earth's interior with depth and through geologic time remains one of the most poorly constrained geochemical variables in the planet. The presence of H in the mantle, even in concentrations of hundreds or thousands of ppm, has major implications for the evolution of the planet. If present in quantities comparable to the samples in this study, the hydration state of the transition zone may be controlling the total amount of liquid water on the surface through geologic time. Wadsleyite and ringwoodite together have the potential to contain more water as hydroxyl bound in their crystal structures than is currently present in the hydrosphere. Actually detecting hydrogen in the mantle will require a quantitative understanding of the effects of hydration on the elasticity of these phases in the context of seismological observation. A detailed understanding of hydration mechanisms and hydrogen sites in the Earth-forming minerals improves our ability to predict the effects of hydration on the physical properties of the high-pressure silicates in Earth's mantle.

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