Coupled substitution of Fe$^{3+}$ and H$^+$ for Si in wadsleyite: a study by polarized infrared and Mössbauer spectroscopies and single-crystal X-ray diffraction

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ABSTRACT

Coupled substitution of Fe$^{3+}$ and H$^+$ for Si in wadsleyite was studied by polarized infrared and Mössbauer spectroscopies and single-crystal X-ray diffraction. Single crystals of Fe-bearing hydrous wadsleyite were synthesized at 16 GPa and 1870 K using a Kawai-type multianvil apparatus. Water and Fe contents of the sample were 0.19-0.26 wt% H$_2$O and Fe/(Mg + Fe) of 0.099(2), respectively. Mössbauer spectra showed 13(4) % Fe$^{3+}$/ΣFe and Fe$^{3+}$ at the tetrahedral site with 5(3) % IVFe$^{3+}$/ΣFe. Crystal structure refinement by single-crystal X-ray diffraction indicated that Fe (presumably Fe$^{3+}$) occupied 4.9(5) % of the tetrahedral site. Infrared light polarized with the electric vector $\mathbf{E} // a$ and $\mathbf{c}$ was absorbed at 3477(2) cm$^{-1}$.
while no absorption was observed at the region in spectra with \( E \parallel \mathbf{b} \). The pleochroic behavior of the 3477 cm\(^{-1}\) band can be interpreted as protonation of silicate oxygen O3 in Fe-bearing hydrous wadsleyite. The protonation of O3 together with the presence of Fe\(^{3+}\) at the tetrahedral site confirms the coupled substitution of Fe\(^{3+}\) and H\(^+\) for Si in Fe-bearing hydrous wadsleyite.

**Keywords:** wadsleyite, hydrogen, ferric iron, polarized infrared spectroscopy, single-crystal X-ray diffraction, Mössbauer spectroscopy

**INTRODUCTION**

Wadsleyite is the most abundant mineral in the upper part of the mantle transition zone (MTZ) (e.g. Irifune and Isshiki 1998) and can incorporate up to 3 wt% water in its crystal structure (e.g. Inoue et al. 1995). Incorporation of water (or hydrogen) in wadsleyite influences its elasticity (e.g. Mao et al. 2011), atomic diffusivity (Shimojuku et al. 2010), creep strength (Kubo et al. 1998), crystallographic preferred orientation (Ohuchi et al. 2014), grain-growth kinetics (Nishihara et al. 2006) and electrical conductivity (e.g. Karato 2011). Moreover, water affects phase boundaries relevant to wadsleyite (e.g. Mrosko et al. 2015; Smyth and Frost 2002). Consequently, determination of the substitution mechanisms of hydrogen in
wadsleyite is fundamentally important to addressing the effects of water on the above properties of the upper MTZ.

The major substitution mechanism of hydrogen in Fe-free hydrous wadsleyite was predicted as protonation of oxygen having no bonding to Si (non-silicate oxygen, O1) (Smyth 1987). Single-crystal X-ray diffraction (SC-XRD) on Fe-free hydrous wadsleyite revealed the protonation of O1 associated with Mg vacancies at the M3 site (Kudoh et al. 1996; Smyth et al. 1997). Moreover, polarized infrared (IR) spectroscopy on Fe-free hydrous wadsleyite indicated the O1 protonation with O-H dipoles on edges of the M3 octahedra, i.e. O1···O1 (2.887 Å), O1···O3 (3.016 Å) and O1···O4 (2.795 and 3.092 Å), and possible protonation of O3 and O4 (Jacobsen et al. 2005). The locations of the O-H dipoles relevant to IR absorption bands at ~3340 cm\(^{-1}\) were further constrained on O1···O4 (3.10 Å) and O3···O4 (3.04 Å) forming ~30° with the c axis by SC-XRD and IR spectroscopy at high pressure and low temperature (Deon et al. 2010). Furthermore, neutron diffraction on Fe-free deuterated wadsleyite confirmed that the O-H dipoles are on O1···O3 (3.035 Å) with a bent hydrogen bond and O1···O4 (3.071 Å) forming 31.9° with the c axis in the b-c plane and 39.8° with the a axis in the a-b plane (Sano-Furukawa et al. 2011).

