

Measurement of water contents in olivine using Raman spectroscopy

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ABSTRACT

We have measured the water contents in forsterites and olivines synthesized in the multi-anvil press using confocal Raman spectroscopy. These samples were previously characterized for water contents by polarized FTIR and contain from 75 to 1300 ppm wt H₂O. We find that both forsterite and olivine follow the same trend in water content vs. integrated Raman OH/Si intensity. In addition three synthetic enstatites also display a linear trend in water vs. OH/Si integrated Raman intensity but with a different slope than for olivine, indicating that the calibration for measuring water by Raman is matrix dependent. Three glasses of different compositions (two rhyolites and one basalt) and different water contents were also analyzed. Comparison with the forsterites and olivines shows that the Raman cross-section of these glasses is very different and their intensities must be corrected by different factors. Therefore, to be able to use glasses as external calibrants, prior knowledge of their behavior compared to well-characterized NAM standards is necessary.

Keywords: Raman spectroscopy, quantification, water content, olivine

INTRODUCTION

To constrain the deep water cycle, the knowledge of the storage capacity of water in nominally anhydrous minerals (NAMs) of the mantle is a key issue (e.g., Bolfan-Casanova 2005; Férot and Bolfan-Casanova 2012; Tenner et al. 2012). This is tackled by studying hydroxyl abundances in natural samples on one hand, and by investigating experimentally the high-pressure and high-temperature solubility of the water component in NAMs. Compared with natural samples, high-pressure synthetic samples are smaller in size, which introduces a limitation on the accuracy of water content measurements because the techniques developed so far, such as Fourier transform infrared spectroscopy (FTIR, Libowitzky and Rossman 1996; Kovacs et al. 2010; Asimow et al. 2006), secondary ion mass spectroscopy (SIMS, Aubaud et al. 2004; Demouchy et al. 2005), elastic recoil detection analysis (ERDA, Bureau et al. 2009; Withers et al. 2012), and proton-proton scattering (P-P, Maldener et al. 2003) provide a spatial resolution that is quite good but not always sufficient for polymineralic samples. Among these techniques, infrared spectroscopy, being a site-specific technique, provides useful information about the different sites of protonation within the mineral structure, one pitfall being that sufficient thickness is necessary to detect small amounts of water and thus the grain size is a limiting factor (typically thicknesses of 50 to 100 μ m are necessary, implying grain sizes of the same order). The beam size of SIMS or ERDA, which are bulk methods, is comparable to that of FTIR. SIMS is also very useful to measure water-rich samples, i.e., that are too absorbing for FTIR, as is the case of wadsleyite for example (Demouchy et al. 2005; Bolfan-Casanova

et al. 2012), and has in addition achieved quite low-detection limits down to 50 ppm wt H₂O (see Koga et al. 2003; Mosenfelder et al. 2011). A limitation of the method is that it relies on external calibrants with a significant matrix effect (Koga et al. 2003; Mosenfelder et al. 2011). Both SIMS, ERDA, or P-P techniques have recently been used to calibrate the infrared absorption coefficients of the Mg₂SiO₄ polymorphs [Withers et al. (2012) for olivine; Deon et al. (2010) for wadsleyite; Koch-Muller and Rhede (2010) for ringwoodite]. Especially ERDA and P-P are calibration-free methods.

In the past, we have used FTIR to analyze samples that were synthesized in chemically simple systems such as MgO-SiO₂-H₂O, MgO-FeO-SiO₂-H₂O, and MgO-FeO-Al₂O₃-SiO₂-H₂O, and with relatively high-bulk water contents from 5 to 1 wt% H₂O. In these cases grain sizes are relatively large and allow absorbance techniques such as FTIR to be used. However, if the peridotite system is to be studied, and also with lower water contents that are more realistic for the mantle, grain sizes may be reduced and the spatial resolution becomes an important issue to measure water contents. Using Raman spectroscopy beam sizes of 1 $\times$ 3 μ m can be achieved (see Thomas et al. 2009) competing with the diffraction limit of infrared spectroscopy.

In the recent years, Raman spectroscopy has been developed to measure water in glasses (Thomas 2000; Di Muro et al. 2006; Thomas et al. 2008) and has also been used to calibrate the water content in garnets (Thomas et al. 2008) down to 50 ppm wt H₂O. In this study we report for the first time Raman spectra of OH in olivine and apply for the first time Raman spectroscopy for the analysis of water in olivine. We measured both iron-free (forsterite end-member Mg₂SiO₄) and iron-bearing olivine (Mg,Fe)₂SiO₄. We also present preliminary data for enstatite, showing that the method can be extended to any NAM.

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EXPERIMENTAL AND ANALYTICAL METHODS

Samples

The samples from this study are doubly polished thin sections of high-pressure synthetic samples. These were synthesized in a multi-anvil press at Laboratoire Magmas et Volcans by Bali et al. (2008) in the MgO-SiO₂-H₂O system and by Férot and Bolfan-Casanova (2012) in the MgO-FeO-SiO₂-H₂O and MgO-FeO-Al₂O₃-SiO₂-H₂O systems, see Table 1. Three glasses were also analyzed: two natural rhyolites and one synthetic basalt (see compositions in Table 2) to test the external calibration method (see Thomas et al. 2008).

