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Water quantification in silicate glasses by Raman spectroscopy: correcting for the effects of confocality, density and ferric iron

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12 Abstract

13 New series of alumino-silicate glasses spanning a wide range of chemical compositions 14 (basanites, tholeiitic basalts, calcalkaline andesites, peraluminous and peralkaline rhyolites) 15 and with water contents from 0.02 to 6.70 wt % were used for improving the method of 16 quantification of dissolved water with a highly confocal Raman micro-spectrometer. After 17 reconsideration of previously proposed methods for spectra acquisition and post-analysis data 18 treatment, we define the main critical steps that allow minimizing glass matrix effects. First, 19 we carefully assess the variation of Raman band intensities, in both water (~ 3000-3800 cm⁻¹) 20 and alumino-silicate vibration (~ $200-1250 \text{ cm}^{-1}$) regions with focus depth of the laser beam 21 inside the sample. Our results indicate that in the first 2-10 µm depth, the intensity increase in 22 the alumino-silicate region is twice as high as that in the water region. Optimal focus depths, 23 where the signal of the water band is maximum and the intensity ratio of the water band to alumino-silicate band is minimum, vary with glass composition and confocal performance of 24 25 the Raman spectrometer. This influences both external and internal calibration slopes. 26 Second, this study recognizes critical parameters related with glass density, presence of ferric iron and dissolved carbonates as mainly responsible for matrix effects on the internal 27

28 calibration method. (a) We provide a procedure for correcting the effect of glass density on 29 water internal calibration based on the observation that the integrated intensity (i.e. the area) 30 of the alumino-silicate envelope generally drops with the increase of water content and 31 decrease of glass density. (b) In CO₂-bearing glasses, the intensity of the v_1 Raman vibration 32 of dissolved carbonate at ~1087 cm⁻¹ has to be subtracted from the intensity of the alumino-33 silicate envelope before applying the density correction. (c) Using peak-fitting, the intensity of the 850-1250 cm⁻¹ envelope of peralkaline rhyolitic glasses is corrected for the effect of the 34 35 presence of four-fold coordinated Fe^{3+} , as revealed by the strong Raman scattering of the vibrational mode at ~980 cm⁻¹. Following this procedure, all the studied glasses define a 36 37 single calibration line in spite of their compositional variability, when using either of the two classical approaches referred to as *external* and *internal* calibration methods. The linear fits of 38 39 the external and internal calibrations reproduce the whole dataset within 0.13-0.11 wt % (high 40 and standard confocality) and 0.17 wt %, respectively. The accuracy of the external 41 calibration is evaluated based upon comparison with ion-probe measurements of water 42 dissolved in natural glass inclusions: the relative standard deviation is $\sim 4\%$ (1 σ) on average, 43 and reaches ~12% (1 σ) for water contents of ~0.1 wt%.

44

45 Keywords: confocal Raman spectroscopy, water quantification, alumino-silicate glasses,
46 glass density, peak fitting, glass inclusions

47 1. INTRODUCTION

48 Concentration, speciation and distribution of volatile species dissolved in silicate melts 49 are key factors that control the physico-chemical evolution of magmas from their genesis to 50 their final emplacement and affect the dynamics, style, and intensity of volcanic eruptions 51 (e.g., Carroll and Holloway, 1994; Cashman 2004; Sanchez-Valle et al., 2015). Volatiles are also important in mantle processes as they control melting and mantle rheology. Crucial information about volatile contents of magmas and behavior of volatiles at depth is usually recorded in small objects, such as phenocryst-hosted melt and fluid inclusions and tiny pockets of glassy matrix (e.g., Andersen and Neumann, 2001; Métrich and Wallace, 2008).

Raman spectroscopy is a useful micro-analytical technique for identification and 56 57 quantification of volatiles contained in a variety of materials, which are of interest in 58 volcanological and petrological studies, in particular water (regardless of speciation) 59 dissolved in natural glasses. With respect to the other micro-analytical techniques used for 60 quantification of water in rock samples, such as Fourier transform infrared spectroscopy 61 (FTIR), secondary ion mass spectrometry (SIMS), and elastic recoil detection analysis 62 (ERDA), Raman spectroscopy has several advantages: (i) it requires minimal sample 63 preparation, (ii) it is non-destructive, (iii) it allows rapid analysis with high spatial resolution, 64 which is of utmost importance for characterization of small samples and samples with small-65 scale heterogeneity, and (iv) it allows analysis of unexposed glass, fluid and solid inclusions 66 contained in transparent minerals and interstitial glass pockets (e.g., Thomas, 2000; Thomas et al., 2006; Chabiron et al., 2004; Zajacz et al., 2005; Di Muro et al., 2006a; Severs et al., 67 68 2007; Frezzotti et al., 2012; Morizet et al., 2013; Freitas et al., 2017).

Since the work by Thomas (2000), several studies have shown that accurate
quantification of water dissolved in natural glasses can be achieved after proper calibration of
Raman spectrometers (Chabiron et al., 2004; Zajacz et al., 2005; Behrens et al., 2006; Di
Muro et al., 2006a, 2006b; Thomas et al., 2006; Mercier et al., 2009, 2010; Le Losq et al.,
2012; Di Genova et al., 2017). These studies investigated the advantages and limitations of
distinct calibration methods. The first method is called "external calibration", as
quantification of water in the unknown sample is obtained by comparing the intensity (i.e. the

76 height, hereafter I_{OH}) or the integrated intensity (i.e. the area, hereafter A_{OH}) of the water band located around 3570 cm⁻¹ (Fig. 1) with water band intensities or integrated intensities of well-77 characterized standard glasses. The relationship between intensity of the water Raman band 78 79 and water concentration (hereafter referred to as "calibration curve") determined in these studies displays a slope that varies as a function of glass type. Dependence of the slope on 80 81 glass composition is especially apparent when glasses belonging to alkaline and sub-alkaline 82 series are compared (Behrens et al., 2006; Di Muro et al., 2006b; Mercier et al., 2010). 83 According to Mercier et al. (2010), glass reflectance and density, as well as water 84 environment, are the main parameters causing matrix effects on the external calibration. Thus, 85 a set of glass standards spanning a wide range of compositions seems required for accurate 86 quantification of water in natural glass samples.

87 The second calibration method is known as "internal calibration" because the intensity 88 of the Raman water band is normalized to the intensity of bands located in the silicate region: either in the entire alumino-silicate region between 200 and 1250 cm⁻¹ (Behrens et al., 2006; 89 90 Le Losq et al., 2012; Di Genova et al., 2017), the band located at high wavenumbers between 850 and 1250 cm⁻¹ (Zajacz et al., 2005; Behrens et al., 2006; Severs et al., 2007; Mercier et 91 al., 2009), or the band at low wavenumbers ranging from 200 to 650 cm⁻¹ (Thomas, 2000; 92 93 Chabiron et al., 2004; Behrens et al., 2006; Mercier et al., 2009) (Fig. 1). Intensity versus 94 content relationships obtained with an internal calibration procedure are expected to be less 95 affected by instrumental and analytical conditions, such as laser power fluctuations, focusing 96 errors, and differences in confocal volume size, light absorption and reflectance that depend 97 on glass structure and composition. In reality, internal calibrations also depend on glass 98 chemical composition, because both bands in the alumino-silicate region and the average 99 Raman scattering cross section of all the different alumino-silicate structural units (Qⁿ) 100 depend on glass composition (Franz and Mysen, 1995).

101 In order to correct the calibration of water concentration for compositional dependence, 102 some authors have proposed additional normalization procedures taking into account the 103 degree of glass polymerization (Zajacz et al., 2005; Mercier et al., 2010). Le Losq et al. 104 (2012) defined a new protocol for spectra background subtraction that partly eliminates the 105 effects of matrix composition. However, this method tends to overestimate and underestimate 106 the water content of iron-poor and iron-rich samples, respectively (Di Genova et al., 2017). 107 According to Di Genova et al. (2017), the use of different baseline procedures is not sufficient 108 to remove the dependence of the internal calibration procedure on the iron content and 109 oxidation state.

110 So far, there is no satisfactory methodology that allows quantifying the water content in 111 glasses of variable composition using Raman spectroscopy. In this study, we reconsider 112 previously proposed strategies for spectra acquisition and post-analysis data treatment, with 113 the aim to establish the procedures under which a composition-independent calibration can be 114 obtained when applying both external and internal calibration methods. For this purpose, we 115 have studied glasses spanning a wide range of compositions belonging to both sub-alkaline 116 and alkaline magma series. First, we investigate in detail how confocal performance and focus 117 depth of the laser beam affect the calibration and highlight the importance of considering 118 these parameters. Then, the effects of physico-chemical characteristics of alumino-silicate 119 glasses, in particular those in relation to density and presence of ferric iron, are quantified, 120 and we propose correction strategies to minimize matrix effects on the internal calibration. 121 Finally, we test our method by analyzing natural glass inclusions of variable composition, 122 whose water content was measured using SIMS or FTIR techniques.

123 **2. METHODOLOGY**

124 **2.1** Starting materials

125 Thirty alumino-silicate glasses including basanites, tholeiitic basalts, calcalkaline 126 andesites, peraluminous and peralkaline rhyolites were used for calibration of water contents 127 by Raman spectroscopy (Table 1, Fig. 1S). Their polymerization degree (expressed as the 128 ratio of nonbridging oxygens per tetrahedrally coordinated cations, NBO/T) calculated on an 129 iron-free and H₂O-free basis varies from 0.0 to 0.78 (Table 2).

130 Two distinct sets of rhyolitic glasses were synthesized from the Güney Dag obsidian 131 (Turkey; Druitt et al., 1995) and from a peralkaline rhyolite (labeled as NSL) from New 132 Zealand, whose exact provenance is unknown (Behrens and Jantos, 2001) (Table 1). Both 133 rhyolites are very poor in microlites. The Güney Dag rhyolite is mildly peraluminous, SiO₂-134 and Al₂O₃-rich (~77 and 12.5 wt %, respectively), FeO- and CaO-poor (0.8 and 0.25 wt %, 135 respectively) and contains 1.39 wt % H₂O (Mourtada-Bonnefoi and Laporte, 2002). This 136 relatively large H₂O content is due to the water contained in the glass phase of the obsidian 137 $(1.05 \pm 0.05 \text{ wt }\%; \text{Mourtada-Bonnefoi and Laporte, 2002})$ and to the presence of biotite and 138 amphibole microlites (Cluzel et al., 2008). The rhyolite from New Zealand has lower SiO₂ 139 (~75 wt %) and Al₂O₃ (~10 wt %), higher Fe (as total FeO ~4 wt %) and Na₂O (~5.5 wt %) 140 contents, and contains 0.1-0.4 wt % H₂O.

141 Two sets of basaltic glasses were synthesized starting from a primitive high-alumina 142 basalt erupted from the Giant Crater Lava Field (Medicine Lake volcano, California; Médard 143 and Grove, 2008; Malfait et al., 2011) and from tephra erupted from Holuhraun volcano 144 (Iceland) in 2014 (Haddadi, 2016). The composition of the Medicine Lake volcano basalt 145 (labeled as 82-72f) is very close to that of primitive mid-ocean ridge basalts, with a higher 146 Al₂O₃ content (~18.5 wt %). The composition of the basalt from Holuhraun is richer in FeO (~12.5 wt %) and poorer in Al₂O₃ (~14 wt %) and is typical of lavas erupted from the 147 148 Bárðarbunga magmatic system (Sigmarsson and Halldorsson, 2015).

A set of reference glasses with basanitic composition and bearing different amounts of H₂O and CO₂ were synthesized from a natural basanitic tephra sampled at Thueyts volcano (Ardèche, France). The tephra composition is characterized by low SiO₂ (~45 wt %) and high total alkali (~6 wt %).

We also synthesized an intermediate (andesitic) composition closely reproducing the andesites erupted at Mt. Shasta (California, Grove et al., 2002) with a slight difference in Na₂O concentration. The details of the syntheses are presented below.

