Revision 1

Tetrahedral ferric iron in oxidized hydrous wadsleyite

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ABSTRACT

Crystals of ferrous and ferric iron-bearing hydrous wadsleyite have been synthesized at 1400°C and 12-13.5 GPa in a multi-anvil press. Crystal structures (atom positions, occupancies, and cell parameters) have been refined by single-crystal X-ray diffraction at ambient conditions. Assuming cation vacancies to be in the M3 site only, their concentration has been estimated from the unit cell parameter *b/a* ratio. Total refined site Fe contents are consistent with microprobe chemical analysis. There appears to be up to 11 percent iron (presumably ferric) in the tetrahedral site, consistent with reduced silica content (<1 Si per 4 oxygens) in the chemical analysis. Also the volume of the tetrahedron increases with increasing ferric iron content. Strong ordering of Fe in the octahedral sites is apparent in the order FeM3 $\geq$ FeM1 >> FeM2. The presence of ferric iron in the mantle transition zone is expected to partition preferentially into wadsleyite and may expand the stability region of wadsleyite relative to olivine and ringwoodite. Also, the observation of tetrahedral ferric iron in these samples increases the likelihood that there is compositional continuity between wadsleyite and the spinelloid III phase field observed in the Mg-free system fayalite-magnetite.

Keywords: wadsleyite, crystal structure, ferric iron, crystal chemistry, transition zone

INTRODUCTION

Wadsleyite (β-Mg_2SiO_4) is generally believed to be the most abundant phase in the Earth's transition zone from depths of 410 to about 525 km. Although its polymorphs, olivine and ringwoodite, are orthosilicates, wadsleyite is a sorosilicate with Si_2O_7 groups and a non-silicate oxygen (Morimoto et al, 1969; Moore and Smith, 1970). As such, it has a limited Fe content but a much greater ability to incorporate trivalent cations as well as hydrogen (Smyth, 1987, 1994, Inoue et al 1995; Kohlstedt et al, 1996; Kohn et al 2002; Gudfinsonn and Wood, 1998). Wadsleyite is thought to be among the five most abundant solid phases in the Earth's interior, so its chemistry may have an impact on the bulk chemistry and dynamics of the planet (e.g. Berkovici and Karato, 2003). It can incorporate more H than the planet's oceans and may be a very significant host phase for water in the interiors of terrestrial planets, buffering H activity and sustaining liquid water on planetary surfaces. Also, because the solubility of ferric iron in wadsleyite is much higher than that in olivine, the olivine to wadsleyite transition may represent a discontinuity in the mantle oxygen fugacity (O'Neill et al., 1996). Thus, the crystal chemistry of wadsleyite may be of general interest to geochemists and planetary scientists.

The wadsleyite crystal structure is that of spinelloid III (Akaogi et al., 1982) and is based on a cubic-close-packed array of oxygens. The space group is *Imma*, although ordering of cation vacancies can result in a dilution of this symmetry to *I*2/*m* with a β-angle up to 90.4° if water content exceeds about one percent by weight (Smyth et al 1997, Kudoh et al., 2001, Holl et al 2008; Jacobsen et al., 2005). In the *Imma* structure, there are three different octahedral sites, M1, M2, and M3, all fairly regular and roughly equal in size, and there is a single silicate tetrahedron which is unusually large and highly distorted with one very long T-O distance (>1.7 Å) to the overbonded bridging oxygen (O2) (Smyth, 1987). The structure is capable of incorporating several weight percent of H_2O as hydroxyl (Inoue et al., 1995), and hydration is thought to occur by protonation of the underbonded, non-silicate oxygen, (O1), principally charge balanced by cation vacancies at M3 (Smyth et al., 1997, Kudoh et al, 2001, Ye et al., 2010).

Although orthosilicate minerals rarely incorporate significant trivalent cations at tetrahedral sites, sorosilicates can do this to partially relieve the overbonding of the bridging oxygen. In particular, the sorosilicate spinelloid minerals commonly have trivalent cations in tetrahedral coordination. However, tetrahedral Fe has not been previously reported in Mg silicate wadsleyites. The spinelloids are derivatives of the spinel structure and are based on a cubic-close-packed array of oxygen atoms. Five different spinelloid structures (I-V) are known in the nickel aluminosilicate system (Akaogi et al, 1982). All contain T_2O_7 or T_3O_{10} groups with bridging oxygens, and all contain oxygen atoms not bonded to tetrahedral cations. Only two spinelloid structures are known with only silicon in the tetrahedral site: wadsleyite has the spinelloid III structure, and wadsleyite II has the spinelloid IV structure (Smyth et al., 1997, Smyth et al 2004). Woodland and Angel (1998), Hazen et al (2000b), Koch et al (2004), and Woodland et al (2012) describe spinelloid III and spinelloid V in the fayalite-magnetite system at elevated pressure. Their spinelloid III structure has about half the tetrahedral site occupied by ferric iron.

