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Hydroxyl groups in β-Mg_2SiO_4

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ABSTRACT

Beta-Mg_2SiO_4 is likely to be an important phase within the transition zone of the Earth's mantle at a depth of 400–500 km. Recent calculations have suggested that β-Mg_2SiO_4 might accept OH groups into its crystal structure and that the phase could be a source for H_2O in the mantle. We have obtained micro-Raman and micro-infrared spectra for well-characterized samples of synthetic β-Mg_2SiO_4 that show a band at 3322 ± 3 cm^{-1} (and perhaps a weaker feature near 3580 cm^{-1}), which suggests that OH groups are present in the nominally anhydrous sample. From the measured absorbance of the 3322 cm^{-1} feature, we estimate that the OH content of the β-Mg_2SiO_4 sample is approximately 0.06% by weight. Also as part of this study, Raman spectroscopy has been used to study the metastable reversion of β-Mg_2SiO_4 to structurally disordered forsterite at 580 °C and a Raman spectrum for the hydrous high pressure phase B has been obtained.

INTRODUCTION

There is currently considerable interest in the state of hydration of the mantle. Wadsleyite (β-Mg_2SiO_4) is stable in a narrow *P-T* region (13–17 GPa at 1800 K) between the phase fields of olivine (α-Mg_2SiO_4) and spinel (γ-Mg_2SiO_4) and would be a major phase in the transition zone of a peridotitic mantle at depths of 400 and 500 km (Anderson, 1970; Jeanloz and Thompson, 1983; Bina and Wood, 1987). The α-β phase transition in $(Mg,Fe)_2SiO_4$ has been suggested as a cause of the seismic discontinuity at 400 km (Ringwood, 1970; Anderson, 1970; Liu, 1979; Jeanloz and Thompson, 1983; Bina and Wood, 1987).

The crystal structure of β-Mg_2SiO_4 contains Si_2O_7 units (unlike the olivine and spinel forms of Mg_2SiO_4 which contain only isolated SiO_4 groups), and one O atom per asymmetric unit (O_1) is not bound to Si, but is coordinated by five Mg atoms in an irregular square pyramidal arrangement (Horiuchi and Sawamoto, 1981). Smyth (1987) recently examined the electrostatic potentials from a point charge model and Pauling bond strength sums at O in a number of hydrous and anhydrous minerals that are believed to be stable under the *P-T* conditions of the upper mantle. He concluded that the O_1 O atom of β-Mg_2SiO_4 would be an ideal candidate for hydration and that this phase could act as a host for H_2O in the mantle. Downs (1989) computed potentials from electron distributions from Horiuchi and Sawamoto's (1981) single-crystal X-ray diffraction data and concluded that a more likely site for protonation would be the O(2) bridging O atom of the Si_2O_7 group, although O(1) protonation would also be possible.

In order to test the original hypothesis, that β-Mg_2SiO_4 might exist as a hydrous phase, we obtained preliminary Raman data for a bulk polycrystalline synthetic sample (McMillan et al., 1987; also in McMillan and Hofmeister, 1988) that had previously been synthesized and characterized for a calorimetry and phase equilibrium study (Akaogi et al., 1984). This Raman study showed the presence of weak bands in the O-H stretching region; however, these bands could have been due to the presence of submicroscopic impurity phases, OH at grain boundaries, or other defects within the β-Mg_2SiO_4 grains. In the present work, we have conducted a more careful investigation of individual β-Mg_2SiO_4 grains from the same sample by micro-Raman spectroscopy and of groups of these grains by micro-infrared spectroscopy, and we have further characterized the sample by scanning and transmission electron microscopy and electron microprobe analysis for all three major elements (Mg, Si, and O). Our results suggest that OH groups are in fact present in this sample at β-Mg_2SiO_4, in general agreement with the suggestion of Smyth (1987). This raises the possibility that β-$(Mg,Fe)_2SiO_4$ phases in the mantle are also hydrated, which would affect their elastic and electrical properties and might modify mineral assemblages of the transition zone.

