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ORIGINAL PAPER

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High-pressure Raman spectroscopic study of Fo_{90} hydrous wadsleyite

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Abstract Raman spectra of monoclinic Fo_{90} hydrous wadsleyite with 2.4 wt% H_2O have been measured in a diamond-anvil cell with helium as a pressure-transmitting medium to 58.4 GPa at room temperature. The most intense, characteristic wadsleyite modes, the Si–O–Si symmetric stretch at 721 cm^{-1} and the symmetric stretch of the SiO_3 unit at 918 cm^{-1}, shift continuously to 58.4 GPa showing no evidence of a first order change in the crystal structure despite compression well beyond the stability field of wadsleyite in terms of pressure. The pressure dependence of these two modes is nearly identical for Fo_{90} hydrous and Fo_{100} anhydrous wadsleyite. A striking feature in the high-pressure Raman spectra of Fo_{90} hydrous wadsleyite is the appearance of new Raman modes above 9 GPa in the mid-frequency range (300–650 cm^{-1} at 1-bar and shifted to 500–850 cm^{-1} at 58.4 GPa) accompanied by a significant growth in their intensities under further compression. In the OH stretching frequency range Fo_{90} hydrous wadsleyite exhibits a larger number of modes than the Mg end-member phase. The higher number of modes may be due to either additional protonation sites or simply that we observe a different subset of all possible OH modes for each sample. The high-pressure behaviour of the OH stretching modes of Fo_{90} and Fo_{100} hydrous wadsleyite is consistent: OH stretching modes with frequencies $< 3{,}530$ cm^{-1} decrease with increasing pressure whereas the higher-frequency OH modes show a close to constant pressure dependence to at least 13.2 GPa. The approximately constant pressure dependence of the OH modes above 3,530 cm^{-1} is consistent with protons being located at the O1···O edges around M3.

Keywords Hydrous wadsleyite · Diamond-anvil cell · High-pressure · Raman spectroscopy · Transition zone

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Introduction

Wadsleyite, β-$(Mg,Fe)_2SiO_4$, the first high-pressure polymorph of olivine, is considered to be the most abundant mineral in the mantle transition zone between 410 and 525 km depth (13–18 GPa). Though nominally anhydrous, it can incorporate up to 3.3 wt% H_2O in the form of hydroxyls in its crystal structure (e.g. Smyth 1987, 1994; Inoue et al. 1995; Kudoh et al. 1996). The hydrogen as well as the iron content of wadsleyite influence its physical and chemical properties and hence, are likely to control the properties of the transition zone globally. The H and Fe^{3+} content (e.g. McCammon et al. 2004) may be particularly important in cooler subduction zone regions.

The crystal structure of Mg end-member wadsleyite belongs to the orthorhombic crystal system space group *Imma* (Horiuchi and Sawamoto 1981). Partial substitution of Fe^{2+} for Mg^{2+}, and Fe^{3+} for Mg^{2+} and Si^{4+} does not change the symmetry of the unit cell (Finger et al. 1993; Hazen et al. 2000b). Also the incorporation of hydrogen in Mg end-member wadsleyite can result in wadsleyite isomorphs (Kudoh et al. 1996). However, the addition of hydrogen or hydrogen with trivalent cations, has been observed to yield a series of modified structures closely related to orthorhombic wadsleyite: Smyth et al. (1997) refined hydrous $Fo_{94.6}$ wadsleyite (2.24 wt% H_2O) in space group $I2/m$ ($\beta = 90°$); Kudoh and Inoue (1999) observed Fo_{100} hydrous wadsleyite samples with small monoclinic distortions ($\beta = 90.1°$); and Jacobsen et al. (2005) found in pure Mg wadsleyite a systematic increase in β-angles with increasing water content above

0.5 wt% (up to $\beta = 90.125(3)°$ for 1 wt% H_2O). The deviation of the β-angle from 90° was suggested to result from ordering of vacancies in the M3 site (Smyth et al. 1997). Kudoh and Inoue (1999) proposed that variations in the stacking arrangement of Mg-vacant structural modules can cause a violation of orthorhombic symmetry. Wadsleyite II, a structurally closely related, hydrous, iron-bearing spinelloid, has a different unit cell (Smyth and Kawamoto 1997; Smyth et al. 2005).

Unlike olivine and ringwoodite, wadsleyite is a sorosilicate characterized by Si_2O_7 groups. O2 is the bridging oxygen of the group and is also bonded to one Mg at M2; the O1 atom is not bonded to Si, but is coordinated by five Mg atoms: four Mg atoms at M3 sites and one Mg atom at an M2 site (e.g. Horiuchi and Sawamoto 1981). O3 and O4 are each bonded to three Mg and one Si and are similar to the oxygen sites in olivine and ringwoodite. Experimental and theoretical studies have shown that the underbonded, non-silicate oxygen atom O1 is the most important protonation site of wadsleyite (e.g. Smyth 1987, 1994; Jacobsen et al. 2005). However, protonation of O2 has also been suggested (Downs 1989; Cynn and Hofmeister 1994; Kohn et al. 2002). The incorporation of H in wadsleyite is compensated principally by octahedral site vacancies. In the Mg end-member phase, the vacancies are strongly concentrated on the M3 site, which is consistent with protonation of O1 (Kudoh et al. 1996; Smyth et al. 1997; Jacobsen et al. 2005). An additional protonation mechanism in Fe-bearing wadsleyite is the reduction of Fe^{3+} to Fe^{2+} that could make possible protonation not only of O1 but also of other O sites (Wright and Catlow 1996).