The wadsleyite (spinelloid III) structure has space group symmetry *Imma*. There are three octahedral cation sites, M1, M2, and M3, a single tetrahedral site, and four distinct oxygen positions. There are eight formula units per cell, so four M1, four M2, eight M3, and eight tetrahedral sites in the cell. There are 32 oxygens per cell, four O1, four O2, eight O3, and sixteen O4. O1 is the non-silicate oxygen bonded to five octahedral cations, and O2 is the bridging oxygen bonded to two tetrahedral cations and one M2 cation. O3 and O4 are each bonded to three octahedral and one tetrahedral cation, as are all of the oxygen atoms in olivine and ringwoodite. O1 is underbonded in the Pauling sense and has a shallow electrostatic potential, whereas O2 is overbonded and has a deep electrostatic potential (Smyth 1987, 1994). Hydration happens by protonation of O1 charge-balanced by octahedral vacancy at M3. Neutron diffraction indicates a proton position on the O1-O4 edge of the M3 octahedron (Sano-Furukawa et al., 2011), consistent with polarized FTIR spectra (Deon et al, 2010). Smyth et al. (1997) report a monoclinic modification of the structure to space group *I*2/*m*, with a β-angle of up to 90.4º in samples with more than one weight percent H_2O.

Thus, whereas olivine and ringwoodite appear to be somewhat limited in their ability to incorporate trivalent cations (O'Neill et al., 1996; Deon et al., 2011), spinelloid III has been reported with compositions up to 30 percent of total iron as ferric (Hazen et al 2000a; Frost and McCammon, 2009; Deon et al 2011, Bolfan-Casanova et al, 2012). Richmond and Brodholt (2000) calculated that ferric iron substitution into the tetrahedral site in wadsleyite is energetically more favorable than in forsterite. This is in contrast to ferrous iron, which would not be stable in tetrahedral sites because it is too large. Compositionally, silicate wadsleyite extends from pure Mg_2SiO_4 (Fo_{100}) to about $Fo_{60}Fa_{40}$.

Additionally, a spinelloid III phase is known from experiments in Fe-rich compositions at pressures of 5 to 7 GPa and is intermediate in composition between fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) with significant (>50%) tetrahedral ferric iron content (Woodland and Angel, 1998, Hazen et al 2000b; Koch et al, 2002; Woodland et al 2012). This phase was synthesized in Mg-free compositions at pressures below 6 GPa, and it is not known if there is a continuous compositional range between Mg silicate wadsleyite and this iron-rich spinelloid III. Woodland et al (2012) report two separate stability fields for spinelloid III in the Mg_2SiO_4 –Fe_2SiO_4 – Fe_3O_4 ternary. They report crystal structure refinements for spinelloid III samples that have ~ 50% Fe^{3+} in the tetrahedral sites from the Fe-rich stability field, but do not identify Fe in the tetrahedral sites of the Mg-rich samples. Their Mg-rich samples were synthesized under low oxygen fugacity and anhydrous conditions, and in their structure refinements, they assume full occupancy of all octahedral and tetrahedral sites. So the possible effects of hydration on ferric iron substitution in spinelloid III are unknown.

In order to document the mechanisms and structural interactions of hydration and trivalent iron incorporation in wadsleyite, we have investigated ferrous and ferric iron-bearing hydrous wadsleyites that were synthesized in co-existence with pyroxene and refined the atom positions and occupancies of the crystals by single-crystal X-ray diffraction. Determinations of bulk compositions by electron probe micro-analysis (EPMA), H contents by secondary ion mass spectroscopy (SIMS) and ferric iron contents by

XANES and micro Mössbauer spectroscopy are presented in a previous study (see Bolfan-Casanova et al., 2012).

EXPERIMENTAL METHODS

Synthesis.

The samples were synthesized in the multi-anvil press under oxidizing and hydrous conditions (Re-ReO_2 buffer, between Ni-NiO and hematite-magnetite, Pownceby and O'Neill, 1994) at pressures of 12 to 13.5 GPa, and temperatures of 1400°C for at least 5 hours. The composition of the samples was analyzed using electron probe microanalysis (**Table 1**). Ferric iron contents were determined by XANES spectroscopy as well as by Mössbauer spectroscopy (see Bolfan-Casanova et al. 2012, for synthesis and analytical details).

Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Bruker Vertex70 FTIR spectrometer coupled to a Hyperion microscope equipped with a 15x objective and condenser. Beam size was varied from 30 to 100 µm. Samples were prepared as doubly polished thin sections of 50 to 100 µm thickness, because the absorption of wadsleyite is too high at greater thicknesses. No epoxy was used in order to avoid contamination of the samples for IR measurements. Unfortunately we could not orient the grains in order to perform polarized measurements along principal directions. We still performed polarized measurements on two samples 1039A and 1039B, which were relatively iron-poor and thus transparent to visible light, so that the extinction under crossed polars could be observed. Unpolarized spectra were also measured over several grains, and averaged in order to obtain a good sampling of the absolute intensity. Here, we only use the infrared information on the relative intensities of the bands and not for water quantification purposes. The aim is to assess the change in proportion of each different type of hydrogen defect.

