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 versus integrated Raman OH/Si intensity. In addition three synthetic enstatites also display a linear trend in water versus OH/Si integrated Raman intensity but with a different slope than for olivine, indicating that the calibration for measuring water by Raman is a matrix dependent. Three glasses of different compositions (two rhyolites and one basalt) and different water contents were also analysed. 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, in order 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

In order 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 to 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 (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 µm 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
Mg$_2$SiO$_4$ 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-SiO$_2$-H$_2$O, MgO-FeO-SiO$_2$-H$_2$O and MgO-FeO-Al$_2$O$_3$-SiO$_2$-
H$_2$O, and with relatively high bulk water contents from 5 to 1 wt% H$_2$O. In these cases grain
sizes are relatively large and allow absorbance techniques such as FTIR. 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 1x3 µm 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 H$_2$O. 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 Mg$_2$SiO$_4$) and iron-bearing olivine (Mg$_x$Fe$_{1-x}$SiO$_4$. We also present
preliminary data for enstatite, showing that the method can be extended to any NAM.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

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-SiO$_2$-H$_2$O system and by Férot and Bolfan-Casanova (2012) in the MgO-FeO-SiO$_2$-H$_2$O and MgO-FeO-Al$_2$O$_3$-SiO$_2$-H$_2$O 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 Vertex70 Bruker spectrometer coupled to a Hyperion microscope equipped with x15 objective and condenser at Laboratoire Magmas et Volcans (Clermont-Ferrand). In order to confine the measurement spot, the size of the aperture was varied from 30 to 50 µm. The spectra were measured through a CaF$_2$ 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 l.mole H$_2$O$^{-1}$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 l.mole H$_2$O$^{-1}$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
L.mol\(^{-1}\).cm\(^{-2}\) (Bell et al., 1995). We used the Beer-Lambert law to calculate the water contents from measured absorbances:

\[ C(\text{ppm wt H}_2\text{O}) = \frac{A}{\varepsilon \cdot t} \cdot X \]  

where \( C \) is the concentration (ppm wt H\(_2\)O), \( A \) is the absorbance, \( \varepsilon \) is the extinction coefficient (l.mole H\(_2\)O\(^{-1}\).cm\(^{-2}\)), \( t \) is the thickness (cm) and \( X \) is the density factor. Density factors of 5358 and 5448 l.moles H\(_2\)O\(^{-1}\) were used for olivine and orthopyroxene respectively to convert water contents from moles H\(_2\)O.l\(^{-1}\) into ppm wt H\(_2\)O, using the formula \( C(\text{ppm wt H}_2\text{O}) = C(\text{mol H}_2\text{O/l}) \cdot X \) with \( X=18.10^6/\rho \) and \( \rho \) 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; HughJones 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 H\(_2\)O-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 = \( A_x + A_y + A_z \), 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 **Figure 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 100x objective at Laboratoire
des Sciences de la Terre de l’Ecole Normale Supérieure de Lyon. In order 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 an
half-wave plate in order to obtain an average spectrum of the silicate and of the OH regions.
Firstly, the spectrum of the silicate region was collected with 0.5 to 5 s collection time (see
**Figure 3** for olivine and enstatite). The Raman spectrum of the forsterite in the silicate region
is similar to that of olivine. In general, no baseline correction was needed for the silicate
region. Then, the OH-region was measured with an acquisition time of 1 to 200 seconds. We
observed that the forsterites display a very steep fluorescence background (see Figure 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 second and 1 mW. In order to correct for random fluctuations in intensity, the integrated OH intensity was normalized to the 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 can not 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 mis-
orientation 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#19, that was repeatedly analysed throughout the Raman session, the average of the integrated water band for this glass is of 162 ± 21 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 Figure 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 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 Figure 7).

The Raman spectra in the OH region of orthopyroxene 1033 (Al-free, containing 600 ppm wt H$_2$O) and 964 (Al-bearing, containing 890 ppm wt H$_2$O) 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.

**Effect of measurement duration**

We performed a test of the effect of the beam on the OH intensity of the most hydrous forsterite (#691). After measuring successive spectra of 10 seconds 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 et al., 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 in order 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 polarised 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 versus integrated OH Raman intensity relationship for forsterite and olivine but also includes 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#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 versus OH/Si. Here, we observe no substantial matrix effect 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 Féro and Bolfan-Casanova, 2012). We believe that the water content versus 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), “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).

In order to quantify OH contents in minerals with Raman spectroscopy, there are two possibilities: either to rely on the water content versus Raman OH/Si ratio and compare to well-known standards of the same mineral (Figure 10a) or rely on the water content versus OH integrated Raman intensity of a glass standard (Figure 10b). 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.
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
$I_{\text{sample,corr}} = I_{\text{sample,meas}} \times \frac{d_{\text{ref}}}{d_{\text{sample}}} (\text{g/cm}^3)$, with $\frac{d_{\text{ref}}}{d_{\text{sample}}} = 0.59 \pm 0.04$. 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. In order 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#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 H$_2$O) in order to measure water in unknown olivine a density
correction factor of $0.75 = \frac{d_{\text{ref}}}{d_{\text{sample}}} (d_{\text{ref}} = 2.4 \text{ g/cm}^3 \text{ and } d_{\text{olivine}} = 3.2 \text{ g/cm}^3)$ must be applied to
the integrated intensity of the unknown olivines.