EXPERIMENTAL

Experiments were carried out using samples of β-Mg_2SiO_4 similar to those used in the calorimetric and spectroscopic studies of Akaogi et al. (1984) and McMillan and Akaogi (1987). This sample was synthesized from

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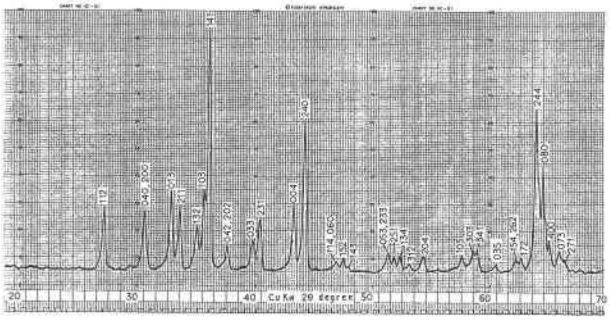

Fig. 1. Powder X-ray diffraction pattern for the sample of β-Mg_2SiO_4 used in these studies.

a "reactive forsterite" starting mix, to avoid the sluggish α-β transition of well-crystallized forsterite. A gel of forsterite composition was precipitated from a mixture of aqueous ethyl orthosilicate and magnesium nitrate solutions. The gel was heated at 1123 K for 127 h, resulting in formation of fine-grained α-Mg_2SiO_4 with unreacted MgO and amorphous silica. This was reacted at 14.5 GPa and 1123 K for 1 h to give β-Mg_2SiO_4. SEM and optical examination of the sample showed well-crystallized grains with well-developed crystal faces, most of which were approximately 0.1–10 μm in diameter. The powder X-ray diffraction pattern (Cu*Kα* radiation) could be entirely indexed as β-Mg_2SiO_4 with space group *Imma* (Horiuchi and Sawamoto, 1981) (Fig. 1). The optical examination also indicated the presence of some (<1%) forsterite in the sample, along with specks of Pt from the capsule material. The IR spectroscopic experiments described below also suggested the presence of minor amounts of the hydrous magnesium silicate phase B ($Mg_{23}Si_8O_{42}H_6$: Akaogi and Akimoto, 1986) and poorly crystallized graphite, which may form a coating on the grains. Although the experiment was nominally anhydrous, the pressure medium for the high-pressure synthesis experiment was pyrophyllite, which is known to dehydrate during high temperature experiments, providing a source for H which may have diffused into the sample during the experiment to give a hydrous component. The graphite may have been derived from the furnace material.

Samples were mounted, polished, and analyzed for Mg, Si, and O using a JEOL JXA-8600 electron microprobe with 15 kV accelerating voltage and 20 nA beam current. O analyses were carried out using 3 mm slits and a lead stearate pseudocrystal in one spectrometer, and Mg and Si analyses were obtained with 550 μm slits and thallium acid phthalate pseudocrystals in the other two spectrometers. Single crystalline MgO was used for Mg and O standards, crystalline Brazilian quartz was used for the Si standard (using quartz as an O standard consistently gave low totals), and the analyses were checked against natural olivine standards. Forty point analyses were obtained for three separate grains. The mean and two standard deviations of these analyses are listed in Table 1. No evidence of deviation from the Mg_2SiO_4 composition was detected within experimental error.

Table 1. Electron microprobe results for β-Mg_2SiO_4

	Atom wt%*	Atom ratio
Mg	34.89 ± 2.10	2.07 ± 0.12
Si	19.44 ± 2.34	1
O	45.55 ± 1.75	4.11 ± 0.15
Total	99.86 ± 2.05	

* Given as the mean and ± two standard deviations of the analyses from 40 point analyses from three different grains.

TEM was performed, using a Phillips 400T electron microscope with an operating voltage of 120 kV, principally to search for possible evidence of dislocations in the sample. Kitamura et al. (1987) have recently shown that hydroxyl groups were associated with the presence of dislocations in natural olivine. Standard bright field convergent beam techniques were used (Hirsch et al., 1965) to examine several grains to a magnification of 300 000×. There was no evidence of dislocations in any of the grains examined.

Unpolarized micro-Raman spectra were obtained for 25 clear grains approximately 2–10 μm in diameter using an Instruments S.A. U-1000 micro-Raman system and a Nachet 40× objective that provided a beam diameter of 1.7 μm at the sample. The grains were sprinkled on a glass slide or KBr disc, as in the IR experiments. Samples were excited with the 514.5 nm line of a Coherent Innova 90-4 Ar ion laser. Approximately 50 unpolarized micro-IR transmission spectra were obtained for a β-Mg_2SiO_4 sample sprinkled on a KBr slide and examined using a Digilab FTS 40 interferometer equipped with a UMA-300A IR microscope with a 32× Cassegrain objective and broad-band HgCdTe detector. The rectangular aperture used for the micro-IR spectroscopy was varied between 15 and 30 μm. Even with the smallest aperture, it was never possible to find a single grain which completely filled the aperture, and most experiments were carried out with three or four 2–10 μm grains (with additional smaller particles probably present) in the field of view. In a few experiments, single large grains (approximately 10 μm across) were found isolated on the slide, and their spectra could be obtained separately.