156

2.2 Experimental Procedures

157 The experimental work was carried out at the Laboratoire Magmas et Volcans 158 (Clermont-Ferrand), except for the synthesis of glasses derived from the NSL and 82-72f 159 starting materials. The synthesis of the 82-72f basaltic set is reported in Médard and Grove 160 (2008) and is summarized in Table 1. Hydrous glasses were synthesized from the NSL 161 rhyolitic obsidian using an internally heated pressure vessel at the Institut für Mineralogie of 162 Hannover (Germany). The natural rhyolitic composition and double-distilled water were 163 sealed in gold capsules and held at 1000 °C and 300-500 MPa for 72-120 h before quenching 164 (for further details see Withers and Behrens, 1999).

165 For the synthesis of the andesitic glasses, we used a decarbonated mixture of oxide 166 (SiO₂, TiO₂, Al₂O₃, FeO, MnO and MgO), silicate (CaSiO₃) and carbonate (Na₂CO₃, K₂CO₃) 167 reagent powders. SiO₂, Al₂O₃, and MgO powders were dried in platinum crucibles in air at 168 1000-1100 °C overnight. CaSiO₃ and carbonate powders were dried in air at 250-400 °C 169 overnight. These dried powders were weighed and ground altogether in an agate mortar to 170 ensure a homogeneous starting mixture. For decarbonation and fusion, the mixture was held 171 in a platinum crucible and heated by a gas-mixing furnace at one bar; as temperature changed, 172 the gas mixture was adjusted to maintain fO_2 near FMQ buffering conditions. Temperature

173 was increased to 1000 °C in 6 hours, kept constant overnight, then increased and held for 30 174 min at 1400 °C before quenching the glass in water. In order to obtain a homogeneous glass, 175 grinding and fusion were repeated a second time. Finally, the glass was ground for two more 176 hours in an agate mortar to produce a very fine powder used in hydration experiments.

Cylinders of natural Güney Dag obsidian were drilled (4.5 mm in diameter, 4-5 mm in
length) and cleaned with acetone in an ultrasonic bath. The Holuhraun basaltic tephra were
crushed into small chips, carefully examined in order to remove possible crustal
contaminants, and then ground in an agate mortar for ~ 2 hours. An analogous procedure was
used for preparation of the starting powder with basanitic composition.

182 Anhydrous glasses were synthesized by re-melting the starting materials in a gas-mixing 183 furnace at one bar, 1300 °C and $fO_2 \sim FMQ$ (Table 1). The starting materials were loaded into 184 Au₈₀-Pd₂₀ capsules whose upper side was left open to allow degassing, held at high 185 temperature for several hours, and finally drop-quenched in water.

186 The hydrous glasses were synthesized in a piston-cylinder apparatus using a Pyrex-187 MgO assembly, a graphite heater, an outer NaCl cell, and Au₈₀-Pd₂₀ capsules (5 and 4 mm outer diameter for 3/4" and 1/2" assemblies, 0.2 mm wall thickness, 4-5 mm length). First, 188 189 deionized water was added at the bottom of the capsule using a micro-syringe; after loading 190 and compacting ~100 mg of glass powders (or cylinders), the capsule was welded shut. We 191 checked for leaks during capsule preparation by weighing the welded capsules before and 192 after 1-hour heating at 120 °C in an oven. For the synthesis of H₂O and CO₂-bearing glasses 193 with andesitic and basanitic compositions (Table 1), we added a mixture of water and oxalic 194 acid dihydrate (C₂H₂O₄·2H₂O) to glass powders. After welding, the capsules were placed in 195 an oven first at 350 °C for 1 hour to decompose the oxalic acid, and then at 120 °C overnight 196 to ensure homogenous distribution of the volatiles. In all experiments, the P-T conditions

197 were chosen to be well above the volatile saturation curve (Duan, 2014). The temperature was 198 measured very close to the capsule by a $W_{95}Re_5-W_{74}Re_{26}$ thermocouple. Hydration 199 experiments were ended by switching off the heating power, quenching the samples at cooling 200 rate > 80 °C/s. Experimental conditions are reported in Table 1.

201 The glasses recovered from the experiments were cut and polished on one or both sides 202 for major element characterization by electron microprobe and water and CO₂ concentration 203 measurements by infrared and Raman spectroscopies. Homogeneity of the glasses was first 204 checked under the microscope. All analyzed glasses were bubble- and crystal-free, except for 205 one andesitic water-rich glass (A011215) that contains microlites crystallized upon 206 quenching. The microlite-bearing glass is not suitable as standard; however, since the 207 percentage of microlites is small and glass composition is homogeneous, it was used for 208 comparison in Raman measurements.

209

2.3 Electron microprobe

Major element composition of glass samples was determined with a CAMECA SX100 electron microprobe (EMP) at the LMV. Glass analyses were performed with 15 kV accelerating voltage, 4-8 nA beam current, and a 20 μ m (10 μ m for basanitic glasses) defocused beam in order to reduce Na loss. The acquisition time was 20 s for Al (and for Mg and Ca in basanitic glasses) and 10 s for the other elements. Average major element compositions of the glasses are reported in Table 2. EMP measurements confirm compositional homogeneity of the studied glass samples.

217

2.4 Infrared Spectroscopy

Total water content of reference glasses was determined by Fourier Transform Infrared
Spectroscopy, using a Bruker Vertex 70 spectrometer coupled with a Hyperion microscope

220 system, housed at LMV. Spectra were recorded using a Globar light source, a KBr

221 beamsplitter and a MCT (Mercury-Cadmium-Tellurium alloy) detector. Plane parallel, double 222 polished glass samples were placed on a CaF₂ window. Absorbance and background spectra 223 of the glasses were obtained by acquisition of 300 and 100 scans, respectively. Beam size was $70 \times 70 \,\mu\text{m}$ and spectral resolution was 4 cm⁻¹. Concentrations of OH groups and molecular 224 225 H_2O were determined from the height of the absorbance bands at 4500 and 5240 cm⁻¹, respectively, using the Beer-Lambert law (e.g. Stolper, 1982). The 4500 and 5240 cm⁻¹ bands 226 227 are commonly assigned to a combination of the stretching vibrations of OH groups attached to 228 Si and the combination of the stretching and bending vibrations of the H₂O molecule, 229 respectively. Total water contents of the basaltic glasses belonging to the Holuhraun set, the 230 basanitic glasses and two water-poor andesitic glasses (A030417 and A040417) were derived 231 from the height of the broad asymmetric band at 3570 cm⁻¹, which contains the fundamental 232 OH stretching vibrations of both molecular H₂O and Si-OH (and Al-OH) structural groups 233 (e.g. Stolper, 1982). Baseline correction (see below) and peak integration were performed 234 using OPUS software. On each sample, we carried out several measurements in order to 235 verify compositional homogeneity. Homogeneity was confirmed by small relative standard 236 deviations (RSD < 5 %) associated with water measurements on each sample.

Sample thickness was typically measured with a Mitutoyo digital gauge, except for very thin or small samples. In the latter case, we measured the sample thickness by reading the vertical displacement of the microscope stage between the top surface of the polished sample and the sample holder accurately determined when the Raman laser beam is focused. The accuracies of the two methods are $\pm 1 \mu m$ and $< 1 \mu m$, respectively. Thicknesses (and associated standard deviations) reported in Table 1 are average values of 4-8 measurements.

Glass density (ρ) was accurately measured with a microbalance using Archimedes'
method and deionized water as the immersion liquid. Two to six repeated measurements on

each glass sample gave reproducibility better than 2 % relative. Densities of the studiedreference glasses are reported in Table 1 and Figure 2.

The largest uncertainty in water contents determined by FTIR analysis is due to the 247 248 uncertainty on the molar absorptivity (i.e. extinction coefficient) for the absorbance bands at 249 4500 and 5240 cm⁻¹. As estimated absorptivity coefficients depend on the baseline subtraction method (e.g. Ohlhorst et al., 2001), we followed guidelines provided by Ohlhorst 250 251 et al. (2001) and Mandeville et al. (2002) for proper choice of baseline fitting procedure and 252 molar absorptivity values. 253 In rhyolitic glass spectra, a linear baseline was fitted as tangent through the minima on both sides of the 5240 cm⁻¹ band and then extrapolated below the 4500 cm⁻¹ band (GG 254 255 baseline of Withers and Behrens, 1999). For peraluminous rhyolites, we used the absorption coefficients provided by Withers and Behrens (1999): $1.52 \pm 0.08 \text{ L mol}^{-1} \text{ cm}^{-1}$ for ε_{4500} (OH) 256 257 and $1.72 \pm 0.06 \text{ L mol}^{-1} \text{ cm}^{-1}$ for ε_{5240} (H₂O). Measured water concentrations in rhyolitic 258 glasses match with target compositions (i.e. the amount of water loaded into the capsule) and 259 are close to the difference of EMP analyses total from 100 wt %. 260 For andesitic glasses, we used the average values of the extinction coefficients determined by King et al. (2002) and Mandeville et al. (2002): 0.97 L mol⁻¹ cm⁻¹ for ε_{4500} 261 (OH), 1.08 L mol⁻¹ cm⁻¹ for ε_{5240} (H₂O), and 66.32 L mol⁻¹ cm⁻¹ for ε_{3570} (total water). 262 263 Mandeville et al. (2002) showed that ε_{4500} and ε_{5240} molar absorptivities have significant

264 compositional dependency and can be predicted if the tetrahedral (Si⁴⁺, Al³⁺) cation /total
265 cation fraction of the glass is known. Molar absorptivity values calculated for the andesitic

266 glasses using the regression line equations provided by Mandeville et al. (2002) are ~ 1.00

and 1.19 (L mol⁻¹ cm⁻¹) for ε_{4500} and ε_{5240} , respectively, which are very close to the adopted

268 values. The baseline of andesitic glass spectra was fitted as tangent through three points: the

269 minima on both sides of the 4500 cm^{-1} band and the minimum on the low wavenumber side of

the 5240 cm⁻¹ band. On its high wavenumber side (at ~ 5400 cm⁻¹), the linear baseline
intersects the absorbance curve. This baseline fitting procedure is analogous to the one
performed by Mandeville et al. (2002). Measured water concentrations in andesitic glasses are
slightly lower than target amounts loaded into the capsule due to minor loss either during
capsule preparation or upon the synthesis experiments.

275 We determined water contents in the basanitic and Holuhraun basaltic glasses based on 276 the height of the absorbance band at \sim 3570 cm⁻¹. This choice was driven by the observation 277 that the spectrum background around the 4500 and 5240 cm⁻¹ bands is strongly affected by 278 the absorption of near infrared and visible electronic transitions or crystal field bands of iron 279 (Ohlhorst et al., 2001). Consequently, baseline fitting around these bands becomes more 280 laborious and the choice of ε_{4500} and ε_{5240} for basanites and iron-rich basalts may be less 281 accurate. In contrast, the linear baseline under the large band at 3570 cm⁻¹ is unambiguously 282 defined. For basanites, we used the molar absorption coefficient provided by Shishkina et al. (2014), 57.3 \pm 1.8 L mol⁻¹ cm⁻¹. For basalts, we adopted the molar absorption coefficient 283 provided by Mercier et al. (2010), $62.8 \pm 0.8 \text{ L mol}^{-1} \text{ cm}^{-1}$, which is very close to the 284 285 coefficient measured by Dixon et al. (1995).

Carbon dioxide concentrations in four basanitic and two andesitic glasses were determined from the heights of the absorbance bands at 1430 and 1520 cm⁻¹, which correspond to antisymmetric stretching of distorted carbonate groups (Dixon et al., 1995). For basanitic and andesitic glasses, we adopted respectively the molar absorption coefficients provided by Shishkina et al. (2014) ($306 \pm 32 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ for 1430 and $349 \pm 25 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$ ¹ for 1520) and those given by King et al. (2002) (269 and 271 L mol⁻¹ cm⁻¹ for the 1430 and 1520 bands, respectively).

Water and CO₂ contents of a few andesitic and basanitic samples measured both by
FTIR and elemental analyzer (Flash 2000 CHNS Thermo Electron housed at LMV) match
within 5 %.