Recently, coupled substitution of Fe\(^{3+}\) and H\(^{+}\) for Si was proposed as a new protonation mechanism in Fe-bearing hydrous wadsleyite (Bolfan-Casanova et al. 2012; Smyth et al. 2014). This hypothesis was supported by the following observations: (1) presence of Fe\(^{3+}\) at the tetrahedral (T) site; (2)
negative correlation between Si content and Fe$^{3+}$ plus H$^+$; (3) positive correlation between intensity of the IR absorption band at 3495 cm$^{-1}$ and Fe$^{3+}$ content. However, Si content also decreased with Fe$^{3+}$ content in dry wadsleyite (Frost and McCammon 2009). Moreover, the 3495 cm$^{-1}$ band may be related to another coupled substitution of Fe$^{3+}$ and H$^+$ for two divalent cations (Mg$^{2+}$ or Fe$^{2+}$). On the other hand, hydrogen should bond to oxygen atoms bonded to Si (silicate oxygen, i.e. O$_2$, O$_3$ and O$_4$) if this hypothesis is valid. However, the protonation of the silicate oxygen has not been reported in Fe-bearing hydrous wadsleyite.

Polarized IR spectroscopy can provide strong evidence for the protonation of the silicate oxygen by constraining orientations of hydrogen bonds and distances of O-H···O (cf. Jacobsen et al. 2005).

In the present study, we tested the hypothesis of the coupled substitution of Fe$^{3+}$ and H$^+$ for Si in wadsleyite by analyzing single crystals of Fe-bearing hydrous wadsleyite. We synthesized crystals large enough for polarized IR spectroscopy using a Kawai-type multianvil apparatus (Kawazoe et al. 2015). Presence of Fe$^{3+}$ at the T site in the sample was determined by SC-XRD and Mössbauer spectroscopy. Pleochroic behavior of IR absorption bands was examined at ~3200-3650 cm$^{-1}$ by polarized IR spectroscopy. We confirm the coupled substitution of Fe$^{3+}$ and H$^+$ for Si in Fe-bearing hydrous wadsleyite and discuss its implications for mantle dynamics in the MTZ.

**METHODS**
Synthesis experiment

San Carlos olivine powder ((Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$) was packed as starting material in a Re capsule with no additional water. The synthesis experiment (run H4181) was performed using a Kawai-type multianvil apparatus. We used second-stage anvils made of tungsten carbide with 8-mm truncation, and a pressure medium made of Cr-doped MgO with 14-mm edge length and pyrophyllite gaskets. A LaCrO$_3$ furnace was adopted with a ZrO$_2$ thermal insulator. We fired the ceramic parts of the cell assembly at 1273 K. The sample was first compressed to 8.0 MN (815 tonf) at room temperature and then temperature was increased to 1870(50) K and held constant for 3 h. Further details of the synthesis are described in our previous paper (Kawazoe et al. 2015).

Sample preparation and analyses

Two single crystals were oriented parallel to the (100) and (001) planes using X-ray diffractometers with a CCD detector (Oxford Diffraction, Xcalibur2) and a point detector (Huber, SMC9000, operating system SINGLE 2014 (Angel and Finger 2011)) operating with Mo $K\alpha$ radiation (40 kV and 30 mA). The crystals were polished on both sides to thicknesses of 101(1) or 102(1) $\mu$m using
0.25-µm diamond powder. The crystals were then oriented to the other crystallographic axes using electron backscatter diffraction in a field-emission scanning electron microscope (LEO, Gemini 1530).

SC-XRD data were collected using a diffractometer with a CCD detector (Bruker, P4 and APEX II) using Mo Kα radiation (50 kV and 250 mA). Crystal structure refinement was performed using the program SHELXL97 (Sheldrick 1997). Scattering factors of ionized cations (Mg2+, Fe2+ and Si4+) and O2- were adopted from Cromer and Mann (1968) and Tokonami (1965), respectively. Occupancy of the T site was refined allowing Fe and Si occupancies. Cation vacancy was assumed to be at the M3 site only and was determined from the b/a ratio (Jacobsen et al. 2005; Smyth et al. 2014).

Chemical compositions of four crystals were measured using an electron microprobe in wavelength-dispersive mode (JEOL, JXA-8200) operated at 15 kV and 15 nA. Mössbauer spectra were taken on a crystal with dimensions of ~0.3 × 0.4 × 0.5 mm³ at room temperature in transmission mode using a constant acceleration Mössbauer spectrometer with a ⁵⁷Co source. Mössbauer spectra were collected along each of three orthogonal directions of the crystal for 1-5 days and were fitted using Lorentzian doublets with Fe²⁺ at M sites and Fe³⁺ at M and T sites using the program MossA (Prescher et al. 2012). Only one Fe²⁺ quadrupole doublet could be statistically resolved (not two as in previous work) because ⁵⁷Fe was not enriched in the sample. Fe²⁺ quadrupole doublets were assumed to have equal component widths but different component areas due to orientation effects, while Fe³⁺ doublets were fitted assuming equal
component areas and widths. Abundances of Fe$^{2+}$ and Fe$^{3+}$ and their uncertainties were calculated from relative areas and statistical fitting errors, respectively.