RAMAN AND IR RESULTS AND DISCUSSION

Raman spectra were obtained for three spectral regions: 600–1000 cm^{-1}, 1200–1800 cm^{-1}, and 3000–4000 cm^{-1}. The 600–1000 cm^{-1} region was recorded to check that the grain was in fact β-Mg_2SiO_4 (McMillan and Akaogi, 1987). A few grains of forsterite were detected in this way, and their spectra in the higher frequency regions were obtained for comparison. All grains, including those in the forsterite samples, showed some fluorescence, which is responsible for the rising background in the 3000–4000 cm^{-1} region (Fig. 2). The absolute intensity of the fluorescence varied from sample to sample and, for some grains, was strong enough to obscure the weak features in the 3000–4000 cm^{-1} region.

In the O-H stretching region, all but two of the micro-

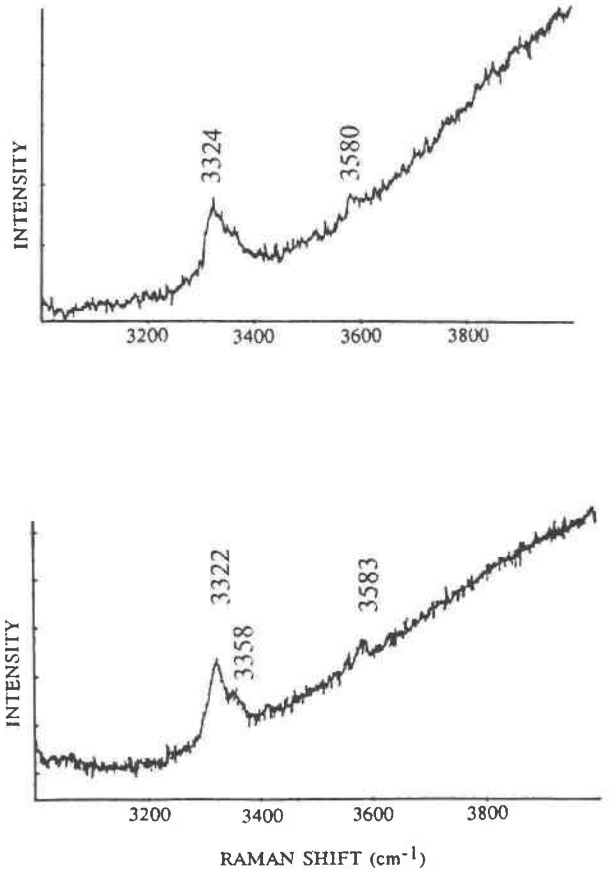

Fig. 2. Micro-Raman spectrum for a typical single grain of β-Mg_2SiO_4 in the region 3000–4000 cm^{-1}, showing the fluorescence background and the features due to O-H stretching (**top**). The spectrum obtained previously (McMillan et al., 1987) for a polycrystalline aggregate of a similar sample is also shown for comparison (**bottom**).

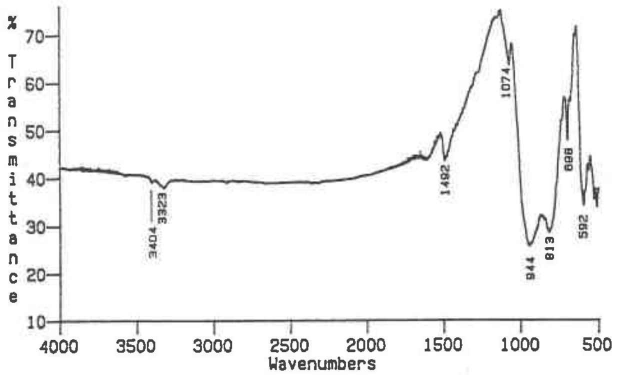

Fig. 3. Micro-IR spectrum of β-Mg_2SiO_4 in the region 500–4000 cm^{-1} obtained with a 30-μm aperture. Several grains filled the field of view.

