

RAMAN AND INFRARED SPECTRA OF HYDROUS β - Mg_2SiO_4

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ABSTRACT

Micro-Raman and micro-infrared spectra of the silicate and OH-stretching regions have been obtained from a well-characterized crystal of hydrous β - Mg_2SiO_4 containing approximately 2.6 wt.% H_2O . Five distinct OH-stretching vibrations were observed in two separate spectral groupings. A Raman-active band at 3355 cm^{-1} and an infrared band at 3351 cm^{-1} comprise the first group; a Raman band at 3583 cm^{-1} and infrared bands at 3596 and 3653 cm^{-1} make up the second group. These results are consistent with the incorporation of H into the O1 site. The apparent division of the OH-stretching bands into a group near 3330 cm^{-1} and a group near 3600 cm^{-1} is due to differences in the lengths of the hydrogen bonds to the nearest-neighbor oxygen atoms in the Mg2 and Mg3 octahedra. Relative intensities of the bands suggest that a majority of shorter, and hence, stronger hydrogen bonds are formed in the hydrated beta phase. Tentative assignments of the observed bands have been made by comparison with the corresponding spectra of anhydrous β - Mg_2SiO_4 .

Keywords: hydrous beta phase, micro-Fourier transform infrared spectroscopy, micro-Raman spectroscopy, mantle.

SOMMAIRE

Nous avons mené une étude par microspectroscopie Raman et dans l'infra-rouge de l'intervalle de vibration des liaisons impliquant la trame silicatée et la région d'étirement du groupe OH dans un cristal bien caractérisé de la forme β hydratée de la composition Mg_2SiO_4 , contenant environ 2.6% de H_2O (poids). Cinq vibrations distinctes impliquant l'étirement du groupe OH ont été documentées, en deux groupes dans les spectres. Une bande active à 3355 cm^{-1} dans le spectre Raman et une bande à 3351 cm^{-1} dans l'infra-rouge constituent le premier groupe. Une bande dans le spectre Raman à 3583 cm^{-1} et deux bandes dans l'infra-rouge, à 3596 et 3653 cm^{-1} , constituent le deuxième. Ces résultats concordent avec l'hypothèse qu'il y a incorporation des atomes H sur le site O1. La division apparente de la fréquence des bandes en deux groupes, un près de 3330 cm^{-1} et l'autre près de 3600 cm^{-1} , serait due aux différences dans la longueur des liaisons O-H impliquant les atomes d'oxygène qui sont proches voisins dans les octaèdres Mg2 et Mg3. D'après l'intensité relative des bandes, une majorité de liaisons plus courtes, et donc plus fortes, caractériserait la phase beta hydratée. Nous proposons une interprétation préliminaire des spectres observés par analogie avec les spectres correspondants de la forme β du Mg_2SiO_4 .

(Traduit par la Rédaction)

Mots-clés: phase hydratée beta, microspectroscopie infra-rouge par transformation de Fourier, microspectroscopie de Raman, manteau.

INTRODUCTION

The state of hydration of the Earth's mantle has been the subject of considerable debate in recent years; the possible existence of hydrated magnesium silicates could alter our current understanding of the phase relationships in the upper mantle and transition zone.

Wadsleyite in its pure form (*i.e.*, β - Mg_2SiO_4) is only stable over a narrow P-T range, from 13 to 17 GPa at 1800 K (Anderson 1970, Liu 1979), although the partial substitution of Fe for Mg may slightly extend the range of stability. At lower pressures, olivine (α - Mg_2SiO_4) is stable in a peridotitic mantle. The $\alpha \leftrightarrow \beta$ phase transition has been suggested as the major cause of the seismic discontinuity at 400 km (Ringwood 1970, Liu 1979, Jeanloz & Thompson 1983, Bina & Wood 1987).