296

2.5 Raman Spectroscopy

Raman spectra were collected at LMV using an InVia confocal Raman microspectrometer manufactured by Renishaw and equipped with a 532 nm diode laser (200 mW
output power), a Peltier-cooled CCD detector of 1024 x 256 pixels, a motorized XY stage and
a Leica DM 2500M optical microscope. Scattered light was collected by a back-scattered
geometry. An edge filter effectively reduced both Rayleigh scattered photons and photons
from the exciting laser source at 0 cm⁻¹ that had been reflected by the sample surface.

303 Laser power on the sample was reduced by filters in order to operate at three different 304 powers of ~1, 8 and 16 mW. Laser power on the sample was periodically checked. A 2400 305 grooves/mm grating was used for the analyses, which resulted in a spectral resolution better 306 than 1 cm⁻¹. A 100x microscope objective (numerical aperture 0.9) was used and the slit 307 aperture was set to 65 µm (standard confocality setting) or 20 µm (high confocality setting). 308 These analytical conditions result in lateral and axial spatial resolutions of ~ 1 and 2-3 μ m, 309 respectively, near the sample surface. Daily calibration of the spectrometer was performed 310 based on a Si 520.5 \pm 0.5 cm⁻¹ peak. The 82-72f#9 basaltic glass was used as internal standard 311 and analyzed several times during each analytical session in order to correct for the 312 dependence of band intensities on delivered energy. The spectra were recorded from ~100 to 1350 cm⁻¹ (alumino-silicate network domain) and from ~2900 to 3800 cm⁻¹ (water domain) 313 314 Raman shifts using Wire 4.2 software. Acquisition times were set to 120-180 s and 120-600 s 315 for the alumino-silicate and water domains, respectively. The longest acquisition was adopted 316 for analysis of water-poor glasses at 1 mW laser power, in order to obtain high signal-to-noise 317 ratios. Under these operating conditions, no melting or water loss was detected. However, we

observed that the Raman signal intensity of the dark H₂O- and Fe-rich basalt from the
Holuhraun set was unstable at the highest laser power we used, possibly due to glass heating
by the laser beam.

321 The lower limit of water detection using the analytical conditions detailed above was
322 measured in olivine-hosted melt inclusions from FAMOUS Zone (Mid-Atlantic Ridge;
323 Schiavi et al., 2016) and was slightly lower than 0.1 wt %.

324 Analytical precision calculated based on repeated daily measurements of reference 325 glasses is generally better than 6 % and 2 % relative, respectively, in water-poor and water-326 rich glasses in highly confocal setting. This difference is mainly related to degradation of the 327 signal-to-noise ratio in spectra of water-poor glasses. Performing measurements under 328 standard confocality conditions yields better analytical precision because the analyzed volume 329 is larger, so Raman signal is more intense and small differences in focusing depth are less 330 critical. We observed that reproducibility decreases for measurements performed on the sample surface, especially for laser powers < 10 mW. When the laser beam is focused on the 331 332 sample surface, in fact, small variations of the excited sample volume are more likely to occur 333 because the beam is not entirely inside the sample and reflectance at the sample surface has a 334 more important effect.

In this study, reference glasses for Raman spectroscopy analysis were prepared as large free chips (i.e. not embedded in epoxy resin or other embedding medium). We verified the homogeneity of the reference glasses by acquiring several spectra on each glass during the same analytical session. In addition, repeated measurements confirmed that no water loss occurred over several months. In A011215, presence of microlites was not detected most likely due to wide spacing between microlites relative to the diameter of the analysis spot.

341

342 **3. GLASS DENSITY**

343 Figure 2 shows the relationship between glass densities, ρ (kg/m³), and water contents, 344 $C_{\rm H2O}$ (wt %), determined by FTIR spectroscopy or SIMS (Table 1). A linear relationship $\rho =$ 345 $\rho_0 + b C_{\rm H2O}$, where ρ_0 is the density of the anhydrous glass and b the slope of the line, is 346 observed. Density diminishes with increasing water content. The slope for mafic glasses is 347 more important than the ones for intermediate and felsic glasses. The slopes defined by the 348 rhyolitic and andesitic sample sets are in agreement with those found by Ohlhorst et al. (2001) 349 and Behrens et al. (2006) for similar glass compositions. Moreover, the measured rhyolitic 350 and andesitic glass densities are very close to densities measured by Withers and Behrens 351 (1999) and Mandeville et al. (2002). The slope obtained for the 82-72f basaltic set is slightly 352 more pronounced than the slope reported by Ohlhorst et al. (2001) for basaltic composition. 353 As expected, the Fe-richer sets of basaltic and rhyolitic glasses are characterized by higher 354 densities than the Fe-poorer sets. The measured basanitic glass densities fall within the range 355 of values calculated by Iacovino et al. (2016). Density of the A011215 sample is aligned with 356 that of the other andesitic glasses, even though it contains microlites.

357 4. RAMAN SPECTRAL TREATMENT

358 *4.1 Baseline fitting*

Raman spectra of glass samples required baseline correction before being used for quantification of volatile species. In fact, a high signal intensity characterizes glass spectra at low wavenumbers (i.e. small Raman shifts, Fig. 3) due to the influence of the intense Rayleigh diffusion tail superimposed by the boson peak (e.g. Le Losq et al., 2012). Long (1977) was the first to highlight the need for correcting the raw spectra for the dependence of Raman scattering on frequency and temperature. Glasses, in particular rhyolitic ones, can be affected by fluorescence, which modifies the shape and intensity of the spectrum background.

Moreover, the slope of the background is influenced by the total glass iron and oxidation degree (Di Muro et al., 2009). As spectrum topology strongly depends on glass composition and degree of polymerization, baseline correction is a critical step in the treatment of Raman spectra, especially in the alumino-silicate vibration region (Figs. 3 and 4). On the other hand, the baseline subtraction procedure does not affect significantly the treatment of the total water band around 3570 cm⁻¹.

372 In previous studies, different approaches were adopted for defining the baseline shape 373 and the choice of anchor points (e.g., Zajacz et al., 2005; Behrens et al., 2006; Severs et al., 374 2007; Di Muro et al., 2009; Mercier et al., 2009, 2010; Le Losq et al., 2012). A first approach 375 consisted in fitting the baseline of raw spectra using either a combination of linear baselines 376 (Severs et al., 2007), a cubic baseline (Mercier et al., 2009) or a cubic spline baseline 377 (Behrens et al., 2006) with three/four anchor points in the alumino-silicate vibration region 378 and two anchor points in the water domain (Fig. 1). Zajacz et al. (2005) used a linear extrapolation of the flat signal from the 1250–1850 cm⁻¹ spectral region towards low 379 380 wavenumbers (Fig. 1). Such an extrapolation is possible only if the spectral background between 1250 and 1850 cm⁻¹ is not too steep. In a second approach, the baseline was 381 382 subtracted from spectra that had been previously corrected for Long's correction (Long, 383 1977). Behrens et al. (2006) and Di Muro et al. (2009) adopted, respectively, a cubic spline 384 and a cubic baseline anchored only at the extremities of the alumino-silicate and water 385 domains, whereas Le Losq et al. (2012) anchored the spline to a limited number of 386 intermediate minima. In general, we observe that discrepancies between different spectral 387 corrections arise from unconstrained concavity of the spline baseline. 388 Difficulties are encountered in fitting the baseline in the alumino-silicate vibration 389 region, because there is no simple *a priori* way to relate the shape of broad Raman bands to

390 specific network vibrations and structures, although statistical analysis and peak fitting

391 algorithms provided interesting results in this direction (e.g., Herzog and Zakaznova-Herzog,

2011; Woelffel et al., 2015). Moreover, overlapping of bending and stretching bands occurs in
the alumino-silicate region (e.g. Mysen et al., 1980), resulting in substantial uncertainty in
selecting physically meaningful anchor points. The observed minima between the bands, in
fact, may include contributions of the vibration bands (e.g. Le Losq et al., 2012).

396 For baseline correction and subsequent peak integration, we used PeakFit package 397 software (Jandel Scientific). We used several procedures based on subtraction of linear (more 398 often a sequence of linear segments) and cubic baselines from raw spectra or Long-corrected 399 data (Fig. 3). Choice of anchor points for definition of linear and cubic baselines was dictated 400 by two requirements (Le Losq et al., 2012): 1) making our procedure simple and reproducible, 401 2) minimizing the arbitrariness due to operators' choices. In the alumino-silicate network 402 domain, we first fixed the anchor points at the two extremities of the spectrum where no 403 Raman signal occurs. In the case of linear baselines, these are tangent points to the curve (Fig. 404 3), whereas a wider range of points on the background was selected for cubic baselines. So, 405 anchor points at the two extremities were fixed at 340-360 and 1190-1200 cm⁻¹ in basanitic glass spectra, at 300-340 and 1200-1220 cm⁻¹ in basaltic glass spectra, at 230-250 and 1230-406 1250 cm⁻¹ in andesitic glass spectra, and 190-210 and 1250-1260 cm⁻¹ in rhyolitic glass 407 408 spectra. For cubic baselines, the background at the high frequencies was extended up to 1350 409 cm⁻¹. Then, a minimal number of intermediate anchor points were set in order to: a) prevent 410 linear baselines from crossing the spectrum, especially in rhyolites, and esites and basalts 411 spectra, and b) minimize the influence of the background characterized by different slopes at 412 the low frequencies, especially in basanites spectra (Fig. 3). For these reasons, an intermediate anchor point was placed near 630 and 640 cm⁻¹ in basanitic and basaltic glasses, and in the 413 645-700 and 670-710 cm⁻¹ ranges in andesitic and rhyolitic glasses, respectively. Around the 414 minimum at 670-710 cm⁻¹ of rhyolitic spectra, linear baselines resemble cubic baselines, as 415

416 several short linear segments are necessary to fit the curve. A second intermediate anchor point was set around 800-830 cm⁻¹ in basalts, 825-840 cm⁻¹ in andesites, and ~840 cm⁻¹ in 417 rhyolites. We did not fix an anchor near 820 cm⁻¹ in basanites because the corresponding 418 419 minimum tends to disappear in H₂O and CO₂-bearing basanites. The defined anchors 420 correspond to minima regions, and in some cases are defined by tangent lines to the spectra. 421 We note that the positions of the intermediate anchor points and that of the anchor at the high 422 wavenumber end of the spectrum shift to higher frequency as the polymerization increases, in 423 agreement with previous observations (Le Losq et al., 2012).

In the water domain of the spectra, linear baselines were anchored (~2980 and 3780 cm⁻¹) and cubic baselines were fit (from 2980 to 3000-3008 and from 3725 to 3780 cm⁻¹) at both band extremities without any distinction between glasses of different composition. As the shape of cubic baseline is more sensitive to the topology and length of the fitted background, the more adequate cubic fitting was considered the one with the closest match of the baseline on the background on both sides of the band.

430

) 4.2 Alumino-silicate band topology and assignment

431 4.2.1 Topology of Raman spectra

In the alumino-silicate region of the Raman spectrum (200 to 1250 cm⁻¹), glass samples typically show two main broad bands. The position of the bands and their topology, i.e. relative band intensities, band shape and FWHM (full width at half maximum), vary from one sample to another (Fig. 4), as they depend on glass structure, chemical composition and oxidation state. Note that the spectral features detailed in the following section are scarcely affected by the chosen method for baseline correction.

In basanitic and basaltic glasses, the most intense band occurs at higher frequency than
the less intense one (Fig. 4). Following previous studies (Mercier et al., 2009), we label these

440 bands as High-Frequency (HF) and Low-Frequency (LF) bands. Increasing water content in 441 basanitic and basaltic glasses has several effects: a) the maximum peak position of the LF bands shifts from 556 to 510 cm⁻¹ and from 532 to 512 cm⁻¹ in basanites and basalts, 442 respectively; b) the maximum peak position of the HF bands shifts from 968 to 975 cm⁻¹ in 443 444 basanites, and from 966 to 990 cm⁻¹ in basalts. c) The FWHM of the HF band slightly decreases from 181 to 164 cm⁻¹ and from 184 to 177 cm⁻¹ in the Fe-rich (Holuhruan) and 445 446 high-Al (82-72f) basaltic sets, respectively (Fig. 2S b). d) In basalts, the ratio of LF band 447 (integrated) intensity to HF band (integrated) intensity increases due to apparent decrease of 448 the HF band height (Fig. 2S d). The latter observation is in agreement with previous observations on different basaltic glasses (Mercier et al., 2009). A shoulder at ~580 cm⁻¹ 449 characterizes the LF bands. A broad weak band centered at ~710 cm⁻¹ defines the spectrum 450 451 topology in the intermediate wavenumber range (650-800 cm⁻¹). In basanites, the relative 452 intensity of this middle-region band with respect to LF and HF bands is higher than in the other glasses, and increases with the volatile content. Dissolved CO_3^{2-} molecules in basanites 453 produce a peak near 1083 cm⁻¹, whose intensity increases with the CO₂ content, in agreement 454 455 with Morizet et al. (2013).