Polarized IR spectra were obtained from 3-4 locations on each crystal with spot diameters of 140-160 µm using a Fourier transform IR spectrometer (Bruker, IFS-120 HR) with an MCT detector. The polarized IR spectra were taken with the electric vector (E) parallel to the crystallographic axes after adjusting crystal orientation by extinction under cross-polarized light. The bands were fitted using the program PeakFit (SeaSolve Software Inc.). Water contents of the sample were determined according to calibrations by Paterson (1982), Libowitzky and Rossman (1997) and Deon et al. (2010). The calibration by Deon et al. (2010) was calibrated specifically for wadsleyite on the basis of water content measurement by secondary ion mass spectroscopy (SIMS). The calibrations by Paterson (1982) and Libowitzky and Rossman (1997) were also used for comparison with the literature data calculated based on these calibrations. Uncertainty in water content corresponds to one standard deviation calculated from the measurements.

**RESULTS AND DISCUSSION**

The chemical composition of the crystals was homogeneous within each crystal and between different crystals with Fe/(Mg + Fe) of 0.099(2) (Table 1). The sample contained 13(4) % Fe$^{3+}$/ΣFe (Fig. 1
and Table 2). The unit-cell and atomic position parameters and site occupancies of the sample are shown in Tables 3, 4 and 5, respectively (CIF is available in Deposit items). The crystal structure refinement revealed the presence of 4.9(5) % Fe at the T site, which is assumed to be Fe$^{3+}$ because of its smaller ionic radius compared to Fe$^{2+}$. Fe/(Mg + Fe) from the structure refinement was 0.137 and higher than that of the chemical analysis. Analysis of the Mössbauer spectra indicated that Fe$^{3+}$ occupied 5(3) % of the T site relative to total Fe (Fig. 1). Thus the presence of Fe$^{3+}$ at the T site in the sample was confirmed by SC-XRD and Mössbauer spectroscopy.

The IR bands are located at 3282(6), 3333(6), 3375(6), 3477(2), 3588(4) and 3614(1) cm$^{-1}$ (Fig. 2). Bolfan-Casanova et al. (2012) and Smyth et al. (2014) reported the IR band at 3498 cm$^{-1}$ for Fe$^{3+}$-rich hydrous wadsleyite and related it to the coupled substitution of Fe$^{3+}$ and H$^+$ for Si while we observed the band at 3477 cm$^{-1}$. The difference in frequency between these bands can be attributed to difference in Fe contents of the samples. Fe/(Mg + Fe) of their representative samples were 0.172-0.410 and higher than that of the present sample (0.099). The increase in Fe content in wadsleyite elongates its O···O distances (e.g. Smyth et al. 2014) and leads to the band shift to higher frequency (Libowitzky 1999). The water content of the sample ranged from 0.191(6) to 0.256(9) wt% H$_2$O depending on the calibrations (Table 6). This water content is comparable with that estimated for the MTZ (~0.1 wt%, Karato 2011).
We assign these IR bands to hydrogen bonds based on the following observations and considerations (c.f. Jacobsen et al. 2005): (1) pleochroic behavior of the bands in the polarized IR spectra (Fig. 2); (2) vacancy at M3 site (Table 5); (3) correlation between O-H stretching frequency and O···O distance (Libowitzky 1999); (4) electrostatic potential of oxygens (Smyth 1987). In the following we refer to O···O with its distance (e.g. O3···O3 (2.858 Å)) to distinguish several crystallographically distinct choices.