X-ray diffraction

Crystals were selected from thin sections and mounted on glass fibers. Diffraction unit cell and intensity data were collected on a Bruker APEX II detector on a Bruker kappa diffractometer using $Mo_{k\alpha}$ radiation at the Department of Chemistry, Université Blaise Pascal, Clermont-Ferrand, France. Data were corrected for absorption and Lorenz and polarization effects. Atom position and occupancy refinements were carried out using the program Shelxl97 (Sheldrick, 1997) in the X-ray program package WINGX (Farrugia, 1999). Unit cell parameters were refined during the intensity data collections from positions of all diffraction data. Unit cell parameters and atomic position parameters are given in **Tables 2** and **3** along with intensity data measurement parameters and final R factors for the structure refinements. The β angles were refined without constraint and found to be within 2σ of 90 degrees and thereafter constrained to be 90 degrees (**Table 2**). This is consistent with H_2O contents below 1.0 wt% (10,000 ppm wt)

In the structure parameter refinements, oxygen was modeled using the scattering parameters of O^{2-} (Tokonami , 1965) as this has been found to give reliable cation occupancy refinements in anhydrous pure Mg phases (Smyth et al., 2004; Ye et al., 2009). For cations, scattering factors from Cromer and Mann (1968) were used for ionized cations (Mg^{2+}, Si^{4+} and Fe^{2+}). Both ferric iron and hydrogen inclusion in the structure may result in high vacancy concentration on the octahedral sites (Ye et al., 2009; Bolfan-Casanova et al., 2012). Based on previous studies of iron-free wadsleyite, cation vacancy was assumed to be in M3 only. Vacancy concentration was determined from the *b/a* unit cell parameter ratio (Jacobsen et al., 2005). Assigning all vacancies to M3, the Fe-Mg occupancies were refined for all octahedra, and Fe, presumable ferric, was allowed in the tetrahedral site. Final position parameters are given in **Table 3**. Occupancies according to this model are reported in **Tables 4 and 5**. The sum of Fe contents of M1, M2, M3 and T sites are reported in **Table 4 and 5**.

RESULTS

Determination of the vacancy concentration by *b/a*.

The incorporation of Fe^{3+} and H^+ in wadsleyite leads to formation of octahedral vacancies as well as occupation of the tetrahedral site by Fe^{3+} and H^+ (see Bolfan-Casanova et al., 2012). Since iron orders strongly among octahedral sites in wadsleyite (Finger et al., 1993), site occupancy refinements require constraints on the amount and nature of vacant sites. The unit cell of wadsleyite has dimensions of about 5.7 x 11.4 x 8.3 Å. Jacobsen et al (2005) pointed out that with hydration, *b* expands whereas *a* contracts. This led them to propose that the *b/a* axis length ratio can be used to indicate water content and thus M3 vacancy content if H is charge balanced by M3 vacancy only. Consistent with this hypothesis Ye et al (2009) report more than 20% vacancy at M3 in a pure Mg wadsleyite with 2.8% H_2O. Following Jacobsen et al. (2005) who have empirically derived the following relationship between vacancy concentration (mainly at M3) and H content:

$$b/a = 2.008 + 1.25 \times 10^{-6} \cdot C_{H2O} \qquad (1)$$

where C_{H2O} is in ppm wt H_2O by weight, we have used the *b/a* cell parameter ratio to estimate the total vacancy content in our samples (**Table 1**). We assumed that the number of M3 vacancies per formula unit is equivalent to one half the number of H atoms per formula unit derived from the above equation.

Thus, we have assumed here that (1) all vacancies are on M3 as is the case in previously studied hydrous samples (Ye et al, 2010, Holl et al, 2008) and that (2) the M3 vacancy is the primary cause of the expansion of *b* and contraction of *a* as in hydrous samples (Jacobsen et al., 2005), whether as a result of hydration or excess of trivalent octahedral over tetrahedral cations. A limitation could be that even if Jacobsen et al. (2005), and also this study, observe that the *b/a* ratio is relatively independent of

Fe/(Fe+Mg), this may not be strictly valid as there are no studies of ferric iron incorporation into anhydrous wadsleyite other than those of extremely Fe-rich spinelloid III (Woodland et al, 2012). Also the latter study does not report H contents or explicitly measured ferrous/ferric ratios. However, using the above assumption yields total Fe contents as refined from X-ray data that are in very good agreement with electron microprobe (see **Figure 1 and Table 4**). Further, some previous studies (Holl et al., 2008, Ye et al., 2010) report small fractional occupancy in a tetrahedral void in the structure near the vacant M3 positions at approximate coordinates (0, 0.375, 0.375). We placed a Si atom at this position but in all cases refined occupancies were less than 0.5%.