There have been several ambient IR and Raman spectroscopic investigations of hydrous wadsleyite (e.g. McMillan et al. 1991; Kohlstedt et al. 1996; Mernagh and Liu 1996; Bolfan-Casanova et al. 2000; Kohn et al. 2002; Jacobsen et al. 2005). The studies by Jacobsen et al. (2005) and Kohn et al. (2002) focused on the hydration mechanism and protonation sites including ordering of hydroxyls within the structure. Both studies reported that the protonation mechanism appears to change with increasing water concentration: using FTIR and ^{1}H MAS NMR Kohn et al. (2002) found that in wadsleyite samples with water concentrations < 0.4 wt% H_2O the hydroxyl ions are ordered over mainly four O–H···O environments, whereas in samples with higher water content (0.8–1.5 wt% H_2O), the hydroxyl ions are highly disordered occupying at least 14 of the 17 possible O–H···O environments. The IR spectra at higher water content are characterized by three main groups: a doublet at 3,614 and 3,581 cm^{-1}, an absorption triplet at 3,360, 3,326, and 3,317 cm^{-1}, and a very broad band centered around 3,000 cm^{-1} (Jacobsen et al. 2005; Kohn et al. 2002). Jacobsen et al. (2005) could explain these six main OH stretching bands by protonation of the O1 site using polarized FTIR spectroscopy and single-crystal X-ray diffraction on oriented single-crystals of Mg end-member wadsleyite with a water content of up to 1 wt%.

Only a few high-pressure Raman and IR spectroscopic studies of hydrous wadsleyite do exist: Cynn and Hofmeister (1994) reported high-pressure IR spectra of Fo_{85} hydrous wadsleyite (0.21 wt% H_2O) to 23 GPa including the pressure dependence of eight OH vibrations to 12 GPa. High-pressure Raman spectroscopic studies of hydrous Mg end-member wadsleyite were performed by Kleppe et al. (2001) and Liu et al. (1998). They established the pressure dependence of the OH stretching modes to 50 and 14 GPa, respectively. Kleppe et al. (2001) found that the incorporation of H into Mg end-member wadsleyite has only a minor effect on the framework lattice dynamics under compression. In the present study, we explore how coupled iron and proton substitution in wadsleyite can affect its vibrational behaviour at ambient conditions and at high-pressures. This is interesting from a crystal chemical point of view and also with regard to modeling the mineralogy of the mantle transition zone. We report the first high-pressure Raman spectra in the region from 80 to 4,000 cm^{-1} on high quality single-crystals of Fo_{90} hydrous wadsleyite (2.4 wt% H_2O) measured in a diamond-anvil cell with helium as a pressure-transmitting medium to pressures of 58.4 GPa. Such high-pressures are well beyond the thermodynamic stability boundary of wadsleyite in terms of pressure (58.4 GPa corresponds to a depth of about 1,400 km in the Earth) and probe its metastability limits under kinetically hindered conditions.

Experiment

Raman spectroscopic studies were performed on single-crystal fragments of two Fo_{90} hydrous wadsleyite samples at ambient conditions and at high pressures up to 58.4 GPa at 300 K. The two samples used in this study have been characterized previously by single-crystal X-ray diffraction, Fourier Transform Infra-red and Mössbauer spectroscopy (Smyth et al. 2000; McCammon et al. 2004). Details of the synthesis conditions and analysis of the samples have been reported in McCammon et al. (2004). Briefly, high quality single-crystals of Fo_{90} hydrous wadsleyite were synthesized at 18–19 GPa and 1,400°C with a heating time of 5 h in the 5,000-t press at the Bayerisches Geoinstitut, Bayreuth, Germany. Sample 1 is a monoclinic ($\beta = 90.183(7)°$) Fo_{90} hydrous wadsleyite with an H_2O content of 2.4 wt% and $Fe^{3+}/\Sigma Fe = 0.44$, and sample 2 is a monoclinic ($\beta = 90.162(7)°$) Fo_{90} hydrous wadsleyite with an H_2O content of 2.2 wt% and $Fe^{3+}/\Sigma Fe = 0.28$ (samples SZ0005 and SZ0006, respectively, in McCammon et al. 2004).

Ambient Raman spectra have been measured in the range 80–4,000 cm^{-1} from single-crystal fragments of sample 1 and 2, and also from a rough powder of sample 2. The powder was prepared by crushing a crystal fragment between two diamond-anvil tips. As the relative intensities of Raman modes do change with changing crystal laser-beam orientation, unpolarized Raman spectra were collected in various, arbitrary orientations of

the crystals relative to the incident laser beam in this study in order to observe and reveal as many of the wadsleyite Raman modes as possible. In the high-pressure micro-Raman spectroscopic experiment, a ~10 μm thick single-crystal fragment with flat surfaces of sample 1, about 25×25 μm in size, was mounted in a diamond-anvil cell (DAC) together with a < 10 μm diameter ruby sphere for pressure calibration (Mao et al. 1978). Fluid helium was loaded at 0.2 GPa (Jephcoat et al. 1987) as a pressure transmitting medium to ensure hydrostatic conditions. A 0.3 mm thick stainless steel gasket preindented to 30 μm with a 100 μm drilled hole and culets of 300 μm diameter formed the sample chamber.

The unpolarized Raman spectra were measured at 300 K in 135° scattering geometry with a SPEX Triplemate equipped with a back-illuminated liquid-N_2-cooled CCD detector. The spectra were excited by the 514.5 nm line of an argon-ion laser focused to a 5 μm spot on the sample and collected through a spatially-filtering (confocal) aperture giving high spatial resolution at the sample. The intrinsic resolution of the spectrometer is 1.5 cm^{-1} and calibrations are accurate to ±1 cm^{-1}. Low laser power was required to avoid heating of the bottle green wadsleyite crystals and only long collection times led to an acceptable signal-to-noise ratio. Raman spectra excited with 488 nm were identical in shift over the entire frequency and pressure range with those excited at 514.5 nm, and hence exclude the observation of fluorescence bands. The frequency of each Raman band was obtained by Voigtian curve fitting using a least-squares algorithm.