Raman spectra for β-Mg_2SiO_4 grains were dominated by a broad peak with maximum at 3322 ± 3 cm^{-1} and with a shoulder extending to higher wavenumber, as reported previously for the polycrystalline sample (McMillan et al., 1987; McMillan and Hofmeister, 1988) (Fig. 2). A weaker feature at 3580–3585 cm^{-1} was also obvious for spectra with better signal-to-noise ratio. In two of the spectra obtained for individual β-Mg_2SiO_4 grains, the shoulder near 3360 cm^{-1} was more intense than the peak at 3322 cm^{-1}. The 3360 cm^{-1} band is discussed further below. The persistent observation of the 3322 cm^{-1} peak for individual grains of β-Mg_2SiO_4 suggests that there are O-H groups associated with the synthetic wadsleyite sample. Grains identified as forsterite by their micro-Raman spectra in the 600–1000 cm^{-1} region showed no evidence of any Raman bands in the 3000–4000 cm^{-1} region, in comparable experimental conditions.

A micro-IR spectrum for a 30-μm region containing several grains of β-Mg_2SiO_4 in the 500–4000 cm^{-1} region is shown in Figure 3. The spectrum is representative of all those obtained in this study, although spectra obtained with smaller apertures could not be obtained to such low wavenumber because of interference fringing. Below 1200 cm^{-1}, the spectrum is generally similar to the powder transmission spectra of β-Mg_2SiO_4 reported by Akaogi et al. (1984) and Williams et al. (1986), which had peaks at 1074, 944, 813, 698, and 592 cm^{-1}. In addition, three obvious peaks appeared in the O-H stretching region for all samples (Fig. 4). (An additional weak peak near 3585 cm^{-1} was also observed in most spectra, as with the Raman spectra discussed above.) One peak, occurring at 3323 cm^{-1}, corresponds to the O-H stretching band observed in the micro-Raman spectra. The other two peaks, at 3346 and 3404 cm^{-1}, correspond to the positions of O-H stretching vibrations of the hydrous magnesium silicate phase B ($Mg_{23}Si_8O_{42}H_6$) (Akaogi and Akimoto, 1986). This phase is stable between 10 GPa and at least 16 GPa at temperatures of 750–1200 °C, and its presence as an impurity phase in the present β-Mg_2SiO_4 syntheses is consistent with H_2O being present during the experiments. The relative intensities of the O-H peaks for phase B and the 3323 cm^{-1} band varied from grain to grain, suggesting that phase B is present as a macroscopic impurity in the β-Mg_2SiO_4 sample. The few spectra obtained for large single grains of β-Mg_2SiO_4 showed least contamination with O-H stretching peaks of phase B, suggesting that phase B was present as submicroscopic (less than 1–2 μm) impurities. Based on the absorbance of the 3404 and 3346 cm^{-1} peaks in the IR spectrum relative to the 3323 cm^{-1} band (see below) and the amount of OH component present in phase B (7 wt%: Akaogi and Akimoto, 1986), we estimate that phase B constitutes approximately 0.4% of the β-Mg_2SiO_4 sample.

There was no obvious evidence for the presence of phase B in the micro-Raman spectra. The unpolarized Raman spectrum for a sample of phase B used for the previous IR study of Akaogi and Akimoto (1986) is shown in Figure 5. The low frequency spectrum is dominated by strong bands at 687, 827, and 877 cm^{-1}. None of these were observed in the Raman spectra obtained in the 600–1000 cm^{-1} region for the β-Mg_2SiO_4 grains studied. Phase B also shows Raman active O-H stretching vibrations at