With increasing polymerization, the relative intensity of the two main silicate bands
inverts and the LF and HF maximum peaks shift, respectively, to lower and higher
frequencies, in agreement with previous studies (e.g., Matson et al., 1983; Mercier et al.,
2009). Moreover, the FWHM of the LF band diminishes with increasing degree of
polymerization (Figs. 2S e,i).

In andesitic glasses, the maximum peak of the LF band occurs at $488 \pm 3 \text{ cm}^{-1}$. The broader HF band is centered at ~1013-1022 cm⁻¹ (with the only exception of the A071215 glass whose maximum peak is at 970 cm⁻¹). The ratio of LF band (integrated) intensity to HF

band (integrated) intensity increases with increasing degree of polymerization (Fig. 2S g). With increasing water content, the FWHM of the LF band decreases from 137 to 114 cm⁻¹ (Fig. 2S f). As in basalts, the LF band exhibits a shoulder at ~580 cm⁻¹. A small asymmetric band centered at 795 cm⁻¹ is present in all andesitic glasses (Fig. 4). Dissolved CO_3^{2-} molecules in A310317 and A030417 glass samples produce a peak near 1078 cm⁻¹, which is more pronounced in A310317.

470 Rhyolitic glasses are characterized by a main asymmetric band centered at 467-484 cm⁻ 471 ¹. Maximum LF peak position shifts to higher frequency with increase of water content 472 dissolved in the glass, contrary to what is observed in basalts. Its FWHM varies from 122 to 130 cm⁻¹ and from 134 to 145 cm⁻¹ in the peraluminous (Güney Dag obsidian) and peralkaline 473 474 (NSL obsidian) glass sets, respectively; there is a negative correlation between FWHM and water content (Fig. 2S j), as pointed in andesitic glasses. In the peraluminous rhyolites, the LF 475 band has a shoulder at ~580 cm⁻¹. A small band centered at 795 cm⁻¹ is present in all rhvolitic 476 477 spectra; its intensity slightly decreases with increased water content of peraluminous glasses. 478 Major differences between the two glass sets and within each set are principally observed in 479 the high wavenumber range (850 to 1200 cm⁻¹). In this range, the spectra are defined by 480 several sub-bands, whose position, shape and relative intensities are strongly affected by glass 481 composition and degree of polymerization (Fig. 4). Peraluminous rhyolites spectra show a 482 less intense band centered at ~930 cm⁻¹ and a more intense band centered at ~1135 cm⁻¹. The intensity of the band near 930 cm⁻¹ slightly increases with water content. In the peralkaline 483 rhyolites, instead, the band occurring at 1135 cm⁻¹ is much smaller than the band located 484 485 around 980 cm⁻¹. Compared to the glasses of the same set, the water-poor NSL-N1 glass 486 differs in that its spectrum has a more pronounced band near 1050 cm⁻¹.

487

4.2.2 *Review of the interpretation of bands*

488	In the 200-1300 cm ⁻¹ region of the Raman spectrum, bands correspond to different
489	bridging and non-bridging T-O vibrations in the glass structure (e.g., Brawer and White,
490	1977; Matson et al., 1983; McMillan, 1984; McMillan et al., 1992). The LF band near 400-
491	500 cm ⁻¹ , which is dominant in polymerized glasses, is traditionally assigned to: a) rocking
492	motion in fully polymerized Q^4 units (where Q^4 denotes a tetrahedron linked by bridging O
493	atoms to 4 adjacent tetrahedra), b) breathing modes of four- and six-membered rings of TO ₄
494	tetrahedra in polymerized glasses (Sharma et al., 1981; Matson et al., 1983; Rossano and
495	Mysen, 2012), but also c) T-O-T symmetric stretching vibrations involving bridging oxygens
496	and four-fold coordinated cations (Zotov et al., 1992) and d) T-O-T bending vibrations in
497	glasses containing non-bridging oxygens (McMillan, 1984; Rossano and Mysen, 2012 and
498	references therein). In rhyolitic glasses, decreasing FWHM of the LF band (Fig. 2S j) and its
499	shift to higher frequency with increasing water content have been explained by a possible
500	decrease in the average T-O-T angle (McMillan and Remmele, 1986).
501	The vibrational mode at 570-580 cm ⁻¹ has been attributed to either structural defects
502	(i.e. broken oxygen bridges, Stolen and Walrafen, 1976; Seifert et al., 1981; McMillan and
503	Remmele, 1986) or a mixed stretch-bend vibration in Q^2 structural units (Furukawa et al.
504	1981). The bands near 700 and 800 cm ⁻¹ have been respectively ascribed to T-O-T bending
505	motions (Mysen et al., 1980; Furukawa et al. 1981; McMillan, 1984; Rossano and Mysen,
506	2012) and to cage-like vibrations of Si atoms mainly in Q^4 tetrahedra (Zotov and Keppler,
507	1998).

The main HF envelope at 900-1200 cm⁻¹ can be decomposed into several bands associated with localized symmetric and asymmetric T-O and T-O-T stretching modes of distinct structural species, i.e. Q^2 , Q^3 , Q^4 (2, 3, 4 being the number of bridging oxygens; Mysen et al., 1980; Matson et al., 1983; McMillan 1984; Zotov and Keppler, 1998; Rossano and Mysen, 2012). Substitution of Al³⁺ and Fe³⁺ for Si⁴⁺ as network-forming cations strongly 513 influences the spectral composition of this band; in particular, increasing the Al content of the 514 glass results in the shifting of Raman bands to lower frequencies (Brawer and White, 1977; 515 Mysen et al., 1980; Neuville et al., 2004). The intensity ratio between the bands near 950 and 516 1135 cm⁻¹ in rhyolitic glasses is indicative of relative proportions of structural units, which are likely Q^2 and a combination of Q^3 and Q^4 units, respectively (Mysen et al., 1980; Zotov and 517 Keppler, 1998). The band near 1050 cm⁻¹ that characterizes the water-poor NSL-N1 glass is 518 tentatively assigned to T-O stretching vibrations in distinct Q^3 or Q^4 units (Mysen et al., 1980; 519 520 Zotov and Keppler, 1998). In the peraluminous rhyolites, the increased intensity of the band at ~930 cm⁻¹ with increasing water content can be attributed to the formation of T-OH units 521 (Zotov and Keppler, 1998). In peralkaline glasses, the sharp increase of the band at 970-980 522 cm⁻¹ is attributed to progressive entry of four-fold Fe^{3+} in alkali-bonded Q^3 units (Wang et al., 523 524 1995; Di Muro et al., 2009; Di Genova et al., 2016).

525 The cause of the HF band shift of the andesitic glass A071215 to lower wavenumber 526 compared to the other andesitic glasses is uncertain: it is probably related to differences in 527 their Fe^{3+}/Fe_{tot} ratios.

528 In basaltic glasses, the increased intensity of the HF envelope and its shift to lower wavenumbers compared to polymerized glasses are consistent with the increase of Q^2 and Q^3 529 530 units. In the high-Al basaltic set, both water content and polymerization degree correlate 531 negatively with the FWHM of the HF band (Fig. 2S a, b) and positively with the intensity 532 ratio of LF band to HF band (Fig. 2S c, d). This seems to be contradictory as water dissolution 533 is expected to enhance depolymerization. Although investigation of dissolution mechanisms 534 of water in basaltic melts is beyond the scope of this study, it is worth noting that the 535 described spectral features likely suggest dissolution mechanisms other than those occurring 536 in more polymerized glasses. In depolymerized CaO-MgO-SiO₂ glasses, Xue and Kanzaki 537 (2004) highlighted formation of (Ca,Mg)-OH groups, in which OH groups are only linked to

network-modifying metal cations, not to the silicate network. This is expected to cause an
increase in the melt polymerization, contrary to the effect of Si-OH formation (Mysen and
Virgo, 1986; Xue and Kanzaki, 2004). These water dissolution mechanisms, associated with
major changes in the local environment of metal cations, are probably responsible for the
trends defined by the high-Al basaltic set.

543

4.3 Water band topology

544 The topology of the water stretching vibration band depends on glass matrix 545 composition and water concentration (Fig. 5), but also on water speciation (e.g., Mysen and 546 Virgo, 1986) and strength of H-bonding (e.g., Zajacz et al., 2005; Behrens et al., 2006; Di 547 Muro et al., 2006). Different water species (metal-hydroxyl and molecular H₂O) contribute to 548 the intensity of the broad water band-envelope (e.g., Mysen and Virgo, 1986). The latter is 549 asymmetric in shape with a long tail on the lower wavenumber side, and is characterized by two shoulders near 3250 cm⁻¹ and 3640 cm⁻¹ that are readily observed in rhyolitic glasses 550 551 (Fig. 5). The exact position of the maximum peak of the water band shifts to lower frequency 552 with increase of polymerization degree and water content (Fig. 5), in agreement with previous studies. The maximum is located within the 3565-3582 cm⁻¹ range in basaltic glasses and at 553 3552-3570 cm⁻¹ in basanitic, and esitic and rhyolitic glasses. In the basanitic, basaltic and 554 555 andesitic glass sets, the FWHM of the band increases by 15-25 % relative with increasing 556 water content.

557 The H₂O bending vibration at ca. 1630 cm⁻¹ (not shown) can be clearly distinguished 558 from the background in spectra of water-rich glasses.

559 4.4 Peak fitting of the HF and water bands

560 We performed spectral deconvolution using OriginPro software in order to quantify561 differences in spectral components of the water band and the HF alumino-silicate envelope of

basanitic and rhyolitic glasses (Tables 1S, 2S and 3S). Spectra were fitted with a finite 562 563 number of Gaussian components using the Multiple Peak Fit tool and following a procedure 564 analogous to the one described by Morizet et al. (2013). This procedure consists of: i) locating 565 a certain number of peaks based on results of previous studies (e.g., Di Muro et al., 2009; 566 Rossano and Mysen, 2012; Morizet et al., 2013); ii) performing a first set of iterations with peak position and/or FWHM fixed until the quality of fit (expressed as χ^2) does not change; 567 and iii) performing a second set of iterations in which peak position and areas are left free to 568 evolve, until the best fit possible (i.e., the lowest χ^2) is obtained. Fitting parameters were 569 570 iterated until the fit converged using both Simplex method and Levenberg-Marquardt 571 algorithm available in OriginPro, and the two algorithms provided comparable results. In our simulations, the γ^2 tolerance value of 10⁻⁹ was always reached. The errors associated with the 572 573 simulations are reported in Tables 1S, 2S and 3S. The proposed simulations may represent 574 one of several possible fits; however, consistency in fitting parameters within each glass 575 series and general agreement with deconvolutions reported in the literature (e.g., Di Muro et 576 al., 2009; Rossano and Mysen, 2012; Morizet et al., 2013) ensure the reproducibility of the 577 calibrations established in the next sections. In fact, we verified that the small changes in the 578 constrained parameters had a negligible effect on the ratios between the areas of different 579 spectral components.

Five components are required to fit the spectra of rhyolitic glasses (Fig. 6). Peak fitting of peraluminous and peralkaline glass spectra differs in the position of component II and in the relative intensities of the five components (Table 1S). Band positions are: I) 901-917 cm⁻¹, II) 975-1000 cm⁻¹ (with the highest frequencies in peraluminous rhyolites), III) 1047-1060 cm⁻¹ 584 ¹, IV) 1113-1126 cm⁻¹, and V) 1174-1182 cm⁻¹. The good quality of the fit is indicated by the randomness of the residuals. Fitting six components instead of five reduces the quality of the fit.