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The crystal structure of β - Mg_2SiO_4 was solved by Moore & Smith (1970) and refined by Horiuchi & Sawamoto (1981). The structure of the β -phase and its relationship to the olivine and spinel structures are fairly well established (Horiuchi *et al.* 1980, 1982, Hazen & Finger 1981, Hyde *et al.* 1982, Price 1983). In contrast to the olivine and spinel forms of Mg_2SiO_4 , the β -phase is a sorosilicate. It contains Si_2O_7 and one less O atom (per asymmetric unit) that is not bound to Si, but is coordinated by five Mg atoms in an irregular square pyramidal arrangement (Horiuchi & Sawamoto 1981). Smyth (1987, 1994) considered a simple point-charge model and Pauling bond-strength sums at O atoms. He concluded that the O1 site of β - Mg_2SiO_4 would be an ideal candidate for hydration, and that this structure might be capable of containing substantial amounts of OH at the underbonded O1 site. In similar calculations of the electrostatic potential for β - Mg_2SiO_4 , Downs (1989) confirmed the suggestions of Smyth (1987, 1994), but also found a minimum in the potential above and below the O2 site and suggested that protonation could take place at O2 as well as O1.

Infrared and Raman spectra of bulk, polycrystalline samples of β - Mg_2SiO_4 were first reported by Akaogi *et al.* (1984). However, the spectra obtained in their preliminary study resemble those of forsterite. A new Raman spectrum of a single grain of β - Mg_2SiO_4 was later published by McMillan & Akaogi (1987). The strongest bands in the latter Raman spectrum were assigned to vibrations of the Si_2O_7 units by analogy with the spectrum of åkermanite . McMillan *et al.* (1991) also have suggested that some of the β - Mg_2SiO_4 grains from their previous studies are hydrated and contain up to 0.06 wt.% H_2O . Young *et al.* (1993) reported infrared spectra for a more hydrous, iron-bearing β - Mg_2SiO_4 -type phase, with up to 0.32 wt.% H_2O .

Kohlstedt *et al.* (1996) and Kudoh *et al.* (1994) have recently synthesized hydrous β - Mg_2SiO_4 -type phases claimed to be almost completely saturated with OH. Kudoh *et al.* (1994) used valence-sum calculations to show that the O1 site is occupied by OH. Their results are consistent with the prediction of Smyth (1987, 1994) that the OH is located at the O1 sites, but they disagree with Smyth's model, which invokes a vacancy at the Mg2 sites and suggests that the O-H bonds are parallel to the *c* axis. The above publications have only presented parts of the infrared and Raman spectra in order to prove that they have actually synthesized the hydrous beta phase. This has prompted us to examine the Raman and infrared spectra of the fully hydrated beta phase (over the full spectral range of our instruments) and to compare them with those of anhydrous β - Mg_2SiO_4 .

EXPERIMENTAL

The specimen used in this study is a single crystal ($\sim 75 \times 30 \times 20 \mu\text{m}$) of the fully hydrated beta phase

synthesized at 1300°C and 15.5 GPa by Inoue (1994) using an MA8-type multi-anvil apparatus at Nagoya University. Electron-microprobe analysis of the present sample gave a Mg/Si value of 1.809 ± 0.049 , and secondary-ion mass spectrometry gave 2.6 ± 0.3 wt.% H_2O . The crystal structure of a very similar sample (almost identical to the present one) having a composition (Mg/Si = 1.803 ± 0.013 ; 2.5 ± 0.3 wt.% H_2O) has been refined by Kudoh *et al.* (1994) and confirmed to have the β -phase structure. Thus the chemical formula of the present sample should be very close to $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$, as calculated by Kudoh *et al.* (1994). The crystal of anhydrous β - Mg_2SiO_4 is the same sample previously studied by Liu & Mernagh (1994).

Fourier transform infrared (FTIR) spectra were recorded from 750 to 4000 cm^{-1} using a Bomen infrared spectrometer and a Spectra-Tech microscope. FTIR spectra were obtained at 4 cm^{-1} resolution by addition of 500 scans for each sample and reference spectrum. To ensure that only the spectrum of the crystal was obtained, a rectangular region approximately $20 \times 15 \mu\text{m}$ was selected for analysis by masking the image at an intermediate focal plane within the microscope. Polarized spectra could not be obtained owing to the small size of the crystal used in these studies and the depolarizing effects caused by the microscope objective.