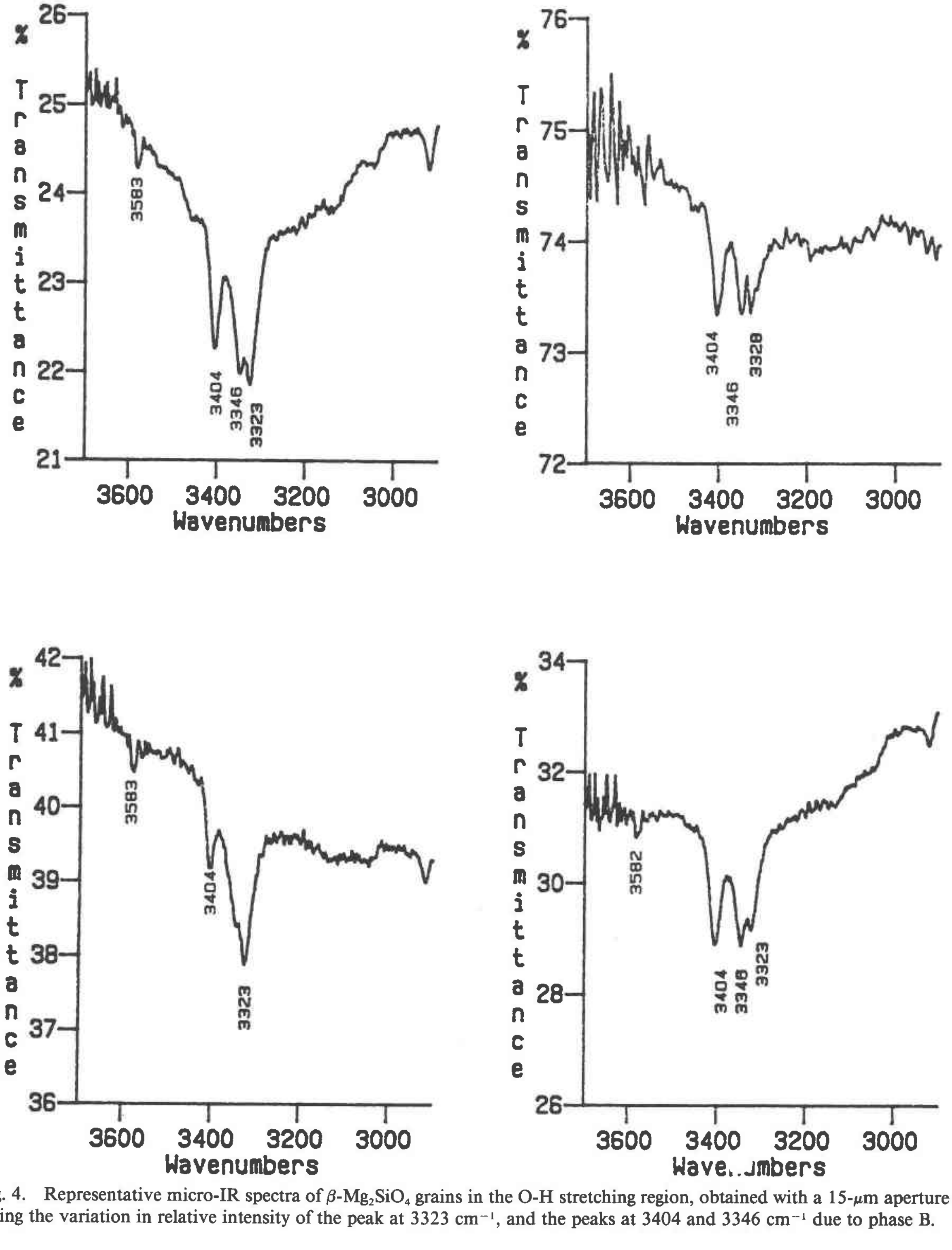

Fig. 4. Representative micro-IR spectra of β-Mg_2SiO_4 grains in the O-H stretching region, obtained with a 15-μm aperture size, showing the variation in relative intensity of the peak at 3323 cm^{-1}, and the peaks at 3404 and 3346 cm^{-1} due to phase B.

3354 and 3414 cm^{-1}, with the higher wavenumber peak approximately twice as intense as that at the lower frequency (Fig. 5; Finger et al., 1989). For this reason, the presence of phase B in the sample cannot be responsible for the shoulder near 3360 cm^{-1}, which was observed for all of the β-Mg_2SiO_4 grains studied and which formed the dominant O-H stretching peak for two of them. The origin of this feature remains unclear, but it is most likely due to an additional OH-containing impurity that has not yet been identified.