H speciation

Figure 2 shows polarized and unpolarized infrared measurements performed on sample 1039A. This figure shows the extent of anisotropy as measured using both polarized and unpolarized radiation and shows that it is similar in both cases when enough grains (i.e. enough different orientations) are measured. **Figure 3** shows the comparison between averaged polarized and unpolarized spectra for the two samples 1039A and 1039B. This figure shows again how similar both types of spectra are when enough grains are measured (here around nine). This good agreement suggests that the use of unpolarized radiation to sample correctly the absolute absorbance is valid. This test is important because only sample 1039 was transparent enough to allow the observation with polarized IR. All other samples were analyzed by unpolarized radiation.

Figure 4 shows the averaged unpolarized measurements of all samples. It displays the effect of changing the composition of wadsleyite on its IR absorption spectrum. In Fe-free wadsleyite (not shown in Fig. 4), the bands are located at 3613 and 3581 cm^{-1}, with the main intensity band being composed of at least three peaks at 3351, 3326, and 3260 cm^{-1} (see Bolfan-Casanova et al., 2000; Jacobsen et al., 2005). In ferrous wadsleyite, represented by 1039B (Fe# 9, Fe^{3+}/Fe_{total} of 15% and 0.7 wt% H_2O), the band at low frequency is the most intense, like in the magnesian end-member, but shifted slightly to higher frequency. The difference lies in the fact that the band at 3613 cm^{-1} is more intense than the one at 3581 cm^{-1} compared to the spectrum of Mg_2SiO_4 wadsleyite. Ferroan wadsleyite, represented here by the sample 961A (Fe# 41, Fe^{3+}/Fe_{total} of 30% and 0.5 wt% H_2O), is characterized by two new features: (1) the most intense band is now the band at high frequency, i.e. the one at 3611 cm^{-1}, the band at 3364 cm^{-1} now being weak; (2) a new band, located at 3498 cm^{-1}, has appeared. Thus in Fe^{3+}-rich wadsleyite, a new population of hydrous point defects is observed.

By fitting each spectra with the PeakFit package (Jandel Scientific, see **Figure 5**), the integrated absorbances of each band could be measured and are shown on **Figure 6** as a function of water content (a) or Fe^{3+} per four oxygens (b). **Figure 6a** shows how the integrated intensity of the low-frequency band, i.e. at 3354 cm^{-1}, increases with increasing water content, whereas that of the new band at 3495 cm^{-1} decreases with increasing water content. The sum of the integrated intensity of the high-frequency bands, at 3613 and 3593 cm^{-1}, is constant as a function of water content. On the contrary, in **Figure 6b** the area of the 3354 cm^{-1} band decreases with increasing Fe^{3+} content, while that of the 3495 cm^{-1} band increases and that of the 3613+3593 cm^{-1} band remains constant. These two opposed behaviors are in agreement with the fact that the water and the ferric iron contents are anti-correlated in these samples (see Figure 11 in Bolfan-Casanova et al., 2012).

The infrared spectrum of iron-free wadsleyite has been interpreted as protonation of edges of vacant octahedral sites, that is, H substituting for Mg^{2+} (Jacobsen et al., 2005; Deon et al., 2010). This agrees well with the fact that most vacancies are located on octahedral sites (Ye et al 2010; Kudoh, 2001), as well as the Mg/Si ratio that decreases substantially with increasing water content (Inoue et al, 1995). The proton positions were reported by Sano-Furukawa et al (2011) from neutron powder diffraction as being primarily on the O1-O4 edge of the partially vacant M3 octahedron. O1 is the non-silicate oxygen which is bonded to five octahedral cations only, whereas O4 is bonded to one tetrahedral cation and three octahedral cations. In Mg_2SiO_4 wadsleyite, most of the integrated intensity is associated with the band centered at 3326 cm^{-1} (Jacobsen et al., 2005), and thus this band is most likely related to H substituting for Mg^{2+} i.e. $(2H_{Me})^X$. This probably holds in oxidized wadsleyite and the band at 3354 cm^{-1} is related to $(2H_{Me})^X$. The correlation between the integrated intensity of the 3495 cm^{-1} band and ferric iron content points to an H defect that is associated with ferric iron. Thus, we link the band at 3495 cm^{-1} to coupling of Fe^{3+} and H^+ substituting for Si^{4+}. The proton is unlikely to be on the tetrahedral edge due to electrostatic repulsion if the tetrahedron is occupied by ferric iron. It is most likely that the proton remains on the O1-O4 edge reported by Sano-Furukawa et al. (2011), but simply moves closer to the O4 oxygen. This would give rise to a new displaced peak at 3496 cm^{-1} in the IR spectrum, but the proton would not be on the tetrahedral edge.