Raman spectra were recorded on a Microdil 28 spectrometer equipped with an Olympus microscope. A 50 $\times$ ULWD Olympus microscope objective lens was used to focus the laser beam to a spot about 2 μm in diameter on the crystal. A complete description of the experimental setup is given in Liu & Mernagh (1990). Spectra were measured at approximately 3 cm^{-1} resolution from 100 to 3675 cm^{-1} using 514.5 nm excitation and 30 mW power at the sample. All spectra were obtained after 15 accumulations using a 25-s integration time. The Raman peaks are accurate to $\pm 1 \text{ cm}^{-1}$, except for the broader bands attributed to H_2O , which are accurate to $\pm 5 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Micro-FTIR spectrum of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$

The micro-FTIR spectrum of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$ is shown in Figure 1. The frequencies of the observed bands are compared with those of anhydrous β - Mg_2SiO_4 in Table 1. The bands at 814 and 948 cm^{-1} in the hydrous β -phase are nearly coincident with those in the anhydrous β -phase, but the band at 890 cm^{-1} is not observed in the anhydrous β -phase. The weak shoulder at 1074 cm^{-1} does not occur in our spectrum of the hydrous β -phase, but a broad band at 1435 cm^{-1} is evident in Figure 1. A similar band at 1492 cm^{-1} was reported by McMillan *et al.* (1991) in their FTIR spectrum of the hydrated beta phase. As the band at

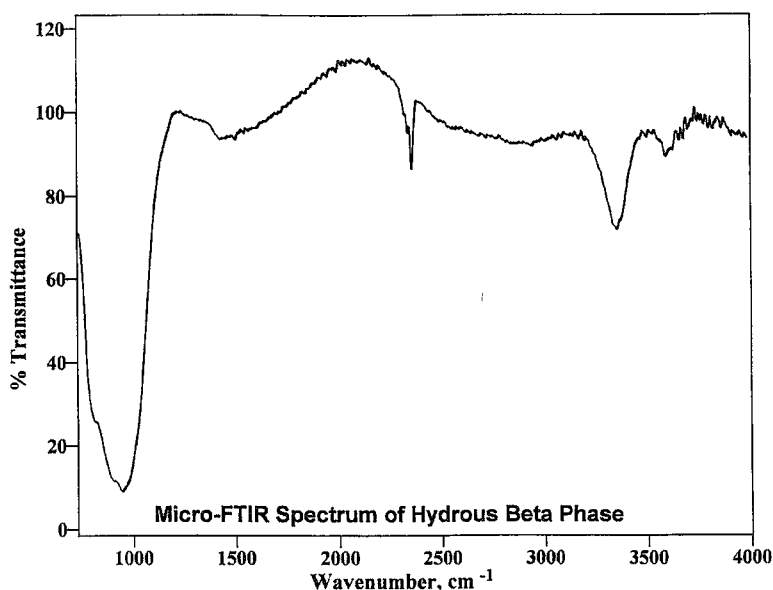


FIG. 1. Unpolarized micro-FTIR spectrum in the region from 750 to 4000 cm^{-1} recorded from a single crystal of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$.

1435 cm^{-1} is only observed in the hydrated samples, it has been tentatively assigned as the $\delta(\text{OH})$ librational mode, although this frequency is near the upper limit for this type of OH vibration. The bands near 2360 cm^{-1} (not listed in Table 1) are due to the

incomplete subtraction of atmospheric CO_2 . It seems unlikely that a significant amount of CO_2 has been incorporated into the crystal structure, as no evidence of CO_2 was found in the X-ray-diffraction study of Kudoh *et al.* (1994) on a crystal synthesized under the same conditions.

Three infrared bands occur in the OH-stretching region at 3351, 3596 and 3653 cm^{-1} (Fig. 1). These are in general agreement with previous studies, although the frequencies reported in each study vary quite considerably. McMillan *et al.* (1991) observed only two bands, at 3323 and 3583 cm^{-1} , in their sample containing 0.06 wt.% H_2O . Young *et al.* (1993) observed three bands, at 3329, 3580 and 3615 cm^{-1} , in their sample containing 0.32 wt.% H_2O , whereas Kudoh *et al.* (1994) reported these bands at 3344, 3587 and 3608 cm^{-1} in a sample of composition similar to that of the present study. In another recent study, Kohlstedt *et al.* (1996) reported at least five distinct OH peaks, at 3270, 3305, 3360, 3590 and 3605 cm^{-1} , in a sample with an estimated 2.4 wt.% H_2O . Furthermore, their experiments on a hydrated α phase clearly showed that the number of observed OH bands and their relative intensity vary dramatically with changes in sample orientation or the polarization of the infrared beam. Nakamoto *et al.* (1955) and Novak (1974) have shown that there is a correlation between the frequency of the OH stretching vibration and the OH...O distance. In general, the frequency of the OH stretching vibration occurs at lower wavenumbers in

TABLE 1. THE OBSERVED INFRARED AND RAMAN BANDS* OF ANHYDROUS AND HYDROUS β - Mg_2SiO_4 .