In an attempt to study the HOH bending region, Raman spectra were also obtained between 1200 and 1800

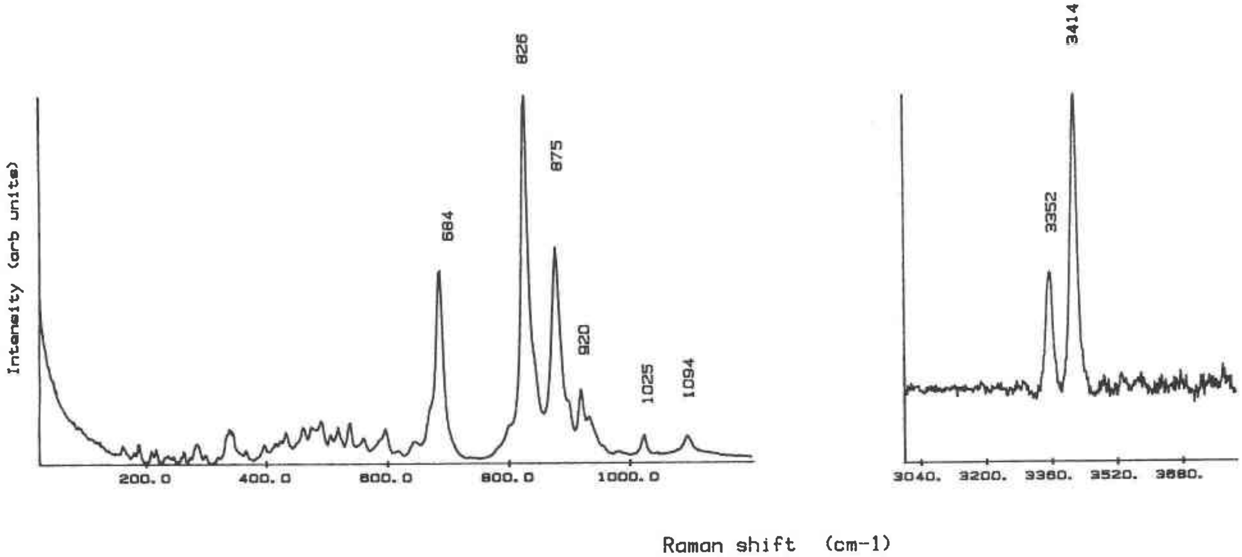

Fig. 5. Unpolarized micro-Raman spectra of phase B.

cm^{-1} (Fig. 6). We observed only two broad bands near 1380 and 1600 cm^{-1}; these bands are characteristic of poorly crystallized graphite (Lespade et al., 1984). This graphite is most likely present as a minor impurity dissolved in or coating our experimental products and probably derived from the furnace material. We are confident that the O-H stretching band at 3322 cm^{-1} is not associated with the graphite impurity, because the disordered graphite bands were also observed in the spectra of forsterite grains within the samples, and these showed no O-H stretching bands.

There is a strong absorption background in the IR spectra above 1400 cm^{-1} (Fig. 3). This could be partly due to the presence of poorly crystallized graphite within our sample (O'Reilly and Mosher, 1983), although the onset of the absorption edge occurs at much lower wavenumbers for both C black and crystalline graphite (Fig. 7). In addition, the micro-IR spectra of forsterite grains within the sample, known to be coated with graphite from the Raman experiments, did not show as intense broad absorption in the IR spectrum. Two peaks at 1494 and 1600 cm^{-1} also appeared consistently in the IR spectra. These could be due to HOH bending vibrations, but their frequencies are a little low for this assignment (especially that of the band at 1494 cm^{-1}) (Aines and Rossman, 1984; Rossman, 1988). Both crystalline graphite and amorphous C show features in this general region (Fig. 6; O'Reilly and Mosher, 1983), but none at precisely the same position. We have no interpretation for these two peaks at the present time.

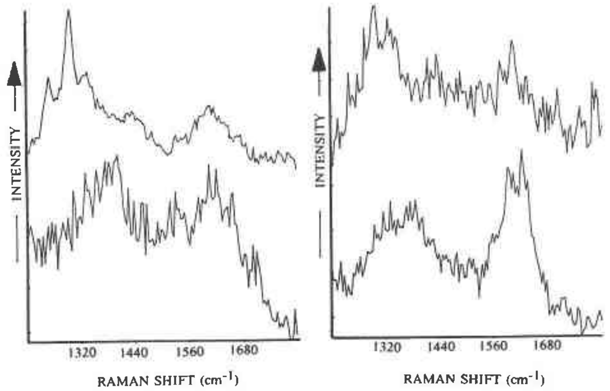

Fig. 6. Representative micro-Raman spectra for individual grains of β-Mg_2SiO_4 in the region 1200–1800 cm^{-1}, showing the bands assigned to poorly crystallized graphite, presumably coating the samples.