Concerning CO₂-bearing basanitic glasses, best fitting in the 630-1200 cm⁻¹ spectral 587 range was achieved with six to seven components, whose positions are: I) 707-715 cm⁻¹, II) 588 779-789 cm⁻¹, III) 864-891 cm⁻¹, IV) 930-963 cm⁻¹, V) 990-1021 cm⁻¹, VI) 1061-1077 cm⁻¹ 589 and VII) 1084-1088 cm⁻¹ (Fig. 3S, Table 2S). The last component refers to the v_1 Raman 590 591 vibration of dissolved carbonate (Morizet et al., 2013). 592 Peak fitting of the total water band requires a minimum of four Gaussian components 593 (Table 3S, Fig. 4S), in agreement with previous studies (e.g., Chabiron et al., 2004; Behrens 594 et al., 2006; Di Muro et al., 2006). The positions of these components are: I) 3080-3098 cm⁻¹, II) 3250-3298 cm⁻¹, III) 3420-3487 cm⁻¹ (with the highest frequencies in rhyolites), IV) 3540-595 3575 cm⁻¹, and V) 3600-3645 cm⁻¹ (with the lowest frequencies in basanites and basalts); 596 597 these positions match those determined by Di Muro et al. (2006). The small component I is 598 only present in water-rich glasses (Fig. 5), as observed by Behrens et al. (2006). In general, 599 the intensity of the low frequency components increases with total dissolved water, in 600 agreement with the expected increase of molecular water (e.g. Mysen and Virgo, 1986).

601 **5. DEPTH PROFILES**

Intensities (i.e. height of the dominant band) and integrated intensities (i.e. total area) of the Raman bands vary with focusing depth of the laser beam (e.g., Behrens et al., 2006; Mercier et al., 2009). Depth profiles measured in the alumino-silicate vibration region and water region, under both high and standard confocality conditions, are shown in Fig. 7 for basaltic, andesitic and rhyolitic compositions. Differences appear between glasses with different compositions and absorptivities.

608 In the alumino-silicate domain of basanitic and basaltic glass spectra, signal intensity 609 increases from the surface to a depth of 2-3 μ m and 3-4 μ m in high and standard confocality, 610 respectively. The maximum intensity is 22% (basanitic) and 35 % (basalt) higher than the

611 signal intensity at the surface in high confocality, whereas it increases by ~45 % in standard 612 confocality (Fig. 7). In andesitic glasses, maximum intensity, which is attained at 3-4 µm 613 depth, is 50 % higher than the signal at the surface. Below the maximum normalized intensity, 614 the intensity decreases with depth by $3 \%/\mu m$ in the first $30 \mu m$ in basanitic glasses and by 615 2 %/µm in both basaltic and andesitic glasses (Fig. 7). Maximum alumino-silicate signal 616 intensity in rhyolitic glasses is attained at ~5 µm depth in a highly confocal setting, but at 7-617 10 µm depth under standard confocality conditions. At these depths the intensity is 55 and 618 65 % higher (in high and standard confocality, respectively) compared to the one measured at 619 the surface; then it diminishes by 1 %/ μ m (high confocality) and 0.5 %/ μ m (standard 620 confocality) for the remainder of the first 30 µm.

Maximum signal intensity of the water band is attained at the same depths as for the 621 622 alumino-silicate bands (Fig. 7). However, the percentages of increase with respect to signal at 623 the surface are lower for water bands than observed for alumino-silicate bands. In the high 624 confocality setting, the increase ranges from 15-18 % in basaltic and basanitic glasses to 20-625 25 % in andesitic and rhyolitic glasses, whereas in the standard confocality setting, it varies 626 from 20-25 % in basaltic and andesitic glasses to 29-35 % in basanitic and rhyolitic glasses. 627 That is, the intensity increase in the alumino-silicate region is twice as high as that in the 628 water region. This causes the observed variability of the ratio between the intensity of the 629 water band and the intensity of the silicate band ("OH/Si"). Below the depth of maximum 630 signal intensity, Raman intensity of the water band decreases more slowly with depth 631 compared to the alumino-silicate bands. Specifically, it drops by 2.6 %/µm in basanites, by 632 1.5 %/ μ m in basaltic and andesitic compositions, whereas it remains almost constant over 12 μ m in rhyolitic glasses before dropping by 0.7 %/ μ m. The evolution with depth of the OH/Si 633 634 band intensity ratio is significantly different in high and standard confocality settings. Indeed, 635 under less confocal conditions this ratio remains almost constant at minimum values within

636 the first 5-20 μ m, irrespective of glass composition. In contrast, the OH/Si band intensity ratio 637 is much more sensitive to depth when using the high confocality setting. Thus, under confocal 638 conditions depth precision is required to get reproducible OH/Si values.

639 Measurements of peak height and area provided consistent results. Moreover, similar depth profiles were obtained at laser power conditions ranging from 1 to 16 mW. In contrast, 640 641 the signal intensities of both alumino-silicate and water bands drop faster with depth when the 642 laser power on the sample is about 75 mW. This is especially relevant for basaltic glasses, in 643 which maximum signal intensity occurs at the glass surface at these high laser-power 644 conditions. These observations are consistent with more intense self-absorption expected in 645 basaltic glasses compared to more silica-rich glasses (e.g., Behrens et al., 2006; Mercier et al., 646 2009). Excitation of (iron-bearing) basaltic samples, in fact, results in attenuation of both the 647 exciting light and the Raman scattered light.

Depths where both signals of the alumino-silicate and water bands are the highest were considered as optimal focusing depths. For measurements performed in high confocality setting, the adopted focusing depths correspond to the depth of minimum OH/Si band intensity ratio. As shown in the following sections, this is a critical step to ensure a good calibration. We highlight that a focusing error of about 1 μ m near the depth of maximum signal intensity causes a relatively small error (< 3% relative) in measured band intensity. Larger focusing errors, however, result in non-negligible drop of the measured intensity.

655 6. CALIBRATION

656

6.1 External calibration method

In the external calibration method, water concentration in an unknown glass sample is
derived from the absolute (integrated) intensity of the band at ~3570 cm⁻¹ compared to band

(integrated) intensities of reference glasses with known water contents defining a calibration
line (e.g., Behrens et al., 2006; Di Muro et al., 2006; Mercier et al., 2010).

661 When spectra are treated using the described procedure for focus depth selection and 662 baseline correction, both I_{OH} and A_{OH} show positive linear correlation with glass water contents determined by FTIR spectroscopy or SIMS. Correlations based on peak height 663 664 measurements, however, are affected by a larger scatter than correlations based on peak area 665 (Fig. 5S), therefore, only calibrations based on area measurements are considered hereafter. 666 Such a difference is explained by the observation that varying amounts of water dissolved in 667 glasses with different compositions produce not only variations in peak height, but also in 668 total band width and distribution of spectral components (as summarized in the previous 669 section).

Figure 8 (a to c) shows calibration lines obtained in high or standard confocality setting
after subtracting a cubic or a linear baseline from raw data. In these plots, reference glasses
define a single composition-independent linear relationship between water band intensity and
water concentration. The calibration based on cubic background subtraction provides the best
fit in both high confocality:

675
$$C_{\text{H2O}} (\text{wt\%}) = 2.403 (\pm 0.033) \cdot A_{\text{OH}} - 0.058 (\pm 0.046) \quad (\text{R}^2 = 0.995), \quad (1)$$

676 and standard confocality setting:

677
$$C_{\text{H2O}}(\text{wt\%}) = 2.057(\pm 0.025) \cdot A_{\text{OH}} + 0.072 (\pm 0.039) \quad (\text{R}^2 = 0.996).$$
 (2)

The data are reproduced with a root-mean-square error of ~0.13 and ~0.11 wt% in high and standard confocality, respectively (Fig. 8, Table 4S). The linear regressions do not take into account the uncertainties on H₂O content of the reference glasses. Their intercepts pass very close to the origin. Linear calibrations with similar slopes (within 15 % difference) were reproduced using a range (1-16 mW) of laser powers in different sessions over severalmonths.

It is worth noting that measurements performed by focusing the laser beam on the surface of the alumino-silicate glasses yielded slightly divergent calibration lines whose slopes depend on glass composition: the slope decreases from basaltic to rhyolitic compositions, as previously observed by Mercier et al. (2010).

688

6.2 Internal calibration method

The internal calibration procedure is based on the correlation between the glass water concentration and the relative (integrated) intensities of the water and alumino-silicate Raman bands. To compare spectra of alumino-silicate glasses with different compositions, and because Mercier et al. (2009) reported a significant effect of bulk chemical composition on internal calibrations based on normalization to either LF or HF band heights, we built our internal calibration procedure on the measurement of band total area, instead of band height (Fig. 9).

696 OH/Si increases with water content and the increase is generally higher for mafic than 697 for felsic glasses (Fig. 9a). Between the two felsic compositions, the increase of the OH/Si 698 ratio with water of the peraluminous rhyolite is noticeably more important than the 699 peralkaline one. More precisely, calcalkaline and tholeiitic glasses bearing less than 3 wt % 700 H₂O and the peraluminous rhyolite with various water contents fit on a single trend, whereas 701 the other glasses diverge from the general trend to higher OH/Si ratios (the water-rich basalts) 702 or lower OH/Si ratios (the basanites and peralkaline rhyolites) (Fig. 9a). Similar trends are 703 obtained when subtracting a linear/cubic baseline from raw or Long-corrected data. 704 Measurements performed in a standard confocality setting (not shown) yield a ~50 % steeper 705 calibration line than measurements done under high confocality conditions.

706 The divergence of water-rich basalts and peralkaline rhyolites from the main trend in 707 Fig. 9a is due to the effect of water content on the integrated intensity of the alumino-silicate region and to the behavior of the band at 980 cm⁻¹, respectively. Careful inspection of spectra 708 709 in the alumino-silicate vibration region reveals that the integrated intensity (hereafter A_{Al-Si}) 710 of this region generally decreases with increasing water content and decreasing density (Fig. 711 10), regardless of analytical conditions (i.e. laser power on sample and confocality) and 712 baseline treatment, except for the peralkaline and basanitic glasses. The effect of water in 713 lowering A_{Al-Si} is maximum in basaltic glasses, in particular in the 82-72f set with 30 % 714 intensity reduction for 15 mol % H₂O (Fig. 10 c), and becomes smaller in andesitic and 715 rhyolitic glasses characterized by < 12 % and 10 % reduction for 18 mol % H₂O and 25 716 mol % H₂O, respectively (Fig. 10 e, g). In CO₂-bearing basanitic glasses, the observed increase of A_{Al-Si} with decreasing density (Fig. 10 b) is due to the presence of CO_3^{2-} dissolved 717 in these glasses; the intensity of the v_1 Raman vibration of dissolved carbonate at ~1087 cm⁻¹ 718 719 (Fig. 3S) has to be subtracted from the intensity of the alumino-silicate envelope (Table 2S). 720 Adjustments of the internal calibration method to take into account the effect of water content 721 on A_{Al-Si}, the behavior of the band at 980 cm⁻¹ in peralkaline rhyolites and the presence of 722 CO_3^{2-} in basanites are presented in the Discussion section.

723 Small deviations from the general trends of Fig. 10 in a given set of glasses reflect 724 differences in glass structure. For instance, the higher A_{Al-Si} measured in the A071215 sample 725 is probably due to a different iron oxidation state compared to the other andesitic glasses (see 726 spectra of Fig. 4c). The HF band in A310317 and A030417 glass spectra contains an 727 additional contribution from the vibration of CO_3^{2-} molecules (Fig. 10 e). The basaltic sample 728 82-72f#10 is characterized by a larger A_{Al-Si} than expected from the general trend of the 82-729 72f basaltic set (Fig. 10 c). This may be due to the slightly higher density of this sample 730 compared to the other glasses of the same basaltic set (Fig. 2). Analogously, the higher

synthesis pressure (and thus the relatively higher density) of the basanite BSN101117-2
compared to the other basanitic glasses (Table 1) may be partly responsible for its

radiation significantly larger A_{Al-Si} (Fig. 10 a, b).