Anhydrous β - Mg_2SiO_4		Hydrus β - Mg_2SiO_4		Assignments
FTIR ^a	Raman ^b	FTIR ^a	Raman ^c	
	231	226	226	{ Lattice vibrations, predominantly involving MgO_4 vibrations
		259	259	
		391	391	
	443	433	433	
		484	484	Translational OH vibration
	551	544	544	
	584	582	582	Complex SiO_4 and MgO_4 vibration
592				SiO_4 bending mode
	620	617	617	SiO_4 bending mode
698				SiO_4 bending mode
	721	714	714	?
	777	769	769	Si_2O_7 symmetric stretch
813	813	814	814	?
	841		848	SiO_4 symmetric stretch
		890		?
	918		912	SiO_4 asymmetric stretch
944		948		SiO_4 symmetric stretch
1074				Si_2O_7 asymmetric stretch
		1435		?
		3351	3355	Hydrogen-bonded O-H stretch
			3583	Hydrogen-bonded O-H stretch
		3596		Hydrogen-bonded O-H stretch
		3623		Hydrogen-bonded O-H stretch

* in cm^{-1} . a. Data on FTIR spectrum from Williams *et al.* (1986). b. Data on Raman spectrum from Liu *et al.* (1995). c. FTIR and Raman spectra generated in this study.

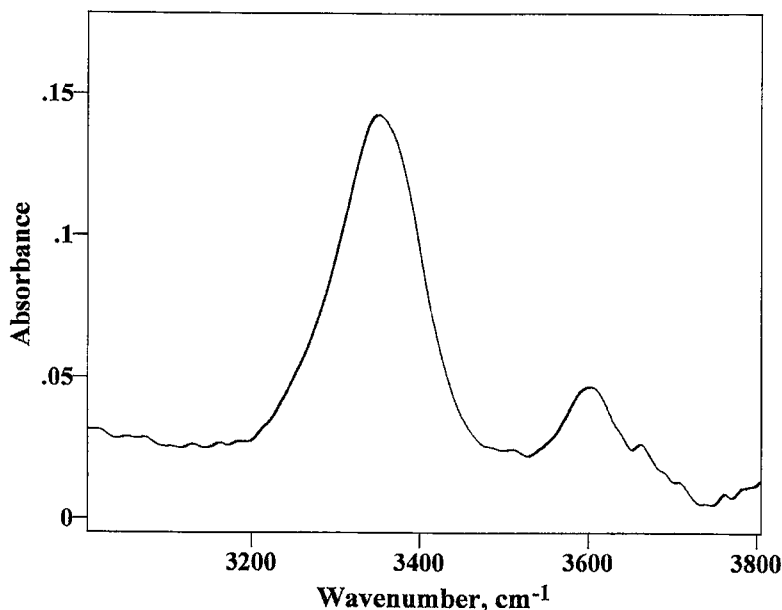


Fig. 2. Unpolarized micro-FTIR spectrum of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$ covering the OH-stretching region and obtained using a $20 \times 15 \mu\text{m}$ intermediate aperture.

systems in which the OH is more strongly hydrogen-bonded. The apparent division of the OH-stretching bands into a group near 3330 cm^{-1} and a group near 3600 cm^{-1} is caused by the differences in the bond lengths of the nearest-neighbor oxygen atoms in the Mg2 and Mg3 octahedra.