Figure 8 shows an expanded view of the O-H stretching region (plotted on an absorbance scale) for a β-Mg_2SiO_4 sample that showed minimal contamination with phase B. The absorbance for the 3323 cm^{-1} peak is approximately 0.025 absorbance units. An approximate value of 200 l/mol·cm can be used for the molar absorptivity of fundamental O-H stretching in minerals (Rossman, 1988) to estimate the OH content of the β-Mg_2SiO_4 sample. For an estimated sample thickness of approximately 10 μm, and using a density of 3.467 g/cm^3 for β-Mg_2SiO_4 (Mizukami et al., 1975), the concentration in wt% OH (i.e., g OH per 100 g β-Mg_2SiO_4) is approximately 0.06%. This is similar to the defect OH content determined for a natural olivine crystal by Beran and Putnis (1983).

PHASE TRANSITION IN β-Mg_2SiO_4

There is some current interest in the mechanism and microstructural changes associated with the α-β transition in Mg_2SiO_4 (Brearley et al., 1989). During our experimental study, we examined the effect of heating, at room pressure, on one sample of β-Mg_2SiO_4. Tsukimura et al. (1988) recently reported results of a single-crystal X-ray study of the lattice parameters and atomic posi-

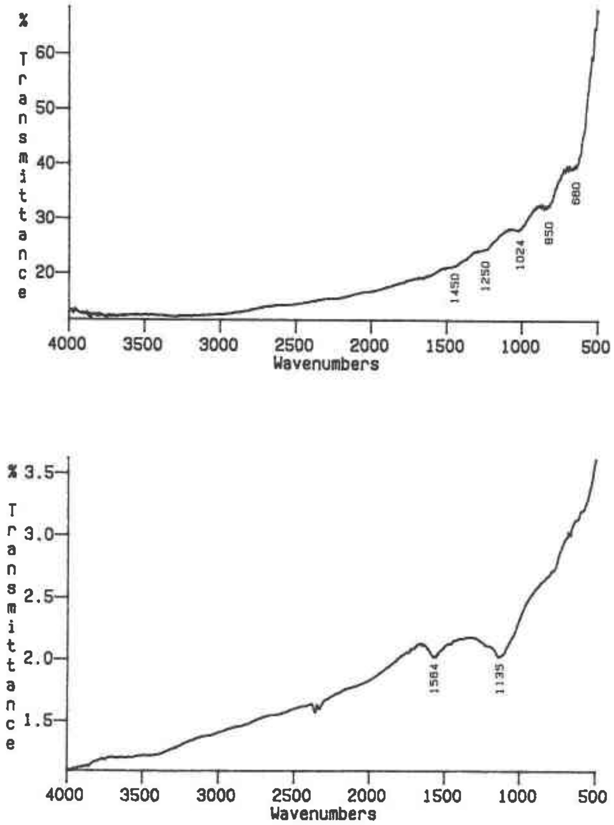

Fig. 7. Micro-IR spectra of crystalline graphite (**top**) and amorphous C black (**bottom**).

tions in β-Mg_2SiO_4 between room temperature and 950 K. These authors observed a sharp decrease in the thermal expansion curves of all three lattice parameters between 800 and 850 K, indicating a structural phase transition. This transition was irreversible and resulted in some cation disorder, but Tsukimura et al. (1988) suggested that the β-Mg_2SiO_4 structure was preserved. On heating to 1050 K, the crystal transformed to the olivine structure, which is the stable form at room pressure.

In our study, the Raman spectra of a sample of β-Mg_2SiO_4 were examined before and after heating to 580 °C (853 K) for approximately 5 min (Fig. 9). After heating, the spectrum resembles that of forsterite (Piriou and McMillan, 1983) except that (1) the bands are broadened and shifted slightly, and (2) additional weak peaks are present in the 600–800 cm^{-1} region. We conclude that the phase transition observed by Tsukimura et al. (1988) represents the metastable reversion of β-Mg_2SiO_4 to forsterite, and that our heated sample corresponds to structurally disordered forsterite (giving rise to the band shifts and broadening) that still contains some SiOSi linkages (responsible for the peaks near 700 cm^{-1}). We made an attempt to study this sample by TEM, but the sample decomposed in the electron beam. We suggest that a study of the β-α Mg_2SiO_4 reversion reaction might prove extremely interesting from a crystal-chemical point of view.