The pleochroic behavior of the bands at 3282, 3333, 3375, 3588 and 3614 cm⁻¹ (Fig. 2) is consistent with Jacobsen et al. (2005). Candidates for the 3614 cm⁻¹ band are O1···O1 (2.905 Å) (Jacobsen et al. 2005) or O1···O2 (4.133 Å) (Deon et al. 2010). We assign the 3614 cm⁻¹ band to hydrogen bonds on O1···O1 (2.905 Å) because of its pleochroic behaviour. The 3581-3612 cm⁻¹ band of Fe-free hydrous wadsleyite was explained by hydrogen bonds on O1···O3 (3.016 Å) (Jacobsen et al. 2005) or O1···O2 (4.1 Å) (Deon et al. 2010). We assign the 3588 cm⁻¹ band to hydrogen bonds on O1···O3 (3.015 Å) confirmed by neutron diffraction (Sano-Furukawa et al. 2011). The bands at 3282, 3333 and 3375 cm⁻¹ were explained by hydrogen bonds on O1···O4 (3.092 Å), O1···O4 (2.795 Å) or O3···O4 (3.045 Å) for Fe-free hydrous wadsleyite (Jacobsen et al. 2005; Deon et al. 2010). We assign these bands to hydrogen bonds on O1···O4 (3.118 Å) confirmed by neutron diffraction (Sano-Furukawa et al. 2011).
The 3477 cm\(^{-1}\) band was observed in spectra with \(E//a\) and \(c\) only. Therefore, the O-H absorber of the band is on the (010) plane and not along the \(a\) and \(b\) axes. Candidates for the 3477 cm\(^{-1}\) band are \(\text{O}_2\cdots\text{O}_2 (2.908 \text{ Å})\) and \(\text{O}_3\cdots\text{O}_3 (2.858 \text{ Å})\) (Fig. 3). Both candidates are appropriate for this band according to the correlation between the O-H stretching frequency and the O\(\cdots\)O distance (Libowitzky 1999). \(\text{O}_2\cdots\text{O}_2 (2.908 \text{ Å})\) is unlikely because O2 is overbonded and has a deep electrostatic potential (Smyth 1987). Therefore, \(\text{O}_3\cdots\text{O}_3 (2.858 \text{ Å})\) is the best choice for the 3477 cm\(^{-1}\) band.

Protonation of O3, one of the silicate oxygens, and presence of Fe\(^{3+}\) at the T site support the coupled substitution of Fe\(^{3+}\) and H\(^+\) for Si in wadsleyite. A previous study suggested that the O-H absorber relevant to the coupled substitution is on the edges of the TO\(_4\) tetrahedron (Bolfan-Casanova et al. 2012). However, the hydrogen bond on O3\(\cdots\)O3 (2.858 Å) determined in the present study is more consistent with expected behavior than the previous model because of electrostatic repulsion from Fe\(^{3+}\) at T site.

**IMPLICATIONS**

Both Fe\(^{3+}\) and H\(^+\) can be brought to the upper MTZ by subduction of oceanic lithosphere and are expected to be accommodated in wadsleyite by the coupled substitution of Fe\(^{3+}\) and H\(^+\) for Si. The incorporation of Fe\(^{3+}\) and H\(^+\) in wadsleyite deepens the 520-km discontinuity by stabilization of wadsleyite relative to ringwoodite (Mrosko et al. 2015). For the 410-km discontinuity, the combined effect of Fe\(^{2+}\) and
water makes the discontinuity shallower (e.g. Smyth and Frost 2002). The incorporation of Fe$^{3+}$ and H$^+$ in wadsleyite may further shift the 410-km boundary to shallower depths by stabilizing wadsleyite relative to olivine. We note that this substitution may be more likely in wadsleyite than in olivine due to the larger polyhedral volume of the T site in wadsleyite (2.30 Å$^3$) relative to that of olivine (2.20 Å$^3$) for pure Mg$_2$SiO$_4$ compositions (Smyth and Bish 1988).

The coupled substitution of Fe$^{3+}$ and H$^+$ for Si in wadsleyite introduces point defects at its T site and may have significant effects on rheological properties of the upper MTZ. Mg-Fe diffusivity in wadsleyite was enhanced by ~1 order of magnitude through increase of its water content from ~0.007 wt% to ~0.12 wt% (Kubo et al. 2004). Moreover, water and oxygen fugacity significantly affect the grain-growth rate of Fe-bearing wadsleyite (Nishihara et al. 2006). The band was observed at ~3475 cm$^{-1}$ in their IR spectra, indicating that Fe$^{3+}$ and H$^+$ substituted for Si in their samples. On the other hand, the effects of Fe and water on Si diffusivity in wadsleyite were determined separately in dry and Fe-free systems, respectively (Shimojuku et al. 2010). The coupled substitution may also have a significant effect on Si diffusivity in wadsleyite.

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**FIGURE CAPTION**

Figure 2. Polarized IR absorption spectra of single crystals of Fe-bearing wadsleyite with \(E\) parallel to the crystallographic axes. IR absorption bands are located at 3282, 3333, 3375, 3477, 3588 and 3614 cm\(^{-1}\).

The water content was 0.256(9) wt% H\(_2\)O using the calibration by Deon et al. (2010).