Infrared spectroscopy

Polarized and unpolarized Fourier transform infrared spectra were acquired using a Vertex 70 Bruker spectrometer coupled to a Hyperion microscope equipped with $\times 15$ objective and condenser at Laboratoire Magmas et Volcans (Clermont-Ferrand). To confine the measurement spot, the size of the aperture was varied from 30 to 50 μm . The spectra were measured through a CaF₂ plate with a resolution of 2 cm^{-1} and with up to 2000 scans. The spectra were integrated from 4000 to 3000 cm^{-1} and OH content quantified using the Beer-Lambert law. In previous studies (Bali et al. 2008; Férot and Bolfan-Casanova 2012), we used the Bell et al. (2003) extinction coefficient of 28450 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$. However, Withers et al. (2012) reported new measurements of a suite of olivines synthesized at high pressures using ERDA. They find a new extinction coefficient of 45200 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$, meaning that the values published by Férot and Bolfan-Casanova (2012) are overestimated and should be multiplied by a factor of 2/3. The olivines of Withers et al. (2012) display the same spectral characteristics as ours and thus their extinction coefficient should be the best suited for our samples. Thus in Table 1, we also display the water contents calculated using the extinction coefficient of Withers et al. (2012). In the following of the paper we will only use these values. For enstatite, we used the integrated molar absorption coefficient of 80600 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ (Bell et al. 1995). We used the Beer-Lambert law to calculate the water contents from measured absorbances

$$C(\text{ppm wt H}_2\text{O}) = \frac{A}{\epsilon t} X \quad (1)$$

where C is the concentration (ppm wt H₂O), A is the absorbance, ϵ is the extinction coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$), t is the thickness (cm), and X is the density factor. Density factors of 5358 and 5448 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ were used for olivine and orthopyroxene, respectively, to convert water contents from $\text{mol H}_2\text{O}\cdot\text{L}^{-1}$ into ppm wt H₂O, using the formula $C(\text{ppm wt H}_2\text{O}) = C(\text{mol H}_2\text{O}/\text{L})\cdot X$ with $X = 18.10/\rho$ and ρ the density of the phase (g/cm^3). We used the densities from the literature [olivine: Fisher and Medaris (1969); pyroxene: Chai et al. (1997); Hugh-Jones and Angel (1997)]. Quantitative OH contents were measured using polarized measurements on randomly oriented crystals. Two polarized spectra were acquired for each crystal at 0° and 90° of the extinction position as determined under crossed polars. Five grains of the same phase were analyzed and generally yield good statistics. The orientation of the spectra were determined based on the comparison of the silicate overtone bands of the sample with those of H₂O-free single crystals cut and polished parallel to the three crystallographic axes. For forsterite we used directly the method of Asimow et al. (2006) to recalculate the OH spectra parallel to the principal crystallographic axes and then use these spectra to quantify the absolute water contents by calculating the total absorbance = $A_a + A_b + A_c$, where A_i are the absorbances parallel to the principal axes (see Libowitzky and Rossman 1996). However, for olivine, the difference in composition between our olivines and San Carlos olivine used as the reference for the principal axes overtone spectra, leads to spectral differences in the overtone region that does not allow for recalculation of the OH spectra along the principal axes. In such cases, we found grains that displayed orientations close to the principal directions (see Férot and Bolfan-Casanova 2012, for more details). This method yielded a maximum error of 20% that was calculated as the relative difference in integrated intensity between the overtone spectra of the unknown sample and the overtone spectra of the oriented standard (see Férot and Bolfan-Casanova 2012). The polarized FTIR spectra of forsterite and olivine are shown in Figure 1. The determination of water contents in forsterite, olivine, and pyroxene using polarized infrared measurements were compared to the average of unpolarized measurements (10 acquisitions on 10 separate grains). The average unpolarized absorbance of randomly oriented grains is equal to one third of the total absorbance (Kovacs et al. 2008; see Fig. 2).

Raman spectroscopy

We used a LabRam HR800 spectrometer from Jobin-Yvon equipped with a motorized XY stage, an Olympus confocal microscope with a long distance 100 $\times$ objective at Laboratoire des Sciences de la Terre de l'Ecole Normale Supérieure de Lyon. To maximize the intensity of the beam we used a grating with 600 grooves/mm and excitation wavelength was 514.532 nm. The spectra were recorded using the LabSpec Software from 100 to 1500 cm^{-1} and 2800 to 4000 cm^{-1} by using a Peltier-cooled CCD detector. The laser power was varied from 50 to 240 mW on the first series of measurements on forsterite. For subsequent measurements the power used was kept at 50 or 70 mW. The laser beam was focused on the sample by monitoring the maximum intensity of the most intense silicate vibration band below 1000 cm^{-1} . Because Raman scattering is polarized we analyzed several grains using a half-wave plate to obtain an average spectrum of the silicate and of the OH regions. First, the spectrum of the silicate region was collected with 0.5 to 5 s collection time (see Fig. 3 for olivine and enstatite). The Raman spectrum of the forsterite in the silicate region is similar to that of olivine. In general, no

TABLE 1a. Water content of the olivine samples

Sample	Water content (ppm wt H ₂ O) ^a		Composition (Fo content) ^b
	Bell et al. (2003)	Withers et al. (2012)	
Forsterite ^c			
556	111 ± 11	74 ± 7	100
559	607 ± 61	405 ± 40	100
691	1189 ± 119	793 ± 80	100
Olivine ^d			
955	126 ± 11	84 ± 7	92.6 ± 0.2
923 ^e	184 ± 52	123 ± 35	91.9 ± 0.5
964 ^e	876 ± 147	584 ± 98	91.3 ± 0.1
949	2071 ± 461	1381 ± 307	92.7 ± 0.2
1033	830 ± 260	553 ± 173	92.7 ± 0.2

^a Water contents calculated using the extinction coefficient of 28450 $\text{L}/(\text{mol}\cdot\text{cm}^2)$ from Bell et al. (2003) or 45200 $\text{L}/(\text{mol}\cdot\text{cm}^2)$ from Withers et al. (2012).