Results

Raman frequencies of Fo_{90} hydrous wadsleyite (sample 1 and 2) at ambient conditions

Figure 1(a) shows ambient, unpolarized Raman spectra of sample 1 and 2 of Fo_{90} hydrous wadsleyite. We resolve 18 modes between 100 and 1200 cm^{-1} (Table 1). A total of 39 Raman modes are expected from symmetry analysis for the wadsleyite structure and 36 modes have been observed at ambient conditions using a single crystal of pure Mg wadsleyite and polarized Raman spectroscopy (Chopelas 1991). Characteristic of the wadsleyite structure are the two most intense modes at 721 and 918 cm^{-1}. They correspond to the Si_2O_7 symmetric stretch (Si–O–Si of the disilicate group) and the symmetric stretch of the SiO_3 terminal unit, respectively. In the OH stretching frequency region, we resolve four bands in the spectrum of sample 1 and two bands in the much weaker spectrum of sample 2. The doublet at 3,588 and 3,563 cm^{-1} of sample 1 corresponds to a single band at 3,575 cm^{-1} in sample 2. 3,575 cm^{-1} is about the average frequency of the doublet suggesting that the doublet components are of approximately equal intensity in the spectrum of sample 2. At lower frequencies, sample 1 exhibits a band at 3,379 cm^{-1}, a peak

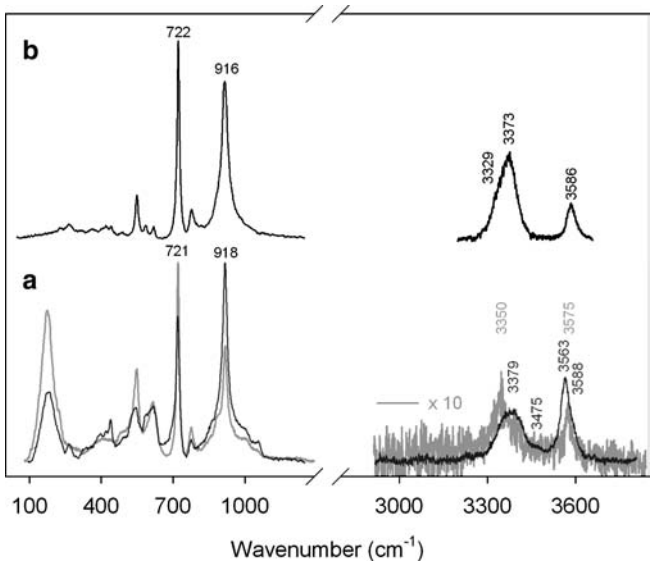

Fig. 1 Ambient Raman spectra of **a** Fo_{90} hydrous wadsleyite (*black*: sample 1, *grey*: sample 2) and **b** Fo_{100} hydrous wadsleyite (Kleppe et al. 2001) for comparison. The relative mode intensities depend on the orientation of the crystal relative to the incident laser beam

position that is significantly different from the band at 3,350 cm^{-1} of sample 2. This frequency difference indicates that the broad 3,379 cm^{-1} band (full width at half maximum is 96 cm^{-1}) might in fact, consist of at least two components: one at 3,399 and one at 3,354 cm^{-1} (Table 1).

A comparison of the Raman spectrum of Fo_{90} and Fo_{100} hydrous wadsleyite measured previously (Fig. 1; Table 1) shows that the Raman mode frequencies are essentially the same in the range 200–1,200 cm^{-1}. Mode shifts due to the incorporation of 10% Fe in wadsleyite are negligible. However, in the Fe-bearing phase, the shoulders of the 918 cm^{-1} mode are expressed more strongly, and modes in the range 200–500 cm^{-1} are less well resolved being slightly broader. The OH stretching bands of Fo_{90} and Fo_{100} samples do not correlate uniformly well: two groups of bands are present in the spectrum of each sample, one around 3,500–3,600 and the other at 3,000–3,400 cm^{-1}, but the resolved peak positions and number of bands differ. This might be connected to compositional differences in iron (Fe^{2+}, Fe^{3+}) and water content of the two samples (2.4 wt% and 1.65 wt% H_2O for Fo_{90} and Fo_{100}, respectively) or it might simply be that we observe a different subset of all possible Raman modes in each spectrum using a single-crystal fragment and unpolarized Raman spectroscopy.

Raman frequencies of Fo_{90} hydrous wadsleyite |(sample 1) at pressures to 58.4 GPa

Representative Raman spectra in the region 80–1,300 cm^{-1} of Fo_{90} hydrous wadsleyite as a function of pressure are shown in Fig. 2. The characteristic wads-

Table 1 Comparison of the mode frequencies of Fo_{90} hydrous wadsleyite and Fo_{100} hydrous wadsleyite