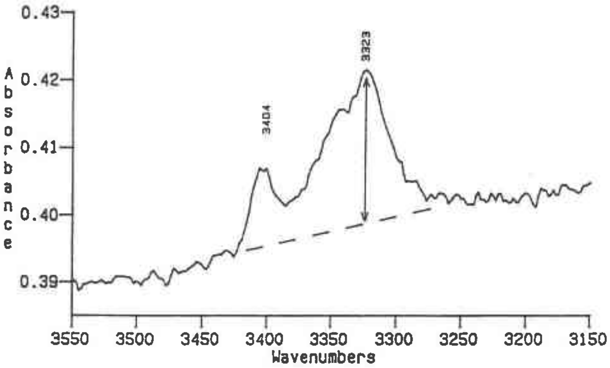

Fig. 8. Micro-IR absorbance spectrum of a large grain (approximately 10 μm across) of β-Mg_2SiO_4 in the O-H stretching region, taken with a 15-μm aperture size. Other smaller grains (less than 1–2 μm) were also probably present in the field of view.

CONCLUSIONS

From our micro-IR and micro-Raman experiments, we conclude that a weak peak at 3322 ± 3 cm^{-1} (and perhaps a weaker peak near 3585 cm^{-1}) in the O-H stretching region is associated with this synthetic sample of β-Mg_2SiO_4. This feature does not appear to be due to an impurity phase. The occurrence of the peak does not ap-

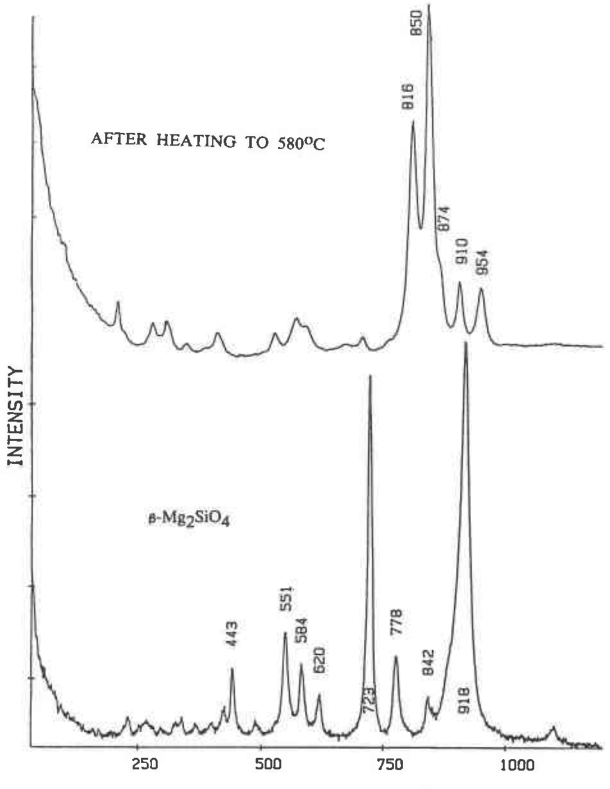

Fig. 9. Raman spectra of β-Mg_2SiO_4 before (bottom) and after (top) heating to 580 °C for 5 min.

pear to depend on the grain size of the samples and is present in both IR and Raman spectra; therefore, we consider that it represents OH in the bulk, and not on the surface, of the sample. From scanning and transmission electron microscopic studies, we saw no evidence for dislocations or inclusions in the β-phase grains, so we suggest that OH is present within the β-Mg_2SiO_4 structure. From the measured IR absorbance, the OH content of the β-Mg_2SiO_4 sample is approximately 0.06 wt%, similar to the concentration of OH defects found in natural olivine samples. The results of this study suggest that β-Mg_2SiO_4 can also accept OH groups into its crystal structure and that crystals coexisting with hydrous phases in the system MgO-SiO_2-H_2O may be partially hydrated. In view of the small amount of OH present, this is unlikely to have dramatic effects on the mineralogy of the transition zone, but could play a major role in impurity-controlled processes such as element interdiffusion and electrical conductivity. Further work will be needed to determine the structural site of these OH groups in β-Mg_2SiO_4 and to determine whether or not samples prepared under different conditions (natural and synthetic) are also hydrated. Finally, our preliminary annealing study of β-Mg_2SiO_4 at room pressure shows evidence of the back reaction to forsterite. Further study of this transition could provide useful insight into the mechanism of the α-β transition in Mg_2SiO_4 at high pressure and temperature.

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