Figure 2 shows an expanded view of the OH-stretching region (plotted on an absorbance scale) for $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$. An approximate value of $100 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ may be used for the molar absorptivity of the fundamental OH-stretching in minerals (Rossman 1988) to estimate the OH content of the hydrous beta phase. The density for $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$ is $3.31 \text{ g}\cdot\text{cm}^{-3}$ (Kudoh *et al.* 1994). Thus, by integrating the infrared spectrum from 3100 to 3800 cm^{-1} and using an estimated thickness of the sample of $20 \mu\text{m}$, the calculated concentration of OH is approximately $1.5 \text{ wt.}\%$. This is lower than the $2.6 \text{ wt.}\%$ H_2O indicated by the formula, but the calculation is subject to large uncertainties in the value of the molar absorptivity and the sample thickness. Note that there is no indication of H_2O in the hydrated beta phase, as no H_2O -bending mode is apparent in the region around 1630 cm^{-1} in Figure 1, and there is also no broad-band absorbance in the OH-stretching region.

Micro-Raman spectrum of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$

The complete Raman spectrum of the hydrous beta phase (Fig. 3) also has three bands in the region $1000 - 3000 \text{ cm}^{-1}$ that are due to the remnants of a previous carbon coating on the sample; it could not be removed owing to the small size of the crystal. Two OH bands are observed at 3355 and 3583 cm^{-1} , and the band at 3583 cm^{-1} correlates with the infrared band at this frequency (Fig. 1). The band at 3355 cm^{-1} is assigned as an O–H vibrational mode. Kudoh *et al.* (1994) observed this band at 3346 cm^{-1} , whereas McMillan *et al.* (1991) reported this band at 3324 cm^{-1} in their samples, which contain only $0.06 \text{ wt.}\%$ H_2O .

Figure 4 compares the Raman spectra of the hydrous and anhydrous beta phases below 1000 cm^{-1} . The Raman frequencies of the hydrous beta phase (Table 1) are lower than the corresponding bands in the anhydrous beta phase (some bands being lower by up to 10 cm^{-1}), and the Raman bands in the hydrous beta phase also are broader than those in the anhydrous beta phase. Both these effects may be due to the deviation of the Mg/Si value from the stoichiometric value for anhydrous $\beta\text{-Mg}_2\text{SiO}_4$. There is a close resemblance between the two spectra, but additional

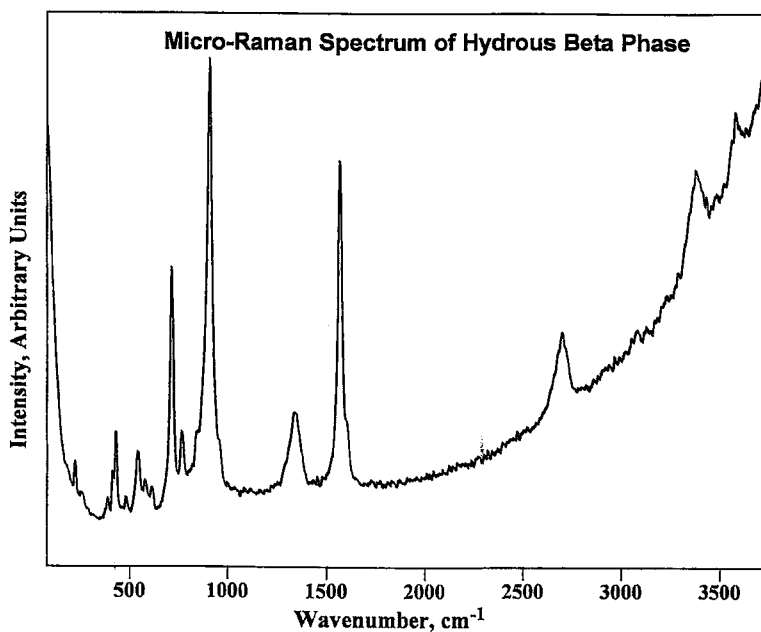


FIG. 3. Micro-Raman spectrum in the region from 100 to 3675 cm^{-1} recorded from a single crystal of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$. Note that the three bands in the region 1000 – 3000 cm^{-1} are due to remnants of a carbon coating on the sample from previous studies (see text for further explanation).