Fo_{90} hydrous wadsleyite (sample 1) to 58.4 GPa, present study			Fo_{90} hydrous wadsleyite (sample 2), present study	Fo_{100} hydrous wadsleyite (Kleppe et al. 2001)	Mode assignment e.g., Mernagh and Liu (1996)
2.4 wt% H_2O monoclinic ($\beta = 90.18°$)			2.2 wt% H_2O monoclinic ($\beta = 90.16°$)	1.65 wt% H_2O orthorhombic ($\beta = 90°$)	
ν (cm^{-1})	$\partial\nu_i/\partial P$ (cm^{-1}/GPa)	γ_{iT}	ν (cm^{-1})	ν (cm^{-1})	
179			176		
			229	229	Lattice vibration
267			[a]	266	Lattice vibration
[a]			[a]	313	
[a]			[a]	363	
398			[a]		Lattice vibration
			[a]	406	
420			[a]	422	
440			[a]	441	Lattice vibration
			488	487	Translational OH vibration(?)
492					
523			522		
543			548	549	Complex SiO_3 and MgO_6 vib
588			588	586	SiO_3 bending mode
619			619	618	SiO_3 bending mode
702					
721	$3.263x - 0.0051x^2$	0.957 (0.804)[b]	722	722	Si_2O_7 symmetric stretch
777	$4.870x - 0.0163x^2$	1.14 (1.07)[b]	777	779	
840			847		
882			889	885	
918	$4.307x - 0.0176x^2$	0.839 (0.833)[b]	919	916	SiO_3 symmetric stretch
955			944		
993			992	978	
				1,028	
1,045			1,054		
ν (cm^{-1})					
				3,280[c]	
				3,329	H-bonded OH stretch
	3,354[d]		3,350		
3,379	3,399[d]			3,373	H-bonded OH stretch
3,475	3,469				
3,563			3,575		
3,588				3,586	H-bonded OH stretch

The modes observed at 398, 492, and 955 (944) cm^{-1} of Fo_{90} hydrous wadsleyite are not additional modes; modes at these frequencies have already been observed for Mg end-member wadsleyite (Chopelas 1991). The shoulders at 702 and 1,045 (1,054) cm^{-1} occur in a frequency range typical of vibrations connected to the Si_2O_7 unit and could be Raman modes of the wadsleyite structure that have not been observed up to now. Grüneisen parameters for the most intense modes of Fo_{90} hydrous wadsleyite are given

[a] Intensity is observed, but modes are not resolved

[b] Value for Fo_{100} anhydrous wadsleyite (Chopelas 1991)

[c] Observed in some of the ambient spectra

[d] Taking the position of the OH mode at 3,350 cm^{-1} of sample 2 into account fitting, a doublet instead of a single mode at 3,379 cm^{-1} is warranted (see Results section). The doublet improves the fit of the spectrum slightly but not significantly

leyite modes at 721 and 918 cm^{-1} (Si_2O_7 and SiO_3 symmetric stretch, respectively) shift continuously up to the highest pressure of 58.4 GPa giving no indication for a major crystal structural change. Their pressure dependence agrees within the error of measurement with the pressure dependence of the modes of the hydrous Mg end-member phase (Fig. 3). Table 1 compares the ambient Raman frequencies of Fo_{90} and Fo_{100} hydrous wadsleyite. The mode Grüneisen parameters determined for the three most intense Raman modes of Fo_{90} hydrous wadsleyite do not deviate significantly from those determined for the anhydrous Mg end-member phase by Chopelas (1991) (Table 1). We determined the mode Grüneisen parameters $\gamma_{iT} = \frac{\partial \ln \nu_i}{\partial \ln V}$ for Fo_{90} hydrous wadsleyite by fitting the ln $\nu_i(P)$ versus ln $V(P)$ values linearly. The $V(P)$ values were taken from Yusa and Inoue (1997) using a Birch–Murnaghan equation of state with bulk modulus $K_T = 155 \pm 2$ GPa and its pressure derivative $K_T' = 4.3$. Yusa and Inoue's values for K_T and K_T' were determined from a Fo_{100} hydrous wadsleyite sample with 2.5 ± 0.3 wt% H_2O compressed to 8.5 GPa. Our sample, a Fo_{90} hydrous wadsleyite with 2.4 wt% H_2O, is of different composition but has a nearly identical state of hydration. As the H_2O content

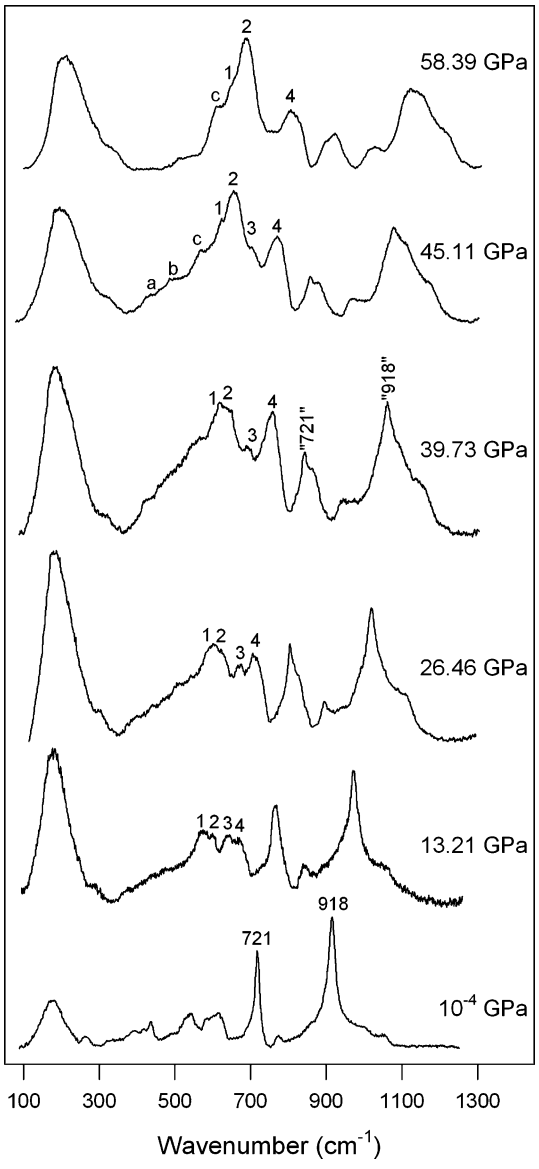

Fig. 2 Selected Raman spectra of Fo_{90} hydrous wadsleyite (sample 1) as a function of pressure in the frequency range 50–1,300 cm^{-1}. The characteristic Si_2O_7 and SiO_3 symmetric stretching mode is labeled as 721 and 918, respectively; modes observed in the mid-frequency range under compression are labeled 1–4 and a–c

influences the bulk modulus significantly (Yusa and Inoue 1997) whereas the Fe-content has little effect on the compressibility of wadsleyite (Hazen et al. 1990, 2000a), Yusa and Inoue's K_T and K_T' values are the literature values that best fit our sample.