^b Forsterite content = $100 \times X_{\text{Mg}}/(X_{\text{Mg}} + X_{\text{Fe}})$, with X being the molar concentration.

^c See Bali et al. (2008) for details.

^d See Férot and Bolfan-Casanova (2012) for details.

^e Samples synthesized in the MFASH system and thus containing trace amounts of aluminum.

TABLE 1b. Water content of the clinopyroxene samples

Sample	Water content (ppm wt H ₂ O) ^a	Composition (En content) ^b
949	1331 $\pm$ 138	92.7 $\pm$ 0.2
964	884 $\pm$ 147	92.8 $\pm$ 0.2 ^c
1033	593 $\pm$ 214	92.7 $\pm$ 0.2

^a Water contents calculated using the extinction coefficient of Bell et al. (1995).

^b Enstatite content = $100 \times X_{\text{Mg}}/(X_{\text{Mg}} + X_{\text{Fe}})$, with X being the molar concentration.

^c Sample synthesized in the MFASH system and containing 0.006 Al per formula unit.

TABLE 2. Composition of the glasses analyzed

Oxides (wt%)	ATHO ^a	Basalt no. 19 ^b	Güney Dag ^c
SiO ₂	74.97 (0.44)	47.3 (5)	76.51
Al ₂ O ₃	11.86 (0.57)	18.6 (2)	12.56
FeO	3.66 (0.11)	8.57 (3)	0.78
MgO	0.10 (0.03)	10.6 (2)	0.01
CaO	1.61 (0.17)	11.73 (13)	0.25
Na ₂ O	4.20 (0.20)	2.24 (11)	4.47
K ₂ O	2.54 (0.08)	0.07 (3)	4.24
TiO ₂	0.24 (0.01)	0.57 (6)	0.03
MnO	0.10 (0.00)	0.15 (2)	0.07
P ₂ O ₅	0.03 (0.02)	0.06 (2)	n.d.
Total	99.30	98.05	98.92
H ₂ O content (wt%)	0.071	0.44	1.10
Densities (g/cm^3) ^d	2.4	2.8	2.3

^a Druitt et al. (1995).

^b Médard and Grove (2008).

^c Olgeir Sigmarsson, personal communication. All water contents measured by FTIR and those of ATHO and Güney Dag by Cluzel (2007).

^d Densities calculated from the data of Lange (1997), Lange and Carmichael (1987), and Ochs and Lange (1997).

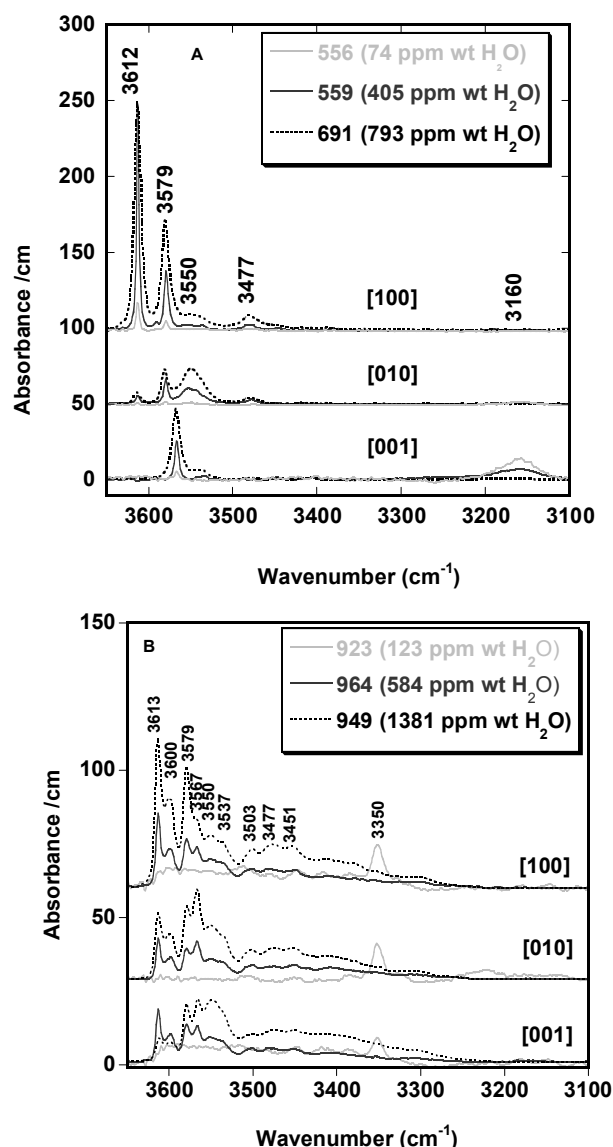


FIGURE 1. Polarized FTIR spectra of (a) forsterite samples from Bali et al. (2008) and (b) olivine samples from Férot and Bolfan-Casanova (2012). Water contents shown are corrected following the extinction coefficient of Withers et al. (2012). Spectra shown are for different orientations and different water contents. The spectra of samples 556 and 923 were multiplied by 5.

baseline correction was needed for the silicate region. Then, the OH-region was measured with an acquisition time of 1 to 200 s. We observed that the forsterites display a very steep fluorescence background (see Fig. 4, due to trace amounts of Cr^{3+} incorporated during synthesis, originating from the LaCrO_3 furnace probably), while the olivines display an almost flat background. The reason why forsterite is contaminated by Cr from the furnace and not olivine is that the forsterite samples were synthesized in Pt capsules while olivine samples were synthesized in double capsules (outer platinum capsule/inner rhenium capsule). The rhenium wall apparently avoids the Cr contamination, while Pt alone does not.