734 **7. DISCUSSION**

735

7.1. Parameters controlling the Raman signal

Raman vibration intensity of a molecule is proportional to the quantity of the analyzed molecule and to its Raman scattering cross-section (which expresses the Raman scattering efficiency of a molecule) (e.g. Dubessy et al., 2012), but it depends also on analytical conditions and instrumental features that influence the excited volume (e.g., laser wavelength and power, confocal aperture of slits or pinholes, microscope magnification, numerical aperture of the objective, grating). These relationships are expressed in the following equation:

743
$$N = N_{V0}/A \cdot d\sigma/d\Omega \cdot \Delta\Omega \cdot N_{\rm m}$$
(3)

where *N* is the total number of Raman photons for a specific vibrational mode, $N_{\rm m}$ is the number of molecules contained in the scattering volume *V* that are responsible for that vibrational mode (i.e. $N_{\rm m} = \rho V$ if ρ is the number of molecules per unit volume), $d\sigma/d\Omega$ is the differential Raman scattering cross-section of a specific Raman mode, N_{V0}/A is the flux of photons of the laser focused onto the sample area *A*, and $\Delta\Omega$ is the solid angle of light collection.

Previous studies showed that the Raman scattering cross-section of different Q^n species and dissolved hydrous species depends on glass composition and structure (Fukumi et al., 1990; Zotov 2001; Zajacz et al., 2005; Behrens et al., 2006; Mercier et al., 2010). Mercier et al. (2010) highlighted that the matrix effect on the total water band is related to differences in glass reflectance and water bonding environment. Moreover, they reported positive
correlations between the slope of the calibration line and both reflectance and density of the
glass.

757 The size of the scattering volume of the glass is affected by its physico-chemical 758 characteristics such as chemical composition, structure, density, reflectance, refractivity and 759 absorptivity. The confocal scattering volume can be expressed by the product of the 760 illumination volume (i.e. the volume of the laser focus) and the detection volume (which is 761 defined by Raman photons generated within the illumination volume that are relayed back 762 into the spectrometer via the confocal aperture, Everall, 2004; Maruyama and Kanematsu, 763 2011). In particular, these two volume components determine the depth resolution of Raman 764 measurements. Therefore, in order to interpret correctly confocal Raman measurements, one 765 should take the spread in focal position due to light refraction into account (Everall, 2004; 766 Maruyama and Kanematsu, 2011). When focusing beneath the surface of a sample with a 767 refraction index above 1, the light rays are slowed down and refracted according to Snell's 768 law. In general, upon moving deeper into the sample the axial laser focus broadens and focus 769 position shifts to lower depth than indicated by microscope vertical displacement, because 770 depth resolution degrades with depth below the surface (Everall, 2004; Maruyama and 771 Kanematsu, 2011). These processes can explain the different depth profiles and distinct slopes 772 of the calibration lines we obtained when changing from high confocality to standard 773 confocality settings (Figs. 7 and 8). Because the observed shapes of OH/Si depth profiles vary 774 with confocality (Fig. 7), we expect these differences to be reflected in calibration lines. 775 Different slopes of the internal calibration lines obtained for high and standard confocality 776 conditions suggest that the internal calibration does not correct for the effect due to changes in 777 confocal volume size.

7.2. External versus internal calibration

779 Concerning the external calibration, the linear relationship between water contents (as 780 determined by FTIR or SIMS) and A_{OH} (Fig. 8) can be explained in two ways: either the 781 scattering cross-section of the water stretching vibration mode is independent of the glass 782 matrix composition, or the procedure established for spectra acquisition and baseline 783 treatment minimizes the differences in Raman cross-section and the effects related with size 784 of the confocal volume, self-absorption and reflectance at the sample surface. Taking into 785 account the findings of previous studies (e.g. Mercier et al., 2010), we believe this second 786 hypothesis is more likely. Small differences in shape and componentry between the water 787 bands of the studied glasses (Fig. 5 and Fig. 4S) are consistent with differences in water 788 bonding environments and speciation, as previously discussed by Behrens et al. (2006), Di 789 Muro et al. (2006b) and Mercier et al. (2010). The external calibration method proposed here 790 yields a single calibration line allowing analysis of all alumino-silicate glasses with the same 791 level of accuracy as previous studies (e.g., Behrens et al., 2006). This suggests that 792 measurements performed following the procedure established in this study (i.e., 793 measurements performed at optimal focus depths rather than on sample surface, and based on 794 quantification of the water band area instead of band height) provide the best conditions for 795 correction of differences in Raman scattering efficiency between glasses with variable 796 subalkaline and alkaline compositions.

In the case of internal calibration, the intensity of the water band is scaled to the alumino-silicate band intensity, resulting in a stronger dependence on glass composition (Fig. 9a), in agreement with previous works (e.g., Zajacz et al. 2005, Mercier et al. 2009). To better compare all the glass sets, the CO₂-bearing glasses need to be corrected for the contribution of the CO_3^{2-} -related spectral component (Fig. 3S). This is simply achieved by multiplying the

 A_{Al-Si} by a factor that takes into account the contribution of the component VII relative to the sum of the areas of all spectral components (Table 2S). In line with the results of Morizet et al. (2013), we found that the relative contribution of the CO_3^{2-} is proportional to the total CO_2 content.

The observed relationships between A_{Al-Si}, glass density and water content (Fig. 10) indicate that glass density strongly affects Raman scattering of the alumino-silicate vibration region. When we consider the glass density dependence, by normalizing the intensity of the alumino-silicate envelopes to the intensity measured in anhydrous glasses, the studied glasses define a single positive linear correlation, except for the peralkaline ones (Fig. 9b). This linear relationship is expressed by the following equation:

812
$$OH/Si = [A_{OH}/(p \cdot t_1)]/[A_{Al-Si}/(p \cdot t_2) \cdot (1 + \alpha_1)]$$
 (4)

813 where $\alpha_1 = 1 - (A_{Al-Si hydrous} / A_{Al-Si anhydrous})$, p is the laser power, and t_1 and t_2 are the acquisition 814 times in the water and alumino-silicate regions, respectively. In other words, the correction 815 factor (α_1 , Table 4S) is proportional to the difference between the A_{Al-Si} of the anhydrous glass 816 and that of the hydrous glasses of each set (Fig. 10). The correction factor depends on both 817 glass composition and water content (see Fig. 2); either density or mol% H₂O estimated with 818 the external calibration method can be used to estimate α_1 (Fig. 10). Up to ~7 wt % H₂O 819 contents, rhyolitic, andesitic and basanitic glasses require a minor correction (< 10-12 % in 820 the studied range of water contents). In contrast, water-rich (> 3 wt % H₂O) basaltic glasses 821 need more important corrections.

Peralkaline glasses are well aligned below the calibration line defined by peraluminous rhyolites (Fig. 9a). In order to understand their distinct behavior, we performed peak fitting of the alumino-silicate HF envelope of both peralkaline and peraluminous glasses (Fig. 6). The spectral components I, IV and V are more important in peraluminous rhyolites than in 826 peralkaline ones, whereas the opposite behavior is observed for the components II and III. 827 The sum of the components III, IV and V represents approximately 50 % of the total area in 828 both glass sets $(51 \pm 6, 1\sigma)$. In contrast, the sum of the areas of the components I, II and III 829 varies significantly from peraluminous (~50 % of the total area) to peralkaline (70-75 % of 830 the total area) glasses, with a 20-25 % difference. This difference can be explained by the 831 higher Fe content and oxidation state of peralkaline glasses, as revealed by the sharp increase 832 of the component (II) at ~980 cm⁻¹, which is attributed to the presence of four-fold coordinated Fe³⁺ in alkali-bonded Q^3 units (e.g., Wang et al., 1995; Di Muro et al., 2009; Di 833 834 Genova et al., 2016). The internal calibration procedure can be improved by taking into account the high Raman scattering of the 980 cm⁻¹ band in peralkaline rhyolites, and this can 835 836 be performed by calculating a correction factor:

837
$$\alpha_2 = [100 - ((I-II-III)_{\text{peralkaline}} - (I-II-III)_{\text{peraluminous}})]/100$$
(5)

838 where (I-II-III) represent the sum of the areas of the components I, II and III (Table 1S). Once 839 the A_{AI-Si} of peralkaline glasses is corrected for the difference in componentry compared to 840 peraluminous glasses, all rhyolitic glasses follow the same calibration line defined by all other 841 compositions (Fig. 9c). This observation suggests that Fe³⁺ has an important effect on the 842 Raman scattering efficiency of alumino-silicate glasses; in rhyolitic glasses the vibrational 843 mode at 970-980 cm⁻¹ has an important Raman scattering cross-section.

844 The linear fit of the internal calibration is expressed by the following equation (Fig. 9c):

845
$$C_{\text{H2O}} (\text{wt\%}) = 2.179 (\pm 0.037) \cdot A_{\text{OH}} / A_{\text{Al-Si corr}} + 0.060 (\pm 0.055) (\text{R}^2 = 0.992),$$
 (6)

where $A_{Al-Si \text{ corr}}$ is the corrected area of the alumino-silicate envelope and $A_{OH}/A_{Al-Si \text{ corr}}$ (i.e., OH/Si in Fig. 9c) = $A_{OH}/(\alpha_1 \cdot A_{Al-Si} + \alpha_2 \cdot A_{Al-Si})$. The linear fit reproduces the whole dataset within 0.17 wt % (root-mean-square error).

849 7.3. Application to natural glass inclusions

850 As a final step, we examine if the calibration procedures described in the previous 851 sections can be applied to the study of natural hydrous glasses. We tested them on natural 852 olivine-hosted glass inclusions from Santorini volcano, Lanzarote Island and FAMOUS Zone 853 (Mid Atlantic Ridge) (Table 3). For the geochemical characterization of Santorini inclusions, 854 including their volatile contents and details on secondary ion mass spectrometry (SIMS) 855 measurements, we refer the reader to Druitt et al. (2016). Inclusions from Lanzarote have 856 been studied by Gómez-Ulla et al. (submitted) and analyzed using a CAMECA ims-4f ion 857 probe at the NERC Ion Microprobe Facility at the University of Edinburgh. The reader is 858 referred to Schiavi et al. (2016) for details on the inclusions from FAMOUS Zone and FTIR 859 measurements.

860 The studied inclusions have variable composition spanning from basanitic to basaltic 861 and andesitic, and contain different amounts of water ranging from 0.1 to 3.3 wt% (Table 3). 862 They contain less than 0.13 wt% CO₂, except for two basanitic inclusions, TAO-ol1 and 863 TGN-ol18 bearing, respectively, 0.43 ± 0.09 and 0.21 ± 0.09 wt% CO₂. As CO₂ contents < 0.2 864 wt% are not detected using Raman spectroscopy (Morizet et al., 2013), only the two basanitic 865 inclusions were corrected for the presence of dissolved carbonate. The relatively large size of 866 the analyzed glass inclusions and the very weak or absent scattering from the embedding 867 olivine crystals allowed focusing the laser beam at depths where the intensity of the water 868 signal was maximum (-2 or -3 μ m). These correspond to the optimal depths reported in Figure 869 7 for the reference glasses.

We were unable to test our calibration procedure on silica-rich glasses with dacitic or rhyolitic compositions because all the tested inclusions contained magnetite nanocrystals, as revealed by the intense scattering of a Raman band near 670 cm⁻¹ (Frezzotti et al., 2012). In line with the findings by Di Genova et al. (2017), we observed that presence of Fe-oxides

874 dispersed in the glass causes underestimation of the water content of the inclusion, most likely

875 due to light absorbance and possible heating and oxidation of the oxide phases.

876 Figure 8d shows the results of the external calibration procedure applied to glass 877 inclusions. The estimated water contents are in very good agreement with SIMS 878 measurements and provide information about the accuracy of the method. The average 879 relative standard deviations (RSD) between Raman and SIMS analyses are ~ 3 % and 5 % (1 σ) 880 when using a cubic or a linear baseline correction, respectively. It is worth noting that SIMS 881 measurements were carried out first, so we cannot exclude that some water loss occurred from 882 the inclusion before Raman analyses. For glass inclusions bearing H₂O contents close to the 883 detection limit of the method (i.e. ~0.1 wt%), the RSD between FTIR and Raman 884 measurements increases (4-22 %, with maximum values for cubic background subtraction), 885 partly due to decreasing signal/noise intensity ratio.