There is a marked increase in the relative intensities of the high-frequency shoulders of the 721 and 918 cm^{-1} mode with increasing pressure. At the highest pressures of this study, these shoulders have approximately the same intensity as the 721 and 918 cm^{-1} mode. Another striking increase in relative intensity under compression occurs in the mid-frequency region, 300–650 cm^{-1} at 1 bar and shifted to 500–850 cm^{-1} at 58.4 GPa. The Raman modes in this frequency range are more intense than the Si_2O_7 and SiO_3 symmetric stretching mode (721 and 918 cm^{-1} at 1 bar, respectively) above 40 GPa. A unique correlation of the intense, high-pressure Raman modes with ambient Raman modes of Fo_{90} hydrous wadsleyite is not obvious: modes in this mid-frequency range are not uniformly well resolved at low pressures. Only above 9 GPa do modes between 550 and 650 cm^{-1} emerge (labeled modes 1–4 in Figs. 2, 3), and above 40 GPa, we resolve modes between 350 and 550 cm^{-1} too (labeled modes a–c in Figs. 2, 3). The latter modes appear to coincide with the pressure dependence of Fo_{100} hydrous wadsleyite modes and hence might be vibrational Raman modes of Fo_{90} hydrous wadsleyite. Out of the four bands appearing above 9 GPa, only mode 2 might agree with the previously established pressure-dependence of a hydrous Fo_{100} wadsleyite mode (the ambient 586 cm^{-1} mode), but this agreement could be coincidental. Modes 1, 3 and 4 do not appear to correlate with ambient Raman modes of wadsleyite.

The observed, pressure-induced spectral changes in the mid-frequency range are reversible without hysteresis indicating that the occurrence of a first-order crystal structural change near 9–10 GPa is unlikely. This is also supported by the fact that the 721 and 918 cm^{-1} mode shift continuously to 58.4 GPa. Furthermore, our observations are not generated or affected by non-hydrostatic stresses in the sample because we used helium as pressure-transmitting medium, and neither the ruby nor the silicate stretching modes gave any evidence for a significant pressure gradient across the sample. Interestingly Cynn and Hofmeister (1994) observed a slight change in the pressure dependence accompanied by intensity changes of some mid-IR modes of hydrous Fe-bearing wadsleyite near 10 GPa confirming a similar observation for anhydrous Mg end-member wadsleyite by Chopelas (1991). The authors interpreted the observations as a second-order phase change.

At low frequencies, a relatively intense feature centered around 175–180 cm^{-1} is observed at 1 bar. Its pressure dependence is relatively weak but it gains intensity relative to the 721 and 918 cm^{-1} mode under compression. Part of the intensity increase is retained on decompression indicating an irreversible modification in the crystal structure. This observation is similar to, but less dramatic than, our observation in the Raman spectra of Fo_{89} hydrous ringwoodite (Kleppe et al. 2002b). However, the degree to which the observations have a common origin needs to be established. In both phases, this low-frequency feature appears to be connected to iron substitution in the hydrous Mg end-member structure as it has not been observed in the spectra of hydrous, pure Mg phases (Kleppe et al. 2001, 2002a). It might be associated with localized modes generated by iron (either Fe^{2+} or Fe^{3+}, or both) substitution in the pure Mg host structure. The partly reversible, pressure-induced intensity increase might be associated with energetically favored site distortions under compression. Additional work is required to