DISCUSSION

We compare the present oxidized and hydrous wadsleyites to those of Finger et al (1993) who reported the crystal structures of a range of Fe-bearing wadsleyites from pure Fo_{100} to $Fo_{60}Fa_{40}$. Their Fe-bearing samples were synthesized in Re capsules at temperatures of 1800°C. They did not measure H contents of their samples and assumed them to be anhydrous. They also assumed all Fe to be ferrous. They did not report evidence of Fe in the tetrahedral site nor did they report significant expansion of the tetrahedron with increasing sample Fe content. Computing *b/a* ratios for their samples we observe that they may have had a minor amount of vacancy or hydration in their samples with Fo_{100} and $Fo_{75}Fa_{25}$ composition because the *b/a* ratio of these samples is higher (2.013 instead of 2.008 for the dry Mg_2SiO_4 wadsleyite, see equation 1). Still, their assumed compositions are likely valid and their study provides a very useful data set representing dry and ferrous wadsleyite for comparison with the current samples that have both significant hydration and ferric iron contents.

Figure 7 shows the change in *b/a* ratio with total iron content in the present wadsleyites compared to those of Finger et al. (1993). One can see that the wadsleyites from this study have higher *b/a* ratios varying from 2.014 to 2.024, indicating a high concentration of vacancies, which can be either due to charge compensation for substitution of Fe^{3+} or H^+ for Mg^{2+}. In this study we report for the first time the occurrence of tetrahedral iron in wadsleyite based on X-ray diffraction. Here, we observe up to 11% of the tetrahedral site occupied by iron based on X-ray scattering. This observation is statistically robust (20σ) and consistent with the large size of the tetrahedron (**Table 5).** In **Figure 8a**, which displays tetrahedral volume as a function of iron content, one can observe that in our oxidized and hydrous samples the tetrahedron is up to 2% larger than in the reference wadsleyites of Finger et al. (1993). **Figure 8b** shows how the volume of the tetrahedron is positively correlated with the amount of iron in the tetrahedron as retrieved from the X-ray data, consistent with Fe^{3+} being larger than Si^{4+}. Also, the incorporation of Fe^{3+} in the tetrahedral site is demonstrated by the low silica content in the chemical analyses (below 1 Si per 4 oxygens, see **Table 1** and **Figure 9**). This is in spite of the high silica activity of the samples that were in co-existence with pyroxene. Indeed, **Figure 9a** shows the decrease in silicon content of the present wadsleyites with increasing total iron content, which is due to the fact that ferric iron content and hence the amount of ferric iron entering the tetrahedron, increases with increasing bulk iron content in agreement with previous results in the reduced system (Frost and McCammon, 2009) (see **Figure 9b**).

In a companion paper Bolfan-Casanova et al. (2012) inferred the occurrence of tetrahedral Fe^{3+} based on composition. They observed that the divalent cation concentrations (i.e., $Mg^{2+} + Fe^{2+}$), the Si as well as the H content in wadsleyite decrease with increasing Fe^{3+} content, indicating an incorporation mechanism via substitution into the metal (Me=Mg^{2+} and Fe^{2+}) and Si sites with a ratio of 5/3 for (Fe^{3+}+H^+):Me and of 5/1 for (Fe^{3+}+H^+):Si, similarly as in the dry system (Frost and McCammon, 2009), see equation 2 below:

$$6(OH)_o^{\bullet}+3V_{Me}^{''}+4Fe_2O_3+6Me_{Me}^{X}+2Si_{Si}^{X} = 6Fe_{Me}^{\bullet}+3V_{Me}^{''}+2Fe_{Si}'+2(OH)_o^{\bullet}+6MeO+2SiO_2+2H_2O+2O_O^{X}+O_2 \qquad (2)$$

where in Kröger-Vink (1956) notation the subscripts refer to the site and the superscripts to the charge, $(^{\bullet})$ for an excess positive charge and $(^{\prime})$ for an excess negative charge. In this model 25% of the ferric iron occupies the tetrahedral sites. This is in near agreement with the current results.

Finger et al (1993) report strong ordering of Fe among the three octahedral sites, M1, M2, and M3, even though their samples were quenched from relatively high temperatures of 1800°C and the octahedra differ little in size, distortion or electrostatic potential (Smyth and Bish, 1988). Also the anisotropic displacement parameters for the octahedral site show no anomalies such as split sites or indication of positional disorder. Finger et al (1993) report that iron avoids M2 and is enriched in both M1 and M3. We observe the same phenomena except in one sample, (1039B) which is about Fo_{90} in composition. All the others show this trend as do most previously reported structure refinements of Fe-bearing wadsleyites.