886 When using the internal calibration approach without applying the corrections (for 887 density and componentry) defined above, a first approximate estimate of the water dissolved 888 in the glasses is obtained (inset in Fig. 9a). Basaltic and andesitic inclusions fall close to the 889 main trend defined by the reference glasses, although some scatter is observed in inclusions 890 bearing \sim 3 wt% H₂O. The basanitic inclusions, instead, are aligned with the basanitic 891 reference glasses below the main trend.

On quantifying water in glass inclusions, we are faced with the difficulty of measuring density of natural glass inclusions. Ardia et al. (2014) studied the evolution of haplogranite glass structure with pressure and water content, and observed that at a fixed water content and glass composition, density is a function of quench pressure. Thus, Raman spectra of melt inclusions trapped over a large pressure range are potentially influenced by the trapping pressure as well. In principle, the relationship observed between density, water content and A_{Al-Si} will hold when a set of natural glass inclusions with similar composition that were

quenched from similar pressure are analyzed, regardless of the absolute value of their density and quench pressure. In this case, corrections can be attempted within each set of glass inclusions based on the relationship between water contents estimated using the external calibration method and A_{Al-Si} . In some cases, calculating the density of glass inclusions could help decreasing the uncertainties of the method. Where these methods cannot be applied, water quantification should be performed based on reference glasses with similar composition, which do not require density-related correction.

906 Attempts to estimate the density-related factor α_1 for the studied inclusions resulted in 907 non-negligible uncertainties on the OH/Si ratio. This is mainly due to the small number of 908 analyzed inclusions with similar composition that did not allow defining trends as in Fig. 10 909 without uncertainty. For a qualitative analysis, the compositions of the inclusions, not 910 corrected for density, are plotted on the main density-corrected trend defined by the reference 911 glasses (inset in Fig. 9c). The observed distribution of the glass inclusions is in line with our 912 expectations based on the behavior of the reference compositions (Fig. 10): the andesitic glass 913 falls on the main trend as it is not expected to be strongly influenced by the density correction, 914 several basaltic inclusions fall slightly above the main trend as observed for non-corrected 915 reference basalts, while basanitic inclusions behave analogously to the reference basanites. 916 Although this may be speculative, the strong similarities observed between reference samples 917 and uncorrected glass inclusions probably suggest that differences of quench pressure in the 918 studied inclusions has a minor influence on the established water quantification procedures.

919 CONCLUDING REMARKS

920 This study contributes to the ongoing research dedicated to the development of precise 921 micro-Raman routines for water quantification in alumino-silicate hydrous glasses. Here we 922 summarize the main new findings of our study.

923 We examined in detail how the Raman intensities of the water band and the alumino-924 silicate envelope change with confocality performance and focus depth of the laser beam, as 925 previously investigated (e.g., Behrens et al., 2006; Mercier et al., 2009). We found that the 926 extent of increase of water band intensity with focus depth is lower than that measured in the 927 alumino-silicate envelope. This results in a variable OH/Si band intensity ratio, and highlights 928 the importance of measuring glasses at their optimal focus depth, which corresponds to the 929 depth of maximum intensity of the water band and minimum OH/Si ratio. The optimal focus 930 depth depends on glass composition and confocal performance of the Raman instrument, and 931 is expected to change with laser wavelength as well. Maximum intensity in both water and 932 alumino-silicate regions is attained at 2-3 µm, 3-4 µm and 5-10 µm depth, respectively in 933 basanitic-basaltic, and esitic and rhyolitic glasses under the instrumental and analytical 934 conditions used in this study.

935 Thirty reference glasses belonging to both alkaline and subalkaline magmatic series and 936 bearing up to ~7 wt % H₂O define a single external calibration line when they are analyzed at 937 their optimal focus depth. In contrast, measurements performed on the sample surface did not 938 yield a single calibration curve for glasses of different compositions. Our study suggests that 939 water content of unknown samples can be determined based on a minimum of two reference 940 glasses whose compositions do not need to match that of the unknown samples. However, 941 using three or more reference glasses is recommended to improve the accuracy of water 942 content quantification. In general, accurate water quantification using the external calibration

method requires careful, repeated measurement of reference glasses because small variationsin laser power can occur during long analytical runs, lowering the analytical precision.

945 For the reasons illustrated above, depth profile measurements are important even when 946 using the internal calibration method for water quantification, because the normalization to 947 the intensity of the alumino-silicate envelope does not cancel completely the differences in 948 confocal volume size, as previously expected. A universal calibration curve for quantification 949 of water content in glasses cannot be established, unless the dependence of the confocal 950 volume on different instrumental parameters is accurately known. Sharing common reference 951 glasses between different laboratories may help future work for establishing a universal 952 calibration.

953 This study recognizes critical parameters related with glass density, presence of ferric 954 iron and dissolved carbonates as mainly responsible for matrix effects on the internal 955 calibration method. We provide simple procedures for correcting and/or minimizing the 956 effects of these parameters. Increasing water content lowers glass density and results in 957 reduction of the area of the alumino-silicate envelope (A_{Al-Si}); we measured up to 30% 958 intensity reduction in a high-Al basaltic glass bearing 15 mol% water. The correction method 959 that we propose is based on the relative difference between A_{Al-Si} of anhydrous and hydrous 960 glasses with similar composition.

Peak fitting of the alumino-silicate high frequency envelope (approximately located between 800 and 1250 cm⁻¹) is required to quantify the intense scatterings around 980 cm⁻¹ and 1080 cm⁻¹ caused, respectively, by Fe³⁺ in four-fold coordination and CO_3^{2-} dissolved in glasses. Concerning the Fe³⁺-related matrix effect, we must point out that, in principle, all Fe³⁺-bearing glasses should be corrected for it. Nevertheless, only peralkaline rhyolites were corrected in this study because the area of the high frequency envelope in peralkaline

967 rhyolites is far more sensitive to changes in Fe³⁺/Fe_{tot} than in mafic compositions (Di Muro et
968 al., 2009; Di Genova et al., 2016). Once the proposed corrections are performed, all the
969 studied glasses define a single internal calibration line in spite of their compositional
970 variability. Alkaline glasses, specifically basanites, behave coherently with the other glass
971 compositions when the analytical strategies and data treatment procedures (i.e., for baseline
972 subtraction, peak fitting and density correction) established in the present study are used.

Accuracy of the external calibration in the high confocality setting was determined by testing our method on olivine-hosted glass inclusions whose water content was measured using SIMS or FTIR. The calculated average RSD is ~4% (1 σ) for most samples, and increases to ~12% (1 σ) for glass inclusions with H₂O contents close to the detection limits (~0.1 wt%).

978 Because of their specific textural complexities, natural glass inclusions provide a979 unique laboratory for testing further the proposed calibration method.

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- 1175

1176 FIGURES









1190 Fig. 2. Glass density versus glass water content determined by FTIR or SIMS measurements (see Table 1). A decrease of slope value from basaltic to rhyolitic glasses is 1191 1192 observed. The dashed line represents the density of rhyolitic glasses calculated from Behrens 1193 et al. (2006). The dashed-dotted line shows the density of andesitic glasses determined by 1194 Ohlhorst et al. (2001). Small grey triangles are calculated basanitic glass densities by Iacovino 1195 et al. (2016). Microlite-bearing A011215 glass is the andesitic glass with the highest water 1196 content (empty circle). WM23-3 and 82-72f#19 glasses are not plotted because their densities 1197 were calculated, not measured.



Fig. 3. Raw Raman spectra of the alumino-silicate vibration bands of the glasses with
basanitic (a), basaltic (b), andesitic (c) and rhyolitic (d) compositions. Linear baselines
adopted for background subtraction are shown with anchor points. Spectra are displaced
vertically for clarity. Intensities were normalized to laser power and acquisition time.



Fig. 4. Alumino-silicate region of raw Raman spectra of basanitic (a), basaltic (b), andesitic (c) and rhyolitic (d) glasses after subtraction of linear baselines. Spectra were measured under the same conditions of laser power and confocality. Intensities were normalized to acquisition time. Laser beam was focused at the optimal depth as defined in the text. Note differences in band topology associated with different major element compositions, water contents, degree of polymerization, and oxidation state (see text).



Fig. 5. Baseline-corrected Raman spectra in the water region of reference glasses:
basanites (a), basalts (b), andesites (c) and rhyolites (d) with different water contents. Spectra
were measured under the same conditions of laser power and confocality. Intensities were
normalized to acquisition time. Laser beam was focused at optimal depths as defined in the
text.



Fig. 6. Peak fitting of the HF alumino-silicate envelope of peraluminous (a), water-poor
(b) and water-rich peralkaline (c) rhyolitic glasses with a finite number of Gaussian
components performed with OriginPro software. The good quality of the fit is indicated by
the randomness of the residuals (d).



Fig. 7. Depth profiles measured in the water and alumino-silicate vibration regions of
basanitic (yellow triangles), basaltic (red diamonds), andesitic (blue circles) and rhyolitic
(green squares) glasses under high (upper row) and standard (lower row) confocality
conditions. Integrated intensities of the water band (A_{OH}) and the alumino-silicate envelope
(A_{Al-Si}) were normalized to laser power and acquisition time; water band intensities were also
normalized to water content.





1235 Fig. 8. External calibration lines for quantification of water contents in glasses, obtained 1236 after subtracting a cubic or a linear baseline from raw data: areas in high confocality setting 1237 (a-b, d), and in standard confocality setting (c). Reference glasses define a composition-1238 independent linear relationship. In (d) glass inclusions are plotted over the reference glasses. 1239 Microlite-bearing A011215 glass (empty circle) is shown but is not considered for calibration 1240 line definition. Water band areas were normalized to the water band area of the 82-72f#9 1241 basaltic glass, which was used as internal standard to eliminate small variations in 1242 measurement conditions. For glass inclusions, errors associated with SIMS measurements are 1243 smaller than symbols.



1246 Fig. 9. a) Internal calibration diagram showing variation of the "OH/Si" ratio (i.e. the 1247 area ratio between the total water band, A_{OH} , and the total alumino-silicate band region, A_{Al-Si}) 1248 versus water content. b) Internal calibration lines after applying the density-related correction. 1249 c) Internal calibration line after correcting for the high Raman scattering of the 980 cm⁻¹ band 1250 in peralkaline rhyolites. All samples define a single calibration line passing through the 1251 origin. The insets show the non-corrected glass inclusion compositions (symbols as in Fig. 8). 1252 Signal intensities were normalized to laser power and acquisition time, and to the areas of the 1253 82-72f#9 internal standard.



Fig. 10. Evolution of the area of the alumino-silicate band (expressed as ratio between the alumino-silicate band area of hydrous glasses and that of the anhydrous glass) with water content (left column) and density (right column) of basanitic (a-b), basaltic (c-d), andesitic (ef) and rhyolitic (g-h) glasses. Grey dashed curves show the main trends. The arrows highlight the different behavior of Fe-rich and Fe-poor glasses with similar compositions. Microlitebearing andesitic glass A011215 is represented by an empty blue circle.

TABLES 1262

 Table 1

 Synthesis conditions and volatile composition of reference glasses.