After acquisition, the OH spectra of the minerals were corrected for a linear baseline using PeakFit Package Software (Jandel Scientific) and the area under the OH peaks was integrated using Kaleidagraph. The integrated intensities of both OH and silicate regions were normalized to 1 s and 1 mW. To correct for random fluctuations in intensity, the integrated OH intensity was normalized to the

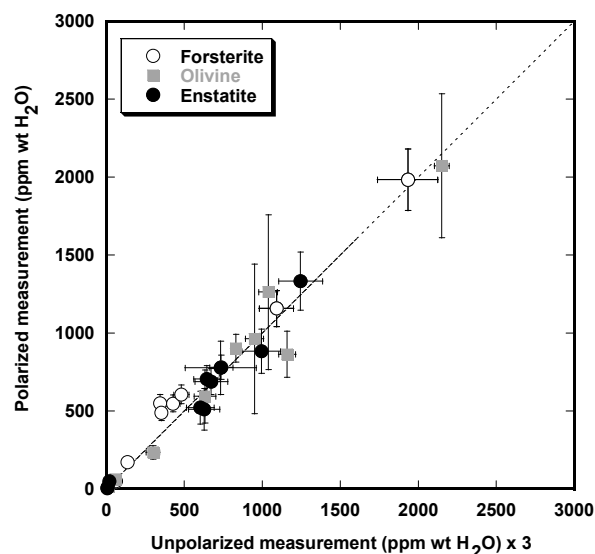


FIGURE 2. Comparison between water concentrations calculated from the average of unpolarized spectra measured on several grains, then multiplied by three following Kovacs et al. (2008) and water concentrations measured using polarized radiation in olivine and enstatite in the MFSH and MFASH systems as measured using selected polarized spectra close to the principal directions from Férot and Bolfan-Casanova (2012) and in forsterite as determined using the method of Asimow et al. (2006) from Bali et al. (2008).

integrated intensity of the silicate region from 200 to 1000 cm^{-1} , and then averaged over all grains from one sample. This defines the OH/Si integrated intensity ratio as introduced by Arredondo and Rossman (2002). The details of the measurements are shown in Table 3. The error in OH/Si due to baseline correction is most of the time within 15% except for the water-poor samples, with a low signal to noise ratio, and for which the error estimated from repeated baseline corrections increases to 50%. The reproducibility of the measurements on olivine was calculated on the basis of two different series of measurements performed at different laser power, see Table 3. When the laser power was similar, 50 and 70 mW, the difference between the values of OH/Si does not exceed 11%. The difference increases to 30% when the power varies from 70 to 140 mW. Concerning forsterite we cannot consider the reproducibility as the variations in power between the different series of measurements were too large (from 240, to 140 to 50 mW).

We also measured an oriented single crystal of San Carlos olivine along the principal directions, and used the polarized spectra in the silicate region to evaluate the degree of misorientation of the final averaged spectra of the olivine unknown samples to analyze. The comparison was performed in the region of major intensity, i.e., between 760 and 900 cm^{-1} . The relative difference between the integrated intensity of the unknowns and that of the standard did not exceed 25%.

The spectra of the glasses are shown in Figure 5. We used a baseline so that the correction was linear under the low-frequency (LF), high-frequency (HF) and water bands. Concerning basalt no. 19 that was repeatedly analyzed throughout the Raman session, the average of the integrated water band for this glass is of $162 \pm 21\text{ cps/mW}$ that is a variability of 13%.

RESULTS

Raman spectra of the forsterites and the olivines in the OH region after baseline correction are shown in Figures 6 and 7. For forsterite, the Raman spectra display the same bands as observed in the FTIR spectra at 3613, 3580, 3550, 3480, 3440, and 3150 cm^{-1} . The latter band is important only in forsterite hydrothermally annealed at pressures of 2.5 GPa. In the case of olivine, the Raman spectra also display bands at 3612, 3599, 3578, 3565, 3544, 3475, and 3352 cm^{-1} . The main difference between Raman and FTIR spectra is that the band at 3613 cm^{-1} has a weak

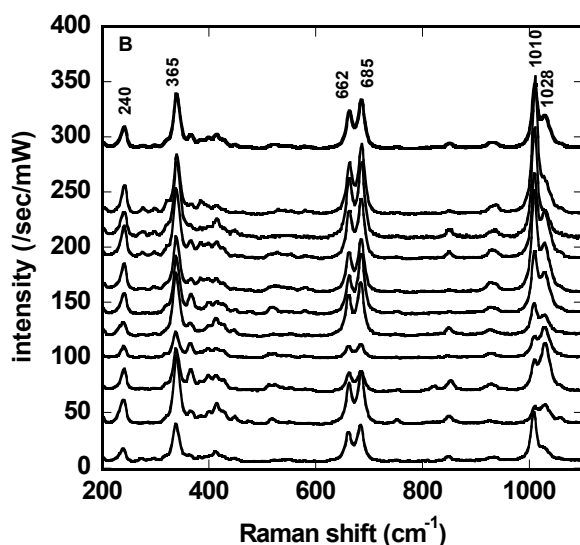
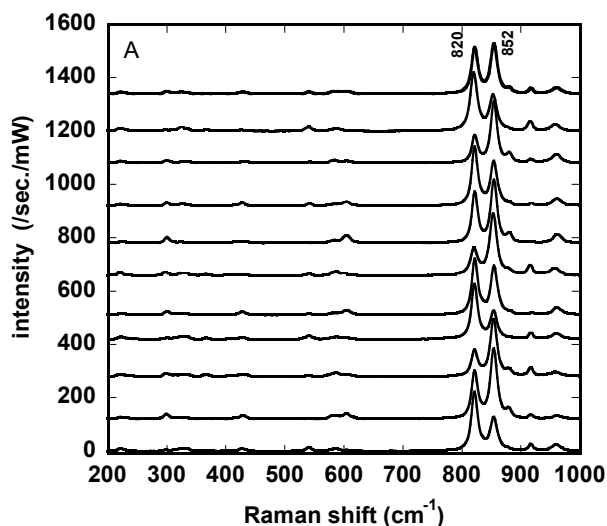


FIGURE 3. Raman spectra of the silicate region of (a) olivine 955 and (b) orthopyroxene 964. The top curves correspond to the average of all spectra. Virtually no baseline correction was necessary.