The observation of significant tetrahedral Fe in wadsleyite in the current study raises the possibility that there is a continuous compositional field between the current samples and the fayalite-magnetite samples described by Woodland and Angel (1998, 2000) and Koch et al. (2004). Woodland et al (2012) show separate compositional fields for the magnesium silicate and the high-Fe spinelloid III, but do not discuss the potential effects of hydration. The presence of trivalent Fe in both the tetrahedral and octahedral sites seems to be restricted to the wadsleyite polymorph since olivine does not seem to incorporate any ferric iron at all. Ringwoodite, on the other hand, easily incorporates ferric iron (McCammon et al., 2004). A recent report by Mrosko et al. (2013) indicates the presence of tetrahedral ferric iron in ringwoodite after oxidation at 500°C at atmospheric pressure. Still, Deon et al. (2011) have reported that ferric iron partitions three times more in wadsleyite than in ringwoodite. Thus, it is likely that the wadsleyite stability field may be increased relative to olivine or ringwoodite in the presence of significant trivalent cations, principally Fe^{3+}, Al, or Cr^{3+}. Gudfinsson and Wood (1998) report a maximum solubility of 0.35-0.45 wt% Al_2O_3 in wadsleyite synthesized at 1400-1600°C and close to 14 GPa, under probably reducing conditions. Under hydrous and oxidizing conditions the solubility of Al_2O_3 in wadsleyite is increased a little up to 0.51 wt% Al_2O_3, i.e. 0.016 Al per formula unit, (Bolfan-Casanova, unpubl.) at 14 GPa and 1400°C, but is still much less than the solubility of ferric iron in hydrous wadsleyite (see **Table 1**).

Magnesium silicate wadsleyite is limited in its iron content and extends only from Fo_{100} to $Fo_{60}Fa_{40}$ compositions. The reason for this may be the distortion of the silicate tetrahedron. Wadsleyite already has the longest Si-O distance of any silicate tetrahedron in common silicate minerals (Smyth, 1987). Even though Finger et al (1993) did not mention this, this distance increases with octahedral ferrous iron content and so may limit the total Fe content of the pure silicate structure. Substitution of trivalent cations (Fe^{3+}, Al, Cr^{3+}) in the tetrahedral site will increase the overall size of the site, especially the distances to the non-bridging oxygens, and thus decrease the distortion of the site. Trivalent cations in the tetrahedron are also expected to relieve the overbonding of the bridging oxygen and should thus stabilize iron in the structure. Indeed, Bolfan-Casanova et al. (2012) observe that hydrous and oxidized wadsleyite can contain more iron, up to an Fe# of 41 (with Fe#=Fe/(Fe+Mg)x100, with all iron considered as ferrous), compared to an Fe# of 32 in the oxidized but dry system (Frost and McCammon, 2009) or 27 in the hydrous but reduced system (Deon et al., 2010). This means that iron is stabilized in wadsleyite under oxidizing and hydrous conditions, and that the stability field of wadsleyite is expanded at the expense of those of olivine and ringwoodite.

In summary, we have refined the crystal structures of seven samples of hydrous Fe-bearing wadsleyite using single crystal X-ray diffraction. Compositions range from about $Fo_{89}Fa_8Mt_3$ to about $Fo_{58}Fa_{30}Mt_{12}$. H contents as ppm wt H_2O range from about 3000 to about 9400. We have refined the unit cell parameters and atom positions and occupancies from X-ray single-crystal diffraction data and observe unambiguous evidence of up to 11% ferric iron in the tetrahedral sites. Site occupancies of Fe, Mg and Si determined from X-ray scattering are consistent with chemical analysis assuming cation vacancy is restricted to M3. We also observe a positive correlation between the intensity of a new band at 3495 cm^{-1} observed only in oxidized wadsleyite and the content of tetrahedral iron. This is consistent with a coupled substitution of Fe^{3+} and H^{+} for Si^{4+}.

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Table 1. Chemical composition data for seven wadsleyites (in parentheses are errors in last decimal places quoted).

	961A	**961B**	**963B**	**966A**	**966B**	**1039A**	**1039B**
SiO_2	34.59(41)	36.52(36)	34.37(31)	34.81(18)	37.68(38)	40.13(36)	41.85(22)
Fe_2O_3 [$]	11.99(2)	8.88(11)	11.56(2)	11.17(6)	6.92(3)	2.64(1)	1.37(1)
FeO	25.17(26)	21.05(40)	23.15(28)	23.11(22)	18.97(11)	13.45(15)	6.97(10)
MgO	29.09(42)	33.31(51)	30.18(40)	30.26(19)	36.53(45)	42.65(43)	48.76(29)
H_2O (SIMS)	0.45(1)	0.55(3)	0.31(6)[£]	0.73(4)	0.70(3)	0.94(4)	0.76(9)
Total	101(1)	100(1)	99(1)	100.1(7)	101(1)	100(1)	99.7(7)
Cations per 4 oxygens							
Si	0.931(7)	0.960(6)	0.935(5)	0.934(3)	0.967(6)	0.996(6)	1.007(4)
Fe^{3+}	0.242(15)	0.176(36)	0.236(14)	0.226(45)	0.134(27)	0.049(2)	0.025(2)
Fe^{2+}	0.567(34)	0.463(92)	0.526(32)	0.519(104)	0.407(81)	0.279(14)	0.140(13)
Mg	1.168(10)	1.305(13)	1.223(10)	1.210(5)	1.398(11)	1.578(11)	1.748(7)
H (SIMS)	0.080(1)	0.097(3)	0.056(7)	0.130(5)	0.120(3)	0.155(5)	0.122(10)
Total	2.99(07)	3.00(15)	2.98(07)	3.02(16)	3.02(13)	3.06(04)	3.04(04)
Vacancy (*b/a*)*	0.082	0.040	0.115	0.108	0.070	0.081	0.057

** calculated using equation: [vacancy]= ½ (b/a- 2.008) x Si x M/11.25, M being the molar mass of the wadsleyite*

[$] ***Ferric iron contents determined by XANES and Mössbauer by Bolfan-Casanova et al. (2012).***

[£] *all water contents measured by SIMS except 963B, see Bolfan-Casanova et al. (2012).*

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Table 2. Unit cell and X-ray data collection parameters for seven wadsleyites.