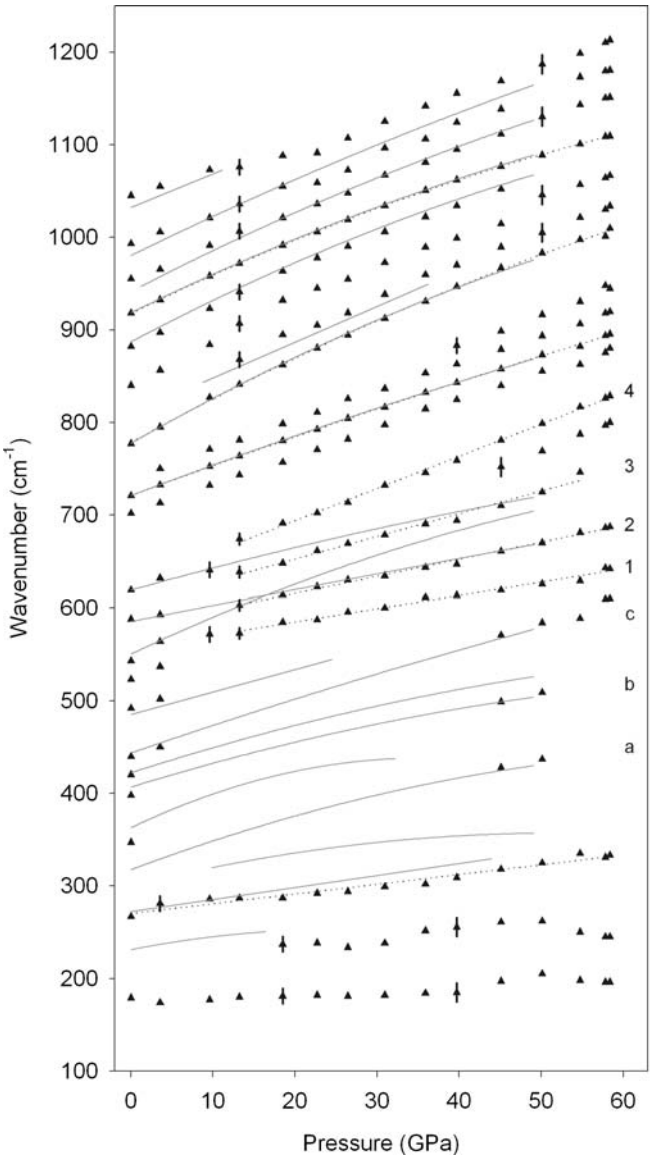

Fig. 3 Pressure dependence of the framework modes of Fo_{90} hydrous wadsleyite (sample 1) (*triangles*, *dotted lines*). The error in measurement of both frequency and pressure is within the size of the symbol except where representative error bars are given. Raman frequencies observed over the entire pressure range have been fitted with a slight quadratic term; weaker bands and shoulders, which could only be located reliably over parts of the investigated pressure range were assumed to vary linearly with pressure. *Grey lines* represent the pressure dependence of the framework modes of Fo_{100} hydrous wadsleyite (Kleppe et al. 2001) for comparison

understand this low-frequency feature and any possible correlation with local disorder in the structure.

Figure 4 shows representative Raman spectra of Fo_{90} hydrous wadsleyite as a function of pressure in the OH stretching region. The OH stretching modes weaken and broaden under compression and have only been unambiguously observed above the fluorescence background of the low-fluorescence, natural diamond-anvils over parts of the investigated pressure range: The doublet at 3,563 and 3,588 cm^{-1} is not resolved at pressure and was tracked as a single mode up to 13.21 GPa; the other OH stretching modes weaken and broaden more strongly and have only been observed to 9.6 GPa. The broadening and weakening of the OH stretching modes, in particular of those modes around 3,330–3,400 cm^{-1}, under compression is in accord with previous studies on hydrous wadsleyite (Kleppe et al. 2001; Cynn and Hofmeister 1994). Figure 5 shows the pressure dependence of the OH Raman bands. It contrasts strongly with that of the framework modes: The OH stretching band centered at about 3,578 cm^{-1} appears to remain constant under compression to at least 13.21 GPa, whereas, the OH modes at lower frequencies decrease with increasing pressure. The pressure dependence is consistent with previous high-pressure Raman and IR studies on Fo_{100} and Fo_{85} hydrous wadsleyite respectively (Cynn and Hofmeister 1994; Kleppe et al. 2001).

Discussion

Effect of iron and proton substitution on the framework Raman modes (200–1,200 cm^{-1}) of wadsleyite

At ambient conditions, protonation of wadsleyite has only a minor effect on its lattice dynamics: a comparison of the Raman spectrum of hydrous with anhydrous pure Mg wadsleyite shows that modes between 200 and 1,200 cm^{-1} are identical for the hydrous and anhydrous phase except for an additional band at 487 cm^{-1} in the spectra of the hydrous phase (Kleppe et al. 2001). This additional band is thought to originate from a translational OH vibration (Mernagh and Liu 1996; Kleppe et al. 2001). Similarly, iron substitution in the hydrated wadsleyite structure does not significantly influence the framework Raman modes. The Raman spectra of Fo_{90} and Fo_{100} hydrous wadsleyite are essentially the same in the region 200–1,200 cm^{-1}. A slight increase in peak width in the Raman spectra of Fo_{90} hydrous wadsleyite reflects a random Fe–Mg substitution as observed in crystal structure refinements of hydrous $Fo_{94.6}$ wadsleyite by Smyth et al. (1997). The authors observed a preference of Fe for the M1 and M2 site without apparent ordering of Fe between these two sites. The prominent shoulders of the 918 cm^{-1} mode in the Raman spectra of hydrous Fo_{90} wadsleyite might be associated with its small deviation from orthorhombic symmetry: a link between monoclinic symmetry of wadsleyite samples and intense, symmetric shoulders of the 918 cm^{-1} Raman mode has been observed before (Kleppe et al. 2001). If we assume this link is true, then the significant gain in intensity of the shoulders of the 918 cm^{-1} mode under compression might be connected with the wadsleyite structure becoming increasingly monoclinic under pressure. High-pressure X-ray diffraction data to at least 40 GPa is needed to test this hypothesis.

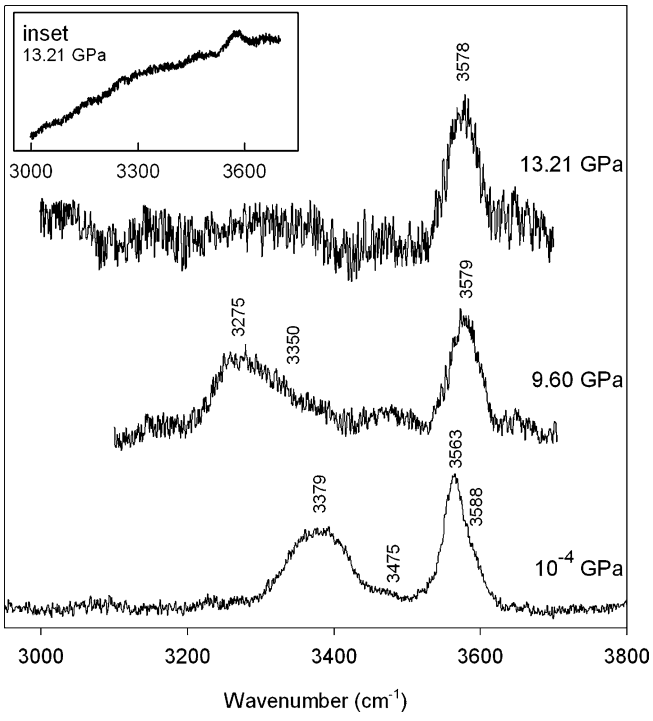

Fig. 4 Selected Raman spectra of Fo_{90} hydrous wadsleyite (sample 1) as a function of pressure in the OH stretching region. The *inset* shows the raw Raman spectrum at 13.21 GPa before subtraction of the background that is caused by the fluorescence of the diamonds