Raman intensity compared to the other bands, the band at 3580 cm^{-1} being the most intense both in forsterites and olivines.

We note a good sensitivity to water content, and a very similar OH/Si ratio of olivine samples 964 and 1033 that contain 580 ± 100 and 550 ± 175 , respectively, as determined by FTIR (see also the similar averaged spectrum in Fig. 7).

The Raman spectra in the OH region of orthopyroxene 1033 (Al-free, containing 600 ppm wt H_2O) and 964 (Al-bearing, containing 890 ppm wt H_2O) display bands at 3672, 3652, 3598, 3371, and 3495 cm^{-1} , as shown in Figure 8, similarly as observed in the FTIR spectra (see Férot and Bolfan-Casanova 2012). The spectrum of the Al-bearing sample also displays a broader band around 3400 cm^{-1} compared to the Al-free sample, in agreement with the FTIR analysis.

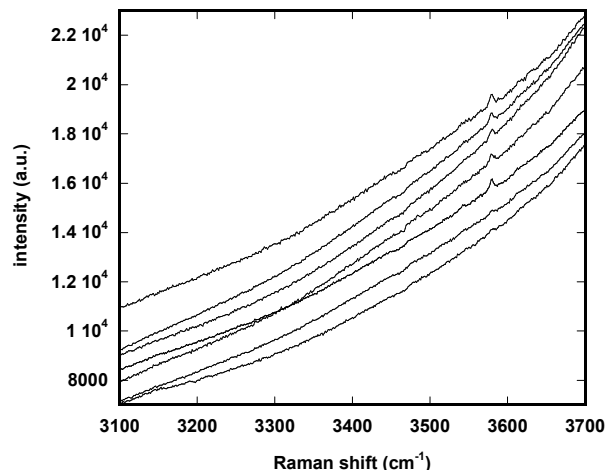


FIGURE 4. Raman spectra of the driest sample used in this study: forsterite 556 containing 75 ppm wt H_2O , measured for 20 s using 140 mW.

Effect of measurement duration

We performed a test of the effect of the beam on the OH intensity of the most hydrous forsterite (no. 691). After measuring successive spectra of 10 s each at 70 mW we note no difference in OH intensity between the six successive spectra, or with the additional spectrum on the same spot but for 60 additional seconds.

Effect of water content on the silicate band region

We note that the integrated intensity of the silicate region decreases with increasing water content as shown in Figure 9. This phenomenon can readily be observed in the Raman spectra of hydrous wadsleyite published in the literature, which usually deteriorate with important band broadening (see for example Frost 1999).

Effect of laser power

Table 3 shows that with increasing laser power from 50 to 240 mW the integrated intensity of the silicate bands and of the OH bands decreases. This is surprising since increasing laser power is expected to increase sampled volume, and hence, Raman intensity. The decrease of Raman bands intensity with increasing laser power could be explained by a self-absorption phenomenon that varies in magnitude with laser power. The net effect on the ratio of OH/Si integrated intensity is that it decreases with increasing laser power. Finally, the effect of laser power on the relationship between water content and OH/Si integrated Raman intensities is that the slope decreases with decreasing laser power. This demonstrates that to quantify the concentration of species using Raman spectroscopy by comparison with the intensity of a reference material, the same laser power should be used.

The relationship between water content, as determined using polarized FTIR and the Raman OH/Si integrated intensity ratio is displayed in Figure 10a. Using this representation, forsterite and olivine both display a linear response and align on the same trend. Also enstatite displays a linear response but with a different slope. Figure 10b displays the water content vs. integrated OH Raman intensity relationship for forsterite and olivine but also includes

TABLE 3. Results of the Raman measurements; only the data in bold were used in Figure 10

Mineral	Sample	Water content (ppm wt H ₂ O)	I_{OH}	I_{Si}	OH/Si ^a	<i>n</i>	Laser power (mW)
Forsterite	556	74 ± 7	3.5 ± 0.9	7310 ± 200	4.8E-04 ± 1.4E-04	3	240
			7.7 ± 2.9	8297 ± 594	9.3E-04 ± 3.8E-04	7	140
	559	405 ± 40	17 ± 11	7420 ± 408	2.3E-03 ± 1.4E-03	4	240
			44 ± 15	9650 ± 938	4.6E-03 ± 1.3E-03	6	50
	691	793 ± 80	64 ± 29	8413 ± 2097	7.6E-03 ± 3.8E-03	4	240
Olivine	955	84 ± 7	84 ± 18	9684 ± 725	1.1E-02 ± 2.1E-03	5	50
			96 ± 34	6840 ± 785	1.4E-02 ± 4.8E-03	12	70
	923	123 ± 35	0.6 ± 0.3	9024 ± 928	6.3E-05 ± 3.6E-05	10	70
	964	584 ± 98	2.8 ± 2.6	6877 ± 542	4.0E-04 ± 3.8E-04	6	215
			64 ± 39	6848 ± 568	9.3E-03 ± 6.5E-03	8	70
	1033	553 ± 173	47 ± 19	4756 ± 825	1.0E-02 ± 4.5E-03	11	70
			46 ± 8	5578 ± 632	8.2E-03 ± 2.1E-03	4	140
	949	1381 ± 307	60 ± 19	5757 ± 425	1.0E-02 ± 3.5E-03	8	70
Enstatite	1033	593 ± 214	117 ± 34	5041 ± 642	2.3E-02 ± 7.0E-03	10	70
			23 ± 3	5907 ± 804	4.0E-03 ± 9.6E-04	8	70
	964	884 ± 147	50 ± 27	5924 ± 1583	7.5E-03 ± 2.3E-03	9	70
	949	1331 ± 138	40 ± 11	4882 ± 1108	8.8E-03 ± 3.7E-03	6	70
Glasses	ATHO	710	44 ± 4			3	70
	Basalt no.19	4400	162 ± 21			12	70
	Güney Dag	11000	581 ± 120			3	70