Parameter	**961A**	**961B**	**963B**	**966A**	**966B**	**1039A**	**1039B**
a	5.7276(2)	5.7237(1)	5.7238(3)	5.7243(2)	5.7194(3)	5.7059(3)	5.6972(2)
b	11.5680(5)	11.5302(4)	11.5844(7)	11.5804(4)	11.5434(6)	11.5315(6)	11.4903(3)
c	8.3072(3)	8.3034(2)	8.3124(5)	8.3108(3)	8.3030(5)	8.2901(5)	8.2655(2)
β	90.00	90.00	90.00	90.00	90.00	90.00	90.00
V	550.41(4)	547.99(3)	551.17(6)	550.92(3)	548.18(5)	545.47(5)	541.1(3)
b/a	**2.0197(2)**	**2.0145(2)**	**2.0239(3)**	**2.0230(2)**	**2.0183(3)**	**2.0298(3)**	**2.0168(2)**
2θmax	70	75	60	125	65	60	85
#Reflections	2450	3117	1675	28054	1853	1527	4114
# unique	676	824	447	2577	558	422	1071
R merge	0.027	0.021	0.024	0.103	0.019	0.018	0.034
R obs	0.029	0.027	0.025	0.045	0.032	0.029	0.036

Table 3. Atom position parameters for seven wadsleyites

Parameter	**961A**	**961B**	**963B**	**966A**	**966B**	**1039A**	**1039B**
Mg2							
z	0.97015(12)	0.97058(7)	0.97039(13)	0.97059(7)	0.97033(20)	0.97049(13)	0.97004(10)
Mg3							
y	0.12497(5)	0.12525(3)	0.12470(5)	0.12500(2)	0.12540(6)	0.12476(5)	0.12528(5)
Si							
y	0.12092(6)	0.12088(3)	0.12103(6)	0.12103(3)	0.12113(6)	0.12090(5)	0.12067(4)
z	0.61647(7)	0.61659(4)	0.61665(8)	0.61661(4)	0.61643(12)	0.61636(7)	0.61633(5)
O1							
z	0.2197(3)	0.2189(2)	0.2204(3)	0.21975(16)	0.2200(5)	0.2202(3)	0.2197(2)
O2							
z	0.7169(3)	0.7168(2)	0.7164(3)	0.71654(17)	0.7164(5)	0.7163(3)	0.7162(2)
O3							
y	0.9878(2)	0.98797(10)	0.9875(2)	0.98738(8)	0.9877(2)	0.98742(13)	0.98815(11)
z	0.2575(2)	0.25698(11)	0.2570(2)	0.25712(10)	0.2566(3)	0.25634(17)	0.25636(12)
O4							
x	0.2616(2)	0.26206(14)	0.2615(2)	0.26140(12)	0.2626(3)	0.26174(16)	0.26160(14)
y	0.12382(10)	0.12363(5)	0.12387(11)	0.12385(4)	0.12407(8)	0.12347(7)	0.12363(7)
z	0.9937(2)	0.99329(9)	0.99366(16)	0.99357(8)	0.9933(3)	0.99327(13)	0.99329(10)

Table 4. Selected Octahedral interatomic distances, coordination parameters, and occupancies