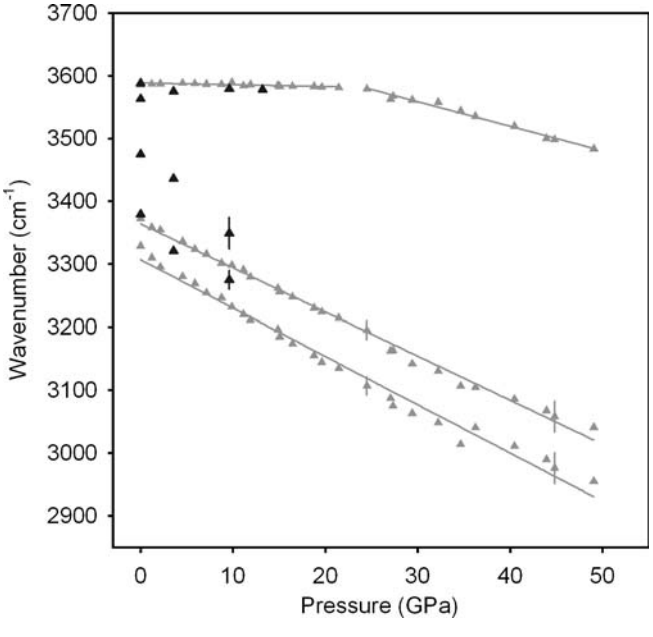

Fig. 5 Pressure dependence of the OH modes of Fo_{90} hydrous wadsleyite (sample 1) (*black triangles*). At higher pressures above 14 GPa, the OH modes could not be observed unambiguously above the fluorescence background of the diamonds. Representative error bars are given where errors are larger than the size of the symbol. The pressure dependence of the OH modes of Fo_{100} hydrous wadsleyite (*grey triangles and lines*, Kleppe et al. 2001) is given for comparison

A striking feature in the high-pressure Raman spectra of Fo_{90} hydrous wadsleyite is the appearance of new Raman modes above 9 GPa in the mid-frequency range (300–650 cm^{-1} at 1 bar and shifted to 500–850 cm^{-1} at 58.4 GPa) accompanied by a significant growth in their intensities under further compression. Similar observations have been reported for wadsleyite II (Kleppe et al. submitted 2005) and Fo_{89} hydrous ringwoodite (Kleppe et al. 2002b), but not for hydrous Mg end-member wadsleyite (Kleppe et al. 2001) and ringwoodite (Kleppe et al. 2002a). Hence, the pressure-induced spectral changes appear to be connected to iron (Fe^{2+}, Fe^{3+})-substitution in the pure Mg wadsleyite and ringwoodite structure. Cation ordering, such as Mg–Fe ordering in octahedral sites, is probably not taking place under pressure because intra-crystalline diffusion is extremely unlikely to occur at room temperature due to the required high activation energies (Hazen and Navrotsky 1996).

Though the pressure-induced changes in spectra of the wadsleyites and ringwoodite look similar, there is a significant difference between them: In the spinel structure, the pressure-induced Raman modes in the mid-frequency range occur at frequencies clearly forbidden for the ideal, cubic spinel host structure, but for the wadsleyite structures the presence of modes in the mid-frequency range is not unusual. Recently, we have argued (Kleppe and Jephcoat submitted) that the pressure-induced modes in Fo_{89} hydrous ringwoodite are likely a result of resonance electronic Raman scattering following the recently reported ambient and high pressure optical and near-infrared absorption spectra of ringwoodite (Keppler and Smyth 2005). Whether the pressure-induced spectral changes observed here for wadsleyite stem from the same effect needs further study. In order to investigate if a subtle reversible structural change occurs in Fo_{90} hydrous wadsleyite around 10 GPa (causing new, pressure-induced modes) structural data to at least 15 GPa would be useful.

Hydroxyls in Fo_{90} hydrous wadsleyite

Raman and IR spectroscopic studies of hydrous wadsleyite (>0.2 wt% H_2O) show consistently two intense groups of OH stretching modes: group 1 comprises a doublet around 3,550–3,620 cm^{-1} and group 2 consists of three components around 3,300–3,400 cm^{-1} (Cynn and Hofmeister 1994; Kleppe et al. 2001; Kohn et al. 2002; Jacobsen et al. 2005). However, the number of resolved modes and individual mode frequencies as well as other spectral details vary depending on the water and iron (Fe^{2+}, Fe^{3+}) content of the wadsleyite sample (Table 2). The influence of water concentration (up to 1.5 wt% H_2O) on the IR active OH stretching modes of Fo_{100} hydrous wadsleyite has been investigated by Kohn et al. (2002) and Jacobsen et al. (2005). Cynn and Hofmeister (1994) studied iron-bearing hydrous wadsleyite with high pressure IR spectroscopy and concluded that

Table 2 Comparison between the ambient OH stretching frequencies of hydrous wadsleyite samples with varying iron and water concentrations

Raman studies		IR studies		
Present study	Kleppe et al. (2001)	Cynn and Hofmeister (1994)	Jacobsen et al. (2005)[a]	
2.4 wt% H_2O, Fo_{90}, monoclinic ($\beta = 90.18°$) ν (cm^{-1})	1.65 wt% H_2O, Fo_{100}, orthorhombic ν (cm^{-1})	0.21 wt% H_2O, Fo_{85}, orthorhombic ν (cm^{-1})	> 0.2 wt% H_2O, Fo_{100}, orthorhombic	
			ν (cm^{-1})	Assignment
			3,000	O4···O4
	3,280	*3,280*		
			3,317	O1···O4 (M3 edge) O1···O4 (M2/M3 edge)
	3,329	*3,329*	*3,326*	
3,354			*3,360*	
3,399	*3,373*	*3,398*		
		3,441		
3,469		3,460		
3,563		3,550		
3,588	**3,586**	**3,582**	**3,581**	O1···O3 (M3/M3 edge)[b]
		3,618	**3,614**	O1···O1 (M3/M3 edge)[b]