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 H$_2$O by applying 1 W and 600 sec.
conditions. In this study we measured concentrations as low as 75 ppm wt H$_2$O in olivine
(#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 H$_2$O 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.

ACKNOWLEDGEMENTS
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REFERENCES CITED


Figure captions

Figure 1. Polarized FTIR spectra of (A) forsterite samples from Bali et al. (2008), and (B) of 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.

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).

Figure 3. Raman spectra of the silicate region of (A) olivine 955 and (B) orthopyroxene 964. The bold curve corresponds to the average of all spectra. Virtually no baseline correction was necessary.

Figure 4. Raman spectra of the driest sample used in this study: forsterite 556 containing 75 ppm wt H₂O, measured for 20 seconds using 140 mW.

Figure 5. Main Raman bands of the glasses (red curve is ATHO, green curve for Basalt #19 and blue 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. Thick curve represents the average spectrum.

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 (the thick curve corresponds to the average of all spectra).

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).

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.
### Table 1a. Water content of the olivine samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content (ppm wt H₂O)³</th>
<th>Composition (Fo content)⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bell et al. (2003)</td>
<td>Withers et al. (2012)</td>
</tr>
<tr>
<td>Forsterite¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>556</td>
<td>111 ± 11</td>
<td>74 ± 7</td>
</tr>
<tr>
<td>559</td>
<td>607 ± 61</td>
<td>405 ± 40</td>
</tr>
<tr>
<td>691</td>
<td>1189 ± 119</td>
<td>793 ± 80</td>
</tr>
<tr>
<td>Olivine²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>955</td>
<td>126 ± 11</td>
<td>84 ± 7</td>
</tr>
<tr>
<td>923 ⁴</td>
<td>184 ± 52</td>
<td>123 ± 35</td>
</tr>
<tr>
<td>964 ⁴</td>
<td>876 ± 147</td>
<td>584 ± 98</td>
</tr>
<tr>
<td>949</td>
<td>2071 ± 461</td>
<td>1381 ± 307</td>
</tr>
<tr>
<td>1033</td>
<td>830 ± 260</td>
<td>553 ± 173</td>
</tr>
</tbody>
</table>

¹ see Bali et al. (2008) for details
² see Férot and Bolfan-Casanova (2012) for details
³ Water contents calculated using the extinction coefficient of 28,450 L.mol⁻¹.cm⁻² from Bell et al. (2003) or 45,200 L.mol⁻¹.cm⁻² from Withers et al. (2012).
⁴ Samples synthesized in the MFASH system and thus containing trace amounts of aluminum.
⁵ Forsterite content = 100 x XMg/(XMg+XFe), with X being the molar concentration.

### Table 1b. Water content of the clinoenstatite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content (ppm wt H₂O)¹</th>
<th>Composition (Fe content)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>949</td>
<td>1331 ± 138</td>
<td>92.7 ± 0.2</td>
</tr>
<tr>
<td>964</td>
<td>884 ± 147</td>
<td>92.8 ± 0.2 ³</td>
</tr>
<tr>
<td>1033</td>
<td>593 ± 214</td>
<td>92.7 ± 0.2</td>
</tr>
</tbody>
</table>

¹ Water contents calculated using the extinction coefficient of Bell et al. (1995).
² Ferrosilite content = 100 x XMg/(XMg+XFe), with X being the molar concentration.
³ Sample synthesized in the MFASH system and containing 0.006 Al per formula unit.
Table 2. Composition of the glasses analyzed