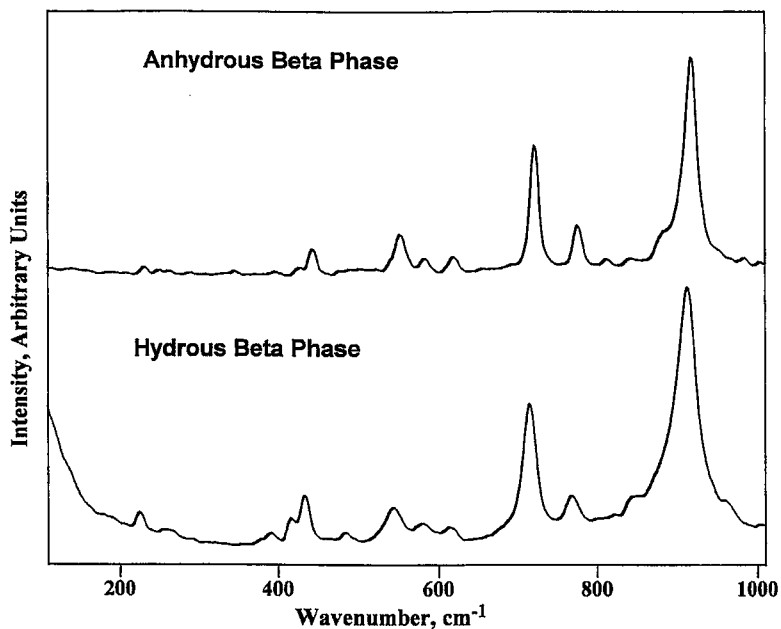


FIG. 4. A comparison of micro-Raman spectra in the region from 150 to 1000 cm^{-1} for anhydrous β - Mg_2SiO_4 (top), and hydrous $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$ (bottom).

bands (absent from the spectrum of the anhydrous β -phase) occur at 259, 391 and 484 cm^{-1} ; these presumably arise from the addition of OH groups. The band at 415 cm^{-1} (not listed in Table 1) may correspond to the main Raman band of the sapphire substrate used to support the crystals.

Mode assignments for $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$

Kudoh *et al.* (1994) reported that the structure of $\text{Mg}_{1.74}\text{Si}_{0.97}\text{H}_{0.65}\text{O}_4$ consists of two distinct layers (a mixed layer of octahedra and tetrahedra and a layer of octahedra) stacked alternately along [201]. The OH group is associated with the Mg-site vacancy, but is mainly governed by the occupancy of the O1 site, as mentioned above. Therefore, our spectra are interpreted in terms of the vibrational modes of tetrahedra (SiO_4) and octahedra (MgO_6), and band assignments are given in Table 1.

As this structure also contains Si_2O_7 units, it is useful to treat the vibrations of the Si–O–Si linkage separately from those of the SiO_3 terminal units. According to the work of Tarte *et al.* (1973), the symmetric and asymmetric Si–O–Si-stretching vibrations should occur in the 600–1200 cm^{-1} region. Jeanloz (1980) assigned a shoulder in the infrared spectrum of $\beta\text{-Co}_2\text{SiO}_4$ to an asymmetric-stretching vibration. As the bond angles of the Si_2O_7 groups are nearly identical in $\beta\text{-Co}_2\text{SiO}_4$ and $\beta\text{-Mg}_2\text{SiO}_4$ (Horiuchi & Sawamoto 1981, Morimoto *et al.* 1974), it is reasonable to assign the infrared band at 948 cm^{-1} to an Si–O–Si asymmetric-stretching vibration. By analogy with the sorosilicate äkermanite, McMillan & Akaogi (1987) have assigned the intense Raman bands at 723 and 918 cm^{-1} in anhydrous $\beta\text{-Mg}_2\text{SiO}_4$ to symmetric stretching of the Si–O–Si linkage and the terminal -SiO_3 groups, respectively. On the basis of the assignments of McMillan & Akaogi (1987) for anhydrous $\beta\text{-Mg}_2\text{SiO}_4$, the corresponding Raman bands at 714 and 912 cm^{-1} for the hydrous beta phase have been assigned to these same vibrations.

Comparison with other sorosilicates (Farmer 1974) indicates that the stretching vibrations of the terminal -SiO_3 groups normally occur between those of the symmetric and asymmetric Si–O–Si stretching vibrations. Therefore, in accord with Williams *et al.* (1986), the infrared bands at 890 and 811 cm^{-1} have been assigned as asymmetric and symmetric stretching vibrations of the terminal- SiO_3 groups, respectively. The spectral feature between the two relatively well-defined Raman bands at 714 and 544 cm^{-1} (Fig. 4) seems to be largely due to closely spaced, low-amplitude SiO_3 -bending modes. From their high-pressure studies, Williams *et al.* (1986) reported that the mode near 544 cm^{-1} is a complex vibration involving coupling of motions of both octahedra and tetrahedra. By analogy with the bands below 400 cm^{-1} in olivine (Iishi 1978), the low-frequency bands

probably represent lattice vibrations predominantly involving motions of the MgO_6 octahedra.