^a The standard deviation represents the anisotropy of absorption. The error due to misorientation of the average compared to an oriented single crystal of San Carlos olivine does not exceed 25% (see text).

the measurements on the three glasses. We observe that only the ATHO glass falls within the trend defined by the forsterite and olivine data. The linear regression on the olivine data in Figure 10b was used to correct the integrated OH intensity of the three glasses knowing their water contents. This allows estimating the correction factors for the three glasses (1.76 for ATHO, 2.4 for Güney Dag, 1.7 for Basalt no. 19). These correction factors are necessary if such glasses are to be used as external calibrants. These factors include differences in densities between the glasses (see Table 2) and the olivine (3.2 g/cm³), but also differences in absorptivity (see Arredondo and Rossman 2002; Thomas et al. 2008; Mercier et al. 2009), which are difficult to calculate a priori.

DISCUSSION

This study demonstrates that Raman spectroscopy can be used to quantify the water content in olivine. The results show a linear relationship between water content determined from polarized IR and Raman OH/Si integrated intensity ratio. The quantification of water content in natural garnets with Raman spectroscopy has been examined previously (Arredondo and Rossman 2002). Although a positive correlation between H₂O content and OH/Si ratio was observed, the correlation was not considered good enough, probably in relation with the differences in composition of the garnets. These authors examined a wide range of composition in the grossular and spessartine-almandine solid solutions, which could explain the variations in the water content vs. OH/Si. Here, we observe no substantial matrix ef-

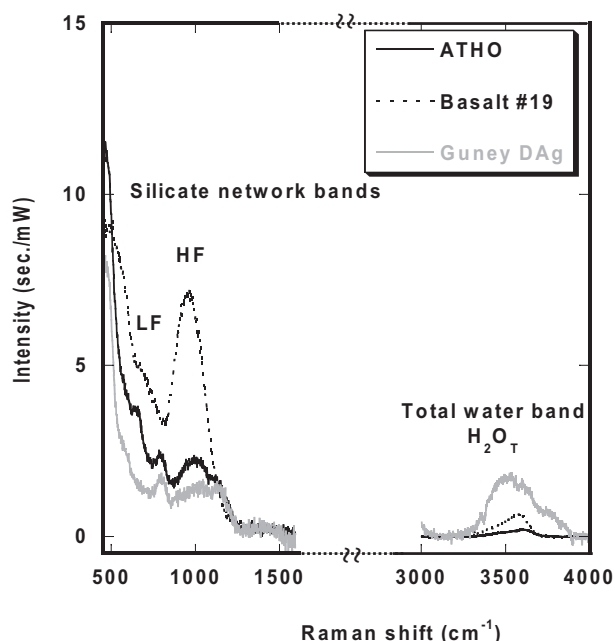


FIGURE 5. Main Raman bands of the glasses (solid black curve is ATHO, dotted curve for basalt no. 19, and gray curve for Güney Dag).

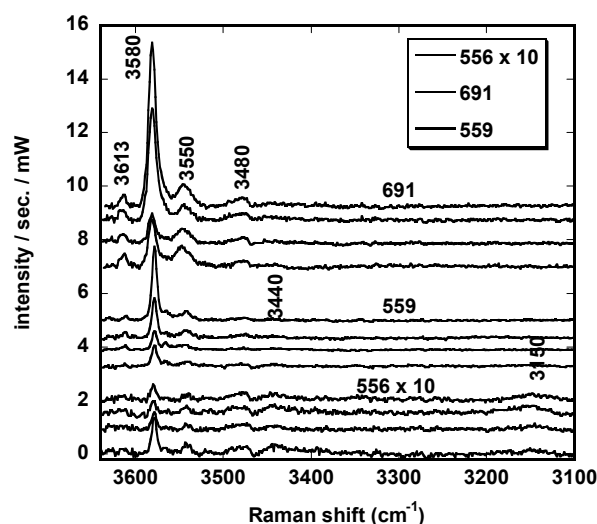


FIGURE 6. Raman spectra of the forsterites in the OH region, recorded at the same power of 240 mW. The spectra measured on several grains are shown and give a representation of the extent of anisotropy sampled. The intensity of the spectra of sample 556 was multiplied by 10 for clarity.