<table>
<thead>
<tr>
<th>Oxides (wt%)</th>
<th>ATHO $^1$</th>
<th>Basalt#19 $^2$</th>
<th>Güney Dag $^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>74.97 (0.44)</td>
<td>47.3 (5)</td>
<td>76.51</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.86 (0.57)</td>
<td>18.6 (2)</td>
<td>12.56</td>
</tr>
<tr>
<td>FeO</td>
<td>3.66 (0.11)</td>
<td>8.57 (3)</td>
<td>0.78</td>
</tr>
<tr>
<td>MgO</td>
<td>0.10 (0.03)</td>
<td>10.6 (2)</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>1.61 (0.17)</td>
<td>11.73 (13)</td>
<td>0.25</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>4.20 (0.20)</td>
<td>2.24 (11)</td>
<td>4.47</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.54 (0.08)</td>
<td>0.07 (3)</td>
<td>4.24</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.24 (0.01)</td>
<td>0.57 (6)</td>
<td>0.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10 (0.00)</td>
<td>0.15 (2)</td>
<td>0.07</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.03 (0.02)</td>
<td>0.06 (2)</td>
<td>n.d.</td>
</tr>
<tr>
<td>Total</td>
<td>99.30</td>
<td>98.05</td>
<td>98.92</td>
</tr>
<tr>
<td>H$_2$O content (wt%)</td>
<td>0.071</td>
<td>0.44</td>
<td>1.10</td>
</tr>
<tr>
<td>Densities (g/cm$^3$) $^4$</td>
<td>2.4</td>
<td>2.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 3. Results of the Raman measurements. Only the data in bold were used in Figure 10.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample</th>
<th>Water content (ppm wt H₂O)</th>
<th>I_{OH}</th>
<th>I_{Si}</th>
<th>OH/\text{Si} \textsuperscript{1}</th>
<th>n</th>
<th>Laser power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>556</td>
<td>74 ± 7</td>
<td>3.5 ± 0.9</td>
<td>7310 ± 200</td>
<td>4.8E-04 ± 1.4E-04</td>
<td>3</td>
<td>240</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>7.7 ± 2.9</td>
<td>8297 ± 594</td>
<td>9.3E-04 ± 3.8E-04</td>
<td>7</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>559</td>
<td>405 ± 40</td>
<td>17 ± 11</td>
<td>7420 ± 408</td>
<td>2.3E-03 ± 1.4E-03</td>
<td>4</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>44 ± 15</td>
<td>9650 ± 938</td>
<td>4.6E-03 ± 1.3E-03</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>691</td>
<td>793 ± 80</td>
<td>64 ± 29</td>
<td>8413 ± 2097</td>
<td>7.6E-03 ± 3.8E-03</td>
<td>4</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84 ± 18</td>
<td>9684 ± 725</td>
<td>1.1E-02 ± 2.1E-03</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>96 ± 34</td>
<td>6840 ± 785</td>
<td>1.4E-02 ± 4.8E-03</td>
<td>12</td>
<td>70</td>
</tr>
<tr>
<td>Olivine</td>
<td>955</td>
<td>84 ± 7</td>
<td>0.6 ± 03</td>
<td>9024 ± 928</td>
<td>6.3E-05 ± 3.6E-05</td>
<td>10</td>
<td>70</td>
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<tr>
<td></td>
<td>923</td>
<td>123 ± 35</td>
<td>2.8 ± 2.6</td>
<td>6877 ± 542</td>
<td>4.0E-04 ± 3.8E-04</td>
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<td>215</td>
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<tr>
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<td>964</td>
<td>584 ± 98</td>
<td>64 ± 39</td>
<td>6848 ± 568</td>
<td>9.3E-03 ± 6.5E-03</td>
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<td></td>
<td>47 ± 19</td>
<td>4756 ± 825</td>
<td>1.0E-02 ± 4.5E-03</td>
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<tr>
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<td>1033</td>
<td>553 ± 173</td>
<td>46 ± 8</td>
<td>5578 ± 632</td>
<td>8.2E-03 ± 2.1E-03</td>
<td>4</td>
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<td>60 ± 19</td>
<td>5757 ± 425</td>
<td>1.0E-02 ± 3.5E-03</td>
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<td>70</td>
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<tr>
<td></td>
<td>949</td>
<td>1381 ± 307</td>
<td>220 ± 68</td>
<td>9457 ± 546</td>
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<tr>
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<td>117 ± 34</td>
<td>5041 ± 642</td>
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<td>23 ± 3</td>
<td>5907 ± 804</td>
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<tr>
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<td>964</td>
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<td>50 ± 27</td>
<td>5924 ± 1583</td>
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<td>70</td>
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<tr>
<td></td>
<td>949</td>
<td>1331 ± 138</td>
<td>40 ± 11</td>
<td>4882 ± 1108</td>
<td>8.8E-03 ± 3.7E-03</td>
<td>6</td>
<td>70</td>
</tr>
<tr>
<td>Glasses</td>
<td>ATHO</td>
<td>710</td>
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<td>Basalt#19</td>
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<td>Güney Dag</td>
<td>11000</td>
<td>581 ± 120</td>
<td></td>
<td></td>
<td>3</td>
<td>70</td>
</tr>
</tbody>
</table>

\textsuperscript{1} the standard deviation represents the anisotropy of absorption. The error due to mis-orientation of the average compared to an oriented single crystal of San Carlos olivine does not exceed 25 % (see text).
Figure 1

A

556 (74 ppm wt H$_2$O)

559 (405 ppm wt H$_2$O)

691 (793 ppm wt H$_2$O)

B

923 (123 ppm wt H$_2$O)

964 (584 ppm wt H$_2$O)

949 (1381 ppm wt H$_2$O)

Wavenumber (cm$^{-1}$)

Absorbance / cm

[100]

[010]

[001]
Figure 2
Figure 3
Figure 4.
Figure 5.
Figure 6.
Figure 7
Figure 8.
Figure 9
Figure 10.