The spectra can be divided into two main OH groups: group 1 is printed in bold, group 2 in italics. Also characteristic of spectra appear to be the weak and broad band centered around 3,000 cm^{-1}, and the less intense bands between 3,440 and 3,550 cm^{-1}

[a]Agrees with Kohn et al. (2002) who resolved 14 out of 17 possible O–H···O environments for Fo_{100} samples with water concentrations between 0.8 and 1.5 wt % H_2O

[b]Bent hydrogen bond

Fe substitution appears to add more hydroxyl sites to the structure. However, their assignment of specific modes (e.g. the 3,582 cm^{-1} mode) to sites with an Fe impurity is inconsistent with the mode assignment of the most recent IR studies of Fo_{100} hydrous wadsleyite (Kohn et al. 2002; Jacobsen et al. 2005). Similarly, the observation of a greater number of Raman active OH stretching modes in our present study (compared to our Raman study of Fo_{100} hydrous wadsleyite) is probably rather connected to the observation of a different subset of all possible OH modes under different experimental conditions than to the incorporation of iron. A correlation of OH modes with site-specific Fe impurities would require high resolution, polarized single-crystal spectroscopic studies of hydrous iron-bearing wadsleyite.

Raman and IR active OH stretching modes of hydrous wadsleyite with frequencies < 3,530 cm^{-1} have a strong, negative pressure dependence whereas OH modes at higher frequencies are less sensitive to pressure with $\partial \nu_i / \partial P$ being approximately constant to about 24 GPa (Kleppe et al. 2001; Cynn and Hofmeister 1994). A nearly constant OH stretching frequency under compression suggests very weak hydrogen bonding. A negative frequency response of OH modes under pressure requires a reduction of the respective O···O distances and reflects a strengthening of the hydrogen bonding. A concomitant lengthening of the O–H bond has often been assumed but is not mandatory; e.g., Parise et al. (1994) demonstrated that in deuterated brucite the O–D bond length is constant under compression to 9.36 GPa.

Jacobsen et al. (2005) argued that the IR absorption triplet in the frequency range 3,310–3,360 cm^{-1} is best associated with protonation of the O1···O4 edges of the M3 octahedron (unshared and shared M3/M2 edge); but the authors could not fully rule out contributions from the O3···O4 edges around M1. The latter protonation sites appear favorable in light of the negative pressure dependence of OH modes below 3,530 cm^{-1}. In detail, the frequency response of the OH mode triplet between 3,310 and 3,360 cm^{-1} is most likely negative under compression requiring a reduction of the respective O···O distances with increasing pressure; this, in turn, is inconsistent with protonation of the O1···O edges around M3 because these edges have been found to be insensitive to pressure, albeit to 3.7 GPa only (Kudoh and Inoue 1998). In order to use the pressure-dependence of the OH stretching modes reliably in the assignment of protonation sites in wadsleyite, structural data to higher pressures, at least 10–15 GPa, is needed. We note that the presence of 2.4 wt% H_2O and 10% of Fe in our wadsleyite sample (compared to Fo_{100} wadsleyites with ≤ 1 wt% H_2O investigated by Jacobsen et al. 2005) might have led to hydration of other O-sites, in addition to the O-sites reported by Jacobsen et al. (2005). The frequencies of the OH bands around 3,550–3,620 cm^{-1} are less sensitive to pressure than the bands at 3,310–3,350 cm^{-1} and hence consistent with the assignment to the O1···O edges around M3 (Jacobsen et al. 2005). Neutron diffraction experiments would best determine the protonation sites in wadsleyite and might become possible with increased neutron flux sources in the future.

Implications for the transition zone

Wadsleyite might be a large reservoir in the transition zone that contains a significant proportion of the global water budget. The wadsleyite sample of the present, high

pressure Raman study has a realistic iron content (~10%) and a hydration state (2.4 wt% H_2O) that is most likely significantly larger than the actual amount in the Earth. The pressure dependencies of the OH stretching modes show that the location of hydrogen remains a complex problem. To improve our understanding of the protonation sites and correlation with bond-lengths in wadsleyite, structural neutron or X-ray diffraction data are needed to pressures well above 10 GPa. A detailed understanding of protonation sites and charge-balancing vacancies in wadsleyite would help to predict the effect of hydration on the physical properties (e.g., density) of transition zone minerals. To connect seismological observations with hydrogen in the transition zone requires a quantitative understanding of the effects of protonation on elasticity of the transition zone phases.

Our high pressure Raman study of Fo_{90} hydrous wadsleyite together with previous studies of hydrous and anhydrous Mg end-member phases has revealed that protonation as well as coupled protonation and iron substitution has only a minor effect on the framework lattice dynamics over the entire pressure stability range for wadsleyite in the mantle. However, the incorporation of iron (Fe^{2+}, Fe^{3+}) into a hydrous wadsleyite structure does appear to result in new, more complex Raman scattering processes associated with resonant phenomena and/or electronic Raman scattering. Pressure-induced, subtle structural changes around 10 GPa can also not be excluded. What the present Raman study does emphasize is that the actual dynamical properties of minerals are likely to depend strongly on small changes in composition, and it is not sufficient to study end-member phases alone. Further, it confirms that iron and hydrogen at least have to be taken into account when modeling the mineralogy of the transition zone.

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