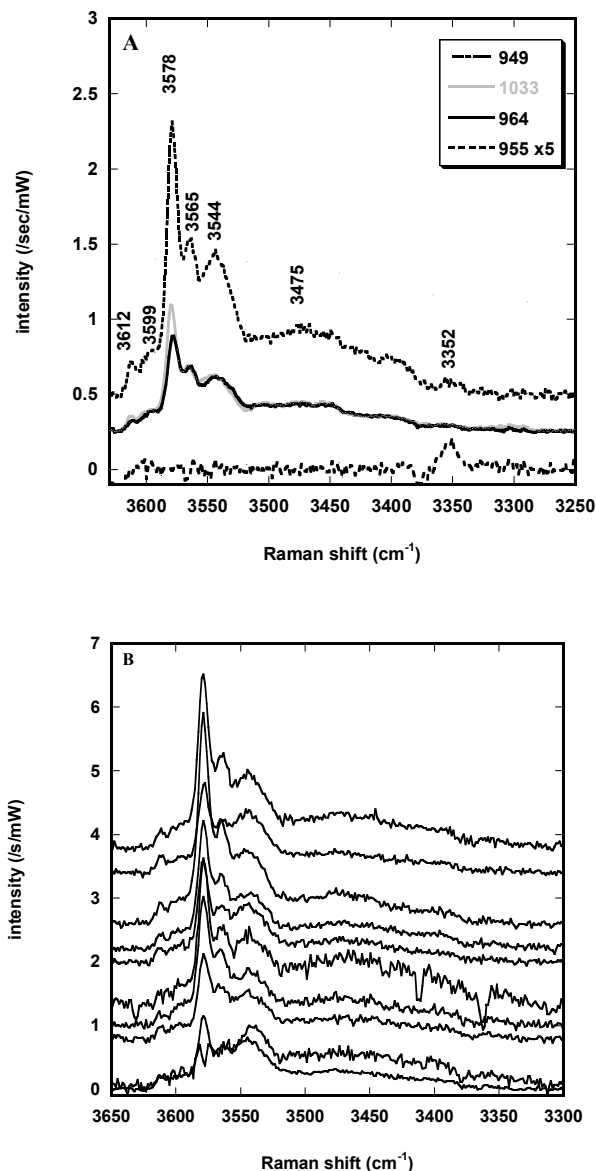


FIGURE 7. (a) Raman spectra of olivines in the OH region. For clarity, only the final total absorbance spectra are shown, which are derived from averaging several measurements on different grains. The intensity of the spectrum of sample 955 is multiplied by 5, also for clarity. (b) Raman spectra of olivine 949 measured along different orientations.

fect as the correlation of water as a function of OH/Si Raman integrated intensity is the same for forsterite and olivine [with composition varying from Fo 91.3 ± 0.1 to 92.7 ± 0.2 , see Férot and Bolfan-Casanova (2012)]. We believe that the water content vs. OH/Si ratio working curve measured here can be used to quantify water in olivines within the range of mantle compositions. More complex variations in garnets are probably due to the complexity of their solid solutions in the natural samples used by Arredondo and Rossman (2002).

As thoroughly explained in the paper by Thomas et al. (2009),

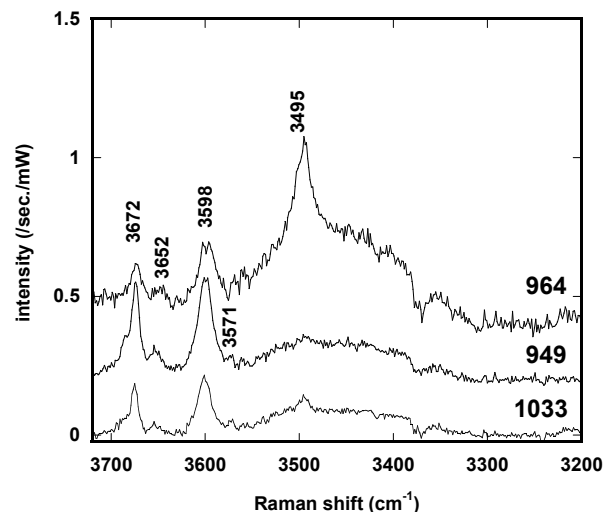


FIGURE 8. Raman spectra of enstatites in the OH region. For clarity, only the averaged spectra are shown. Sample 964 displays a high and broad band at 3495 cm^{-1} , which is due to the presence of Al (in contrast to samples 949 and 1033 that were synthesized in an Al-free system).

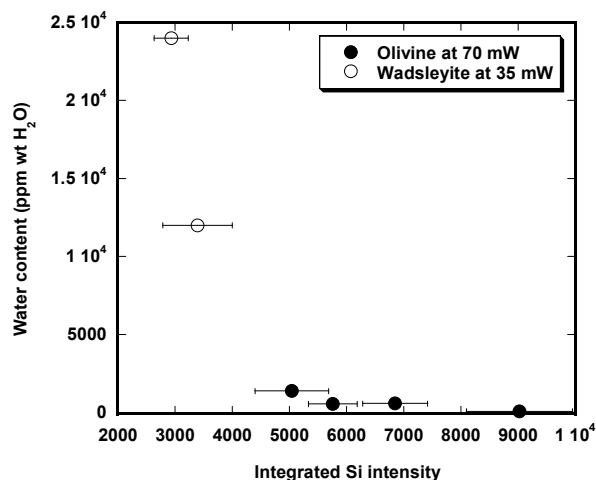


FIGURE 9. Effect of water content on the integrated Raman intensity of the silicate region. Wadsleyite from Bolfan-Casanova (unpublished).

“a linear relationship exists between the measured Raman intensity and the concentration of activated species.” Especially, the relationship between Raman intensity and concentration depends on the scattering cross-section and the excited volume (which includes the effect of density and refractive index). Thus, since the effect of laser power on the intensity is not linear, the measurements on the unknown samples and the standards should be performed under similar conditions of laser beam (laser power and microscope objectives).