Parameter	**961A**	**961B**	**963B**	**966A**	**966B**	**1039A**	**1039B**
b/a	**2.0197(2)**	**2.0145(2)**	**2.0239(3)**	**2.0230(2)**	**2.0183(3)**	**2.0298(3)**	**2.0168(2)**
Vacancy pfu	0.082	0.040	0.115	0.108	0.070	0.080	0.057
Fe/(Fe+Mg)	40.9(4)	32.9(4)	38.4(3)	38.1(3)	27.9(3)	17.2(2)	8.6(1)
Fe# (XRD)	**44.7(5)**	**34.0(5)**	**37.9(5)**	**35.3(4)**	**27.9(4)**	**16.9(4)**	**8.5(3)**
M1							
Femol%	42.2(5)	33.3(5)	39.3(5)	39.8(4)	29.7(4)	20.1(3)	7.0(3)
M1-O3(2)	2.1439(16)	2.1383(9)	2.1410(17)	2.1419(9)	2.1355(25)	2.1300(14)	2.1236(10)
M1-O4(4)	2.0733(13)	2.0700(7)	2.0740(13)	2.0734(6)	2.0718(14)	2.0641(8)	2.0597(8)
<M1-O>	2.0969	2.0928	2.0964	2.0962	2.0930	2.0861	2.0810
PolyVol	12.213	12.135	12.203	12.198	12.142	12.018	11.935
M2							
Fe%	16.3(5)	12.2(5)	16.0(3)	16.5(3)	15.6	7.6(4)	7.4(3)
M2-O1(1)	2.073(3)	2.0617(15)	2.078(3)	2.0707(14)	2.0731(39)	2.0702(24)	2.0642(20)
M2-O2(1)	2.104(3)	2.1069(15)	2.112(3)	2.1114(13)	2.1081(39)	2.1069(23)	2.0980(18)
M2-O4(4)	2.1008(13)	2.0996(7)	2.1005(13)	2.0999(6)	2.0946(15)	2.0964(9)	2.0896(8)
<M-O>	2.0966	2.0945	2.0975	2.0970	2.0947	2.0938	2.0868
PolyVol	12.178	12.148	12.197	12.189	12.151	12.136	12.010
M3							
Fe%	52.0(4)	38.2(4)	48.1(4)	45.9(3)	34.0(4)	19.9(3)	9.1(3)
Vac (*b/a*)	8.2	4.0	11.5	10.8	7.0	8.0	5.7
M3-O1(2)	2.0508(5)	2.0453(3)	2.0531(6)	2.0510(3)	2.0433(6)	2.0449(5)	2.0359(5)
M3-O3(2)	2.1380(16)	2.1346(9)	2.1394(16)	2.1427(7)	2.1386(20)	2.1321(12)	2.1232(8)
M3-O4(2)	2.1301(13)	2.1328(8)	2.1319(14)	2.1321(7)	2.1328(21)	2.1294(11)	2.1247(10)
<M-O>	2.1063	2.1042	2.1069	2.1086	2.1035	2.1008	2.0946
PolyVol	12.353	12.315	12.370	12.392	12.3058	12.2640	12.151

Table 5. Selected Tetrahedral interatomic distances, coordination parameters, and occupancies

Parameter	**961A**	**961B**	**963B**	**966A**	**966B**	**1039A**	**1039B**
Si							
Fe%	10.8(5)	7.1(5)	10.0(5)	8.2(3)	6.0(6)	4.8(4)	3.8(3)
Si%	89.2(5)	92.9(5)	90.0(5)	91.8(3)	94.0(6)	95.2(4)	96.2(3)
Si-O2(1)	1.7105(13)	1.7056(8)	1.7085(15)	1.7089(7)	1.704(2)	1.7039(12)	1.7001(9)
Si-O3(1)	1.6366(20)	1.6363(11)	1.6384(21)	1.6362(10)	1.640(3)	1.6353(16)	1.6343(8)
Si-O4(2)	1.6444(14)	1.6396(8)	1.6450(14)	1.6447(7)	1.640(2)	1.6356(10)	1.6332(8)
<T-O>	1.6589	1.6553	1.6619	1.6586	1.6581	1.6526	1.6502
PolyVol	2.332(2)	2.317(1)	2.345(2)	2.331(1)	2.329(4)	2.306(2)	2.295(1)

Figure 1. Fe contents expressed as ($X_{Fe}/(X_{Fe}+X_{Mg})$x100) in the wadsleyite, measured with electron microprobe and compared to the Fe content measured from the single crystal X-ray refinement.

Figure 2. FTIR spectra of sample 1039A measured using polarized radiation (a) and unpolarized radiation (b) on several grains randomly oriented. The average of polarized and unpolarized spectra are shown as thick black curves and are very similar when enough grains are measured, see figure 3.

Figure 3. Average of polarized and unpolarized spectra of sample 1039A and 1039B showing the similarity of both types of measurements when enough grains are measured (here around nine).

Figure 4. Averaged unpolarized FTIR spectra of all the wadsleyites investigated in this study (the dotted curve represents the A labelled sample and the plain curve the B labelled sample).

Figure 5. Deconvolution of the average spectrum of sample 1039A using the software Peak_Fit (Jandel scientific) into 4 components.

Figure 6. Change in integrated infrared absorption as measured for each band as a function of (a) water content and (b) ferric iron content.

Figure 7. Effect of the iron content of wadsleyite on the cell parameter *b/a* ratio, and comparison with the data from Finger et al. (1993). The error bars from this study have the same size as the symbols.

Figure 8. Effect of composition on the volume of the tetrahedron in wadsleyites of this study (a) as a function of iron content, and (b) as a function of tetrahedral iron content as retrieved form the X-ray single crystal refinement. The data from Finger et al. (1993) are shown in (a) and represent dry and reduced wadsleyite.

Figure 9. Effect of iron content on (a) Si content and (b) tetrahedral ferric iron content as retrieved from single crystal X-ray refinement.