A model with substitution of H at the O1 sites predicts a strong c-axis polarization of the infrared and Raman OH-stretching absorptions and two distinct frequencies of absorption (Smyth 1994). The nearest-neighbor oxygen atoms around O1 are O1 and O4, which form edges of the Mg3 and Mg2 octahedra. The O1–O1 and O1–O4 edges of the Mg3 octahedron are separated by distances of 0.3026 nm and 0.2857 nm, respectively, whereas the O1–O4 edges of the Mg2 octahedron are separated by a distance of 0.2817 nm (Kudoh *et al.* 1994). Therefore, the Raman band at 3583 cm^{-1} and the two infrared bands at 3596 and 3653 cm^{-1} have been assigned to OH-stretching vibrations, with the longer hydrogen-bond distances in the Mg3 octahedra. The differences in frequencies indicate that there may be small perturbations of the OH bond lengths or angles (or both). Similarly, the Raman and infrared bands around 3350 cm^{-1} correlate with the shorter hydrogen-bond distances. The observed bands cannot be assigned to particular OH orientations within the crystal structure because it was not feasible to collect polarized spectra from the very small crystals used in this study.

Skogby & Rossman (1991) have shown that molar absorptivity has a strong wavenumber dependence in the OH-stretching region; thus it is difficult to directly compare the intensities of the infrared OH bands. However, the observation that the hydrogen-bonded OH band at 3351 cm^{-1} in the infrared spectrum is much more intense than the OH bands at higher wavenumber is confirmed by similar observations in the Raman spectrum in Figure 2. This indicates that the majority of the OH groups in the hydrous beta phase form shorter and hence stronger hydrogen bonds.

The weak and moderately broad band at 1435 cm^{-1} noted in the present study has not been observed in infrared spectra recorded from the anhydrous β -phase, but McMillan *et al.* (1991) also observed a similar band near 1492 cm^{-1} in their infrared spectrum of a hydrated beta phase. This band occurs at a lower frequency than that of the H_2O -bending vibration (which always lies near 1630 cm^{-1}) and is possibly due to a small amount of carbonate or nitrate impurity in the crystal. Another Raman band at 484 cm^{-1} , which is absent from the spectrum of anhydrous $\beta\text{-Mg}_2\text{SiO}_4$, could be a translational OH vibration. For example, talc has a translational OH vibration at 465 cm^{-1} (Farmer 1974). However, assignments in these regions remain speculative.

GEOLOGICAL IMPLICATIONS

It is generally accepted that the 400-km seismic discontinuity results from the $\alpha \leftrightarrow \beta$ transition in Mg_2SiO_4 (Ringwood 1970, Liu 1979). Given the high solubility of OH in the beta phase samples used in this

study, it is reasonable to suggest that abundant beta phase present in the transition zone could provide a very significant reservoir for H_2O in the mantle. In fact, more H_2O could be incorporated into the mantle than is currently present in the Earth's oceans. However, because most hydrous minerals are expected to dehydrate at much shallower depths than the α - β phase boundary, possible mechanisms for the transport and trapping of H_2O at these depths can only be postulated at this stage. Liu (1989) suggested that other hydrous silicates, such as magnesian pumpellyite, may exist in the coldest part of a subducting lithosphere down to a depth of at least 300 km, and a similar suggestion also was made by Young *et al.* (1993). Thus, H_2O in the cold core of deeply descending slabs may eventually partition into the β -phase in the appropriate region.

However, the incorporation of OH into β - Mg_2SiO_4 seems to have only a slight effect on the physical properties of this phase. Recent high-pressure and high-temperature studies of the hydrous beta phase (Liu *et al.* 1997) have shown that this phase may be slightly less compressible than the corresponding anhydrous phase, and that the volume thermal expansivity for the hydrous β -phase is only slightly less than that for the anhydrous phase. Therefore, detection and discrimination between the anhydrous and hydrous beta phases may be very difficult, if not impossible, using current geophysical techniques.

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