To quantify OH contents in minerals with Raman spectroscopy, there are two possibilities: either to rely on the water content vs. Raman OH/Si ratio and compare to well-known standards of the same mineral (Fig. 10a) or rely on the water content vs. OH integrated Raman intensity of a glass standard (Fig. 10b).

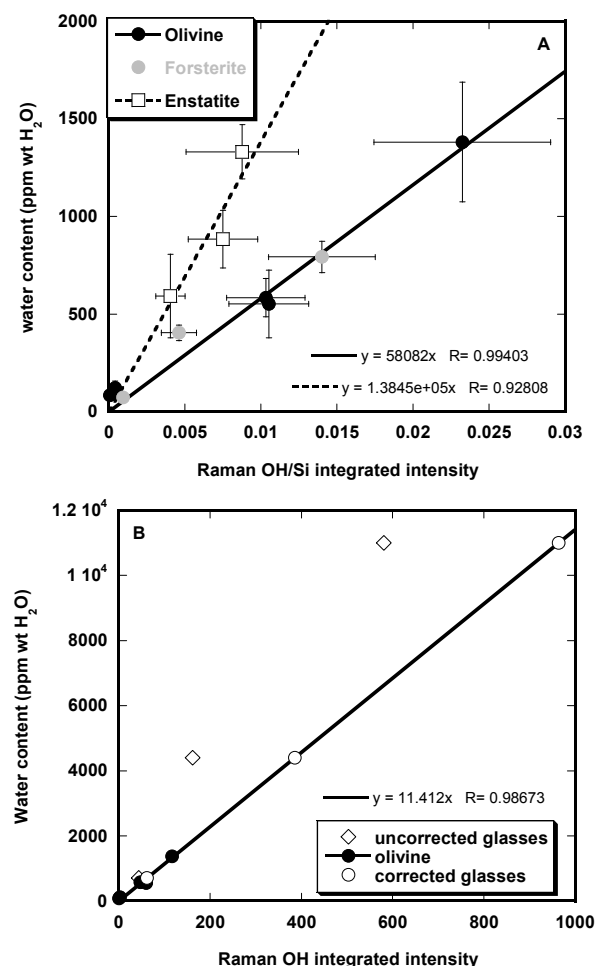


FIGURE 10. (a) Correlation between water content in forsterite and olivine and the integrated OH/Si Raman intensity. Also shown is the trend for enstatite. (b) Correlation between water content and the integrated OH Raman intensity of olivine and of the glasses and the corrected glasses.

In the last case, the correction factor to apply to the intensity of the unknown samples must be known. Indeed, there is a strong matrix effect between glasses and nominally anhydrous minerals. This was treated by Thomas et al. (2008) by correcting for differences in refractive index and density between the glass standard and the minerals they studied, simply through a normalization procedure. This implies knowing the refractive index of our glass which is not the case. For example, in the study of Thomas et al. (2009), they corrected the integrated Raman intensity for density variations between the glass reference material and the garnets $I_{i,\text{sample,corr}} = I_{i,\text{sample,meas}} \times d_{\text{ref}}/d_{\text{sample}}$ (g/cm^3), with $d_{\text{ref}}/d_{\text{sample}} = 0.59 \pm 0.04$. However, this does not take into account for other possible matrix effects such as reflection/refraction, self-absorption, etc. Thus, we find that the best method to constrain the matrix effect, hence the correction factor to apply to the unknowns is to first compare the water-intensity (i.e., water concentration vs. OH Raman intensity) response of the future reference glasses to a pre-established mineral calibration. To align glasses and olivine on the same line, the glasses must be corrected for factors of 1.4,

2.4, and 1.7 for ATHO, basalt no. 19, and Güney Dag, respectively. Such variation in correction factors expresses differences in density and optical properties between the three glasses (see also Table 2). Alternatively, if we want to use ATHO (containing 710 ppm wt H₂O) to measure water in unknown olivine a density correction factor of $0.75 = d_{\text{ref}}/d_{\text{sample}}$ ($d_{\text{ref}} = 2.4 \text{ g}/\text{cm}^3$ and $d_{\text{olivine}} = 3.2 \text{ g}/\text{cm}^3$) must be applied to the integrated intensity of the unknown olivines.

IMPLICATIONS

By using Raman spectroscopy, Thomas et al. (2008) have been able to quantify water in natural garnets and to detect down to 3 ppm wt H₂O by applying 1 W and 600 s conditions. In this study, we measured concentrations as low as 75 ppm wt H₂O in olivine (no. 955) by applying only 70 mW. Also, this work shows how useful Raman spectroscopy can be to analyze water contents in olivines from high-pressure experiments. The method is not as sensitive as FTIR but still water contents of 75 ppm wt H₂O are measurable in olivine. Preliminary data also show that the water content in enstatite can also be quantified by Raman, and thus this method could be extended to all sorts of mantle NAMs. This method should be very useful for analyzing water in small grain sized and polyphasic samples where FTIR or SIMS cannot be applied.

ACKNOWLEDGMENTS

Nathalie Bolfan-Casanova thanks E. Médard and N. Cluzel for providing the glass samples as well as A. Bouhifd for calculating glass densities. The authors also warmly thank Jed Mosenfelder and Istvan Kovacs for their very helpful comments, as well as R. Stalder for the handling of the manuscript. This study was supported by INSU DieTY Program and ANR 11 JS56 015 01 HYDEEP Grant to Nathalie Bolfan-Casanova. This is Laboratory of Excellence ClerVolc contribution no. 68.

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MANUSCRIPT RECEIVED DECEMBER 19, 2012

MANUSCRIPT ACCEPTED SEPTEMBER 10, 2013

MANUSCRIPT HANDLED BY ROLAND STALDER