GLASSES Series		Starting material	Synthesis met		Capsule	P (GPa)	T (K)	Time (h)	Loaded H ₂ O	Analytical	Thickness (cm)	Density ^a	Water co	ontent		CO2	References
					material				wt%	technique		(kg m ⁻³)	wt%	1σ ^ε	mol	wt%	
asanitic																	
SN050417	Alkaline	Thueyts tephra	GMF		Au ₈₀ Pd ₂₀	0	1573	4		FTIR	0.0410(5)	2841(37)	0.023	0.001	0.001		This stud
SN081117-1	Alkaline	Thueyts tephra	PC	1/2"	Au ₈₀ Pd ₂₀	1.5	1598	3		FTIR	0.0054(7)	2811(21)	2.21	0.13	0.072	0.48 ± 0.07	This stud
SN081117-2	Alkaline	Thueyts tephra	PC	1/2"	Au ₈₀ Pd ₂₀	1.5	1598	3		FTIR/CHNS	0.0055(7)	2794(11)	2.48	0.10	0.080	1.76 ± 0.03	This stud
SN101117-1	Alkaline	Thueyts tephra	PC	1/2"	Au ₈₀ Pd ₂₀	1.5	1598	3		FTIR/CHNS	0.0095(1)	2793(43)	1.92	0.07	0.063	0.82 ± 0.03	This stud
SN101117-2	Alkaline	Thueyts tephra	PC	1/2"	Au ₈₀ Pd ₂₀	2.2	1598	3		FTIR/CHNS	0.0022(3)	2790(48)	2.86	0.17	0.092	2.35 ± 0.15	This stud
asaltic																	
2-72f#22	Tholeiitic	Giant Crater Lava Field	GMF			0	1564	5.0				2806	< 0.05				[1],[2]
2-72f#19	Tholeiitic	Giant Crater Lava Field	MHC		Au ₈₀ Pd ₂₀	0.01	1503	2.1		SIMS/FTIR		2795 ^b	0.58	0.05	0.020		[1]
2-72f#10	Tholeütic	Giant Crater Lava Field	MHC		Au ₈₀ Pd ₂₀	0.025	1486	2.0		SIMS		2797	1.39	0.08	0.046		[1],[2]
2-72f#9	Tholeiitic	Giant Crater Lava Field	MHC		Au ₉₀ Pd ₁₀	0.05	1472	2.0		SIMS		2756	2.28	0.13	0.074		[1],[2]
2-72f#7	Tholeiitic	Giant Crater Lava Field	MHC		Au ₉₀ Pd ₁₀	0.10	1446	2.0		SIMS		2739	3.03	0.25	0.097		[1],[2]
2-72f#12	Tholeiitic	Giant Crater Lava Field	MHC		Au ₉₀ Pd ₁₀	0.20	1443	3.1		SIMS		2701	4.40	0.16	0.137		[1],[2]
250317	Tholeiitic	Holuhraun tephra	GMF		Au ₈₀ Pd ₂₀	0	1573	3.0		FTIR	0.0250(4)	2850(33)	0.017	0.001	0.001		This stud
/M23/3	Tholeiitic	Holuhraun tephra	PC	1/2"	Au ₈₀ Pd ₂₀	1.0	1573	68	3.7	FTIR	0.0324(4)	2815 ^b	1.53	0.19	0.051		This stud
6b	Tholeiitic	Holuhraun tephra	PC	1/2"	Au80Pd20	1.0	1473	2.0	5	FTIR	0.0016(1)	2749(11)	4.33	0.41	0.136		This stud
ndesitic																	
040417	Calcalkaline	Synthetic	GMF		Au _{so} Pd ₂₀	0	1573	20		FTIR	0.0181(6)	2580(1)	0.024	0.003	0.001		This stud
030417	Calcalkaline	Synthetic	PC	1/2"	AusoPd20	0.75	1573	24	1.0	FTIR	0.0120(2)	2565(4)	0.95	0.05	0.033	0.28 ± 0.02	This stud
310317	Calcalkaline	Synthetic	PC	1/2"	Au ₈₀ Pd ₂₀	1.1	1573	24	2.7	FTIR/CHNS	0.0451(2)	2542(22)	3.17	0.22	0.104	0.59 ± 0.01	This stud
031215	Calcalkaline	Synthetic	PC	3/4"	Au _{so} Pd ₂₀	1.0	1573	17	2.5	FTIR	0.0357(2)	2551(5)	2.24	0.11	0.075		This stud
131115	Calcalkaline	Synthetic	PC	3/4"	AusoPdan	1.0	1573	18	3.5	FTIR/CHNS	0.0298(5)	2520(5)	3.23	0.15	0.106		This stud
071215	Calcalkaline	Synthetic	PC	3/4"	Au ₈₀ Pd ₂₀	1.0	1573	24	4.0	FTIR	0.0521(2)	2516(9)	3.71	0.18	0.120		This stud
hvolitic																	
SL-N1	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2403	1.16	0.06	0.040		[3]
ISL-N3	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2378	3.30	0.16	0.109		[3]
SL-N3.3	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2375	3.51	0.18	0.115		[3]
SL-N4b	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2366	4.11	0.20	0.133		[3]
SL-N5	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2354	5.06	0.25	0.160		[3]
SL-N6	Peralkaline	obsidian from New Zealand	IHPV		Au		1273			FTIR		2330	6.09	0.30	0.188		[3]
041215	Peraluminous	Güney Dag obsidian	PC	3/4"	Au _{so} Pd ₂₀	1.0	1373	64	2 ^d	FTIR	0.0371(2)	2326(7)	3.15	0.10	0.105		This stue
261115	Peraluminous	Güney Dag obsidian	PC	3/4"	Au ₈₀ Pd ₂₀	1.0	1373	70	4 ^d	FTIR	0.0434(3)	2297(2)	5.21	0.18	0.165		This stu
201115	Peraluminous	Güney Dag obsidian	PC	3/4"	Au ₈₀ Pd ₂₀	1.0	1323	63	6 ^d	FTIR	0.0228(3)	2265(20)	6.70	0.35	0.205		This stue
licrolites-bear	ing																
011215	Calcalkaline	Synthetic	PC	3/4"	AuenPdae	1.0	1573	18	6	FTIR	0.0135(3)	2486(27)	5.65	0.30	0.175		This stur
							W								M		

Notes CMF is gas-mixing furnace; MHC is Molybdenum-Hafnium-Carbide cold-scal pressure vessel; PC is non-endloaded piston cylinder; HHPV internally heated pressure vessel. The numbers in parentheses are 10 standard deviations, given in terms of the last unit cited. References [1] Médard and Groove (2008); [2] Malfait et al. (2011); [3] Withers and Behrens (1999). ^a The sink/float method was used to measure the density of the 82-272 series of basaltic glasses; Archimedes' method for the other glasses. ^b Density calculated using the regression line of Fig. 2. ^c Uncertainty resulting from error propagation in Beer-Lambert equation. ^d In addition to -1.29 wt% H₂O of Giney Dag obsidian starting material.

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Major element composition of reference glass	s.

GLASSES	n	SiO ₂	TiO_2	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P205*	Total	NBO/T ^b
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%		_
BASANITIC*													
BSN050417	12	45.1(2)	2.47(7)	13.64(8)	10.05(11)	0.19(4)	11.16(14)	10.09(10)	3.99(12)	1.77(8)	077-0	98.45	0.780
BSN081117-1	12	43.8(2)	2.40(9)	13.29(9)	9.36(9)	0.19(5)	10.65(9)	9.82(17)	3.83(9)	1.76(7)	-	95.11	0.769
BSN081117-2	12	43.5(2)	2.40(11)	13.42(8)	9.07(14)	0.18(4)	10.09(7)	9.81(11)	3.78(14)	1.75(8)	(m)	93.97	0.739
BSN101117-1	12	43.7(3)	2.46(7)	13.57(13)	9.19(17)	0.18(4)	10.09(13)	10.15(10)	3.94(14)	1.80(9)	-	95.05	0.749
BSN101117-2	12	42.7(3)	2.48(11)	13.58(13)	9.19(17)	0.20(6)	9.69(7)	8.77(8)	3.90(14)	1.87(5)	-	92.37	0.693
BASALTIC													
82-72f#22	15	47.6(4)	0.60(6)	18.43(14)	8.13(11)	0.16(3)	10.58(10)	11.57(9)	2.33(16)	0.08(3)	0.07(3)	99.57	0.572
82-72f#19	20	46.4(5)	0.56(6)	18.26(2)	8.41(3)	0.15(2)	10.40(2)	11.51(13)	2.20(11)	0.07(3)	0.06(2)	98.05	0.571
82-72f#10	20	46.7(3)	0.52(6)	18.14(13)	8.39(23)	0.16(3)	10.44(10)	11.41(15)	2.17(11)	0.08(3)	0.06(2)	98.08	0.570
82-72f#9	20	46.9(1)	0.54(9)	18.17(12)	7.20(13)	0.15(3)	10.43(10)	11.40(15)	2.23(14)	0.07(3)	0.06(2)	97.18	0.567
82-72f#7	20	45.8(2)	0.55(7)	17.82(10)	7.41(14)	0.15(3)	10.24(14)	11.16(12)	2.18(12)	0.08(3)	0.05(2)	95.43	0.569
82-72f#12	10	45.0(2)	0.54(7)	18.25(17)	7.10(10)	0.10(2)	10.02(9)	11.28(9)	2.09 (9)	0.07(3)	0.05(2)	94.52	0.554
B250317	15	49.7(3)	1.87(6)	13.67(14)	11.88(25)	0.21(3)	6.72(17)	11.55(21)	2.26(24)	0.21(3)	0.21(7)	98.24	0.515
WM23/3	15	48.8(2)	1.80(9)	13.31(10)	12.00(22)	0.21(4)	6,87 (9)	11,46(22)	1.98(42)	0.20(3)	0.17(5)	96.80	0.524
B6b	12	47.3(3)	1.71(11)	12.89(10)	11.54(18)	0.19(5)	6.45(10)	11.03(17)	2.08(11)	0.20(3)	0.19(5)	93.55	0.519
ANDESITIC													
A040417	10	60.0(4)	0.75 (7)	17.00(13)	4.77(11)	0.17(3)	4,32(7)	6.82(9)	4.05(45)	1.38(5)	-	99.29	0.215
A030417	10	60.5(3)	0.67 (7)	15.53(18)	5,19(10)	0.15(3)	3,69(6)	6,79(17)	3,43(34)	1.32(5)	-	97.27	0.200
A310317	10	60.0(4)	0.69 (5)	15.57(11)	4.08(13)	0.17(3)	3.44(8)	6.50(5)	3,28(38)	1.33(7)	-	95.10	0.180
A031215	9	59,9(6)	0.72(11)	16.23(20)	4,51(22)	0.18(5)	4.03(15)	6.36(23)	3.71(15)	1.42(11)	-	97.05	0.199
A131115	8	58 5(3)	0.79(10)	16.18(15)	4 41(15)	0.15(4)	4.08(9)	6.42(9)	3,73(9)	1.46(9)	-	95.71	0.207
A071215	8	57.8(3)	0.67 (6)	15.81(13)	4.79(10)	0.16(3)	3.86(16)	6.71(13)	3.70(7)	1.39(7)		94.87	0.214
RHYOLITIC													
NSL-N1	12	72.3(2)	0.26(5)	10.45(4)	4.15(4)	0.07(3)	0.008(3)	0.20(1)	5,28(28)	4.45(1.6)	-	97.15	0.049
NSL-N3	12	72 1(2)	0.21(5)	10.25(3)	4 05(5)	0.08(4)	0.011(4)	0.19(2)	5 45(31)	4 28(16)		95.63	0.054
NSL-N3.3	12	70.4(3)	0.22(7)	10.25(6)	4 22(5)	0.10(3)	0.006(5)	0.19(2)	5.09(37)	4 30(21)	-	94 79	0.047
NSL-N4b	12	71.3(3)	0.22(6)	10.24(5)	3 93(8)	0.09(2)	0.010(3)	0.20(2)	516(39)	4.22(1.3)	-	95.40	0.047
NSL-N5	12	70.6(3)	0.20(3)	10 17(7)	4 05(4)	0.08(2)	0.008(7)	0.19(2)	4 55(37)	4 21 (9)	_	94.02	0.034
NSL-N6 ^c		70.4	0.20	9.86	3.87	0.07	0.004	0.17	517	4 18		93.91	0.051
R041215*	10	75.1(4)	0.04(5)	12,22(8)	0.74(1.0)	0.07(4)	0.03(2)	0.42(5)	4.09(14)	4.46(26)		97.20	0.004
B261115*	10	73.4(3)	0.05(5)	11.89(12)	0.74 (4)	0.08(6)	0.02(2)	0.41(6)	3.92(17)	4.24(19)		94.76	0.001
R201115*	10	72.3(4)	0.04(4)	11.69(13)	0.72 (8)	0.07(4)	0.02(2)	0.32(4)	3.82(15)	4.16(24)	-	93.12	0.000
Microlites-bearing	nσ												
A011215	11	57 7(3)	0.71(5)	15.60(14)	4 49(1.0)	0.14(2)	3.74(10)	6.08(13)	3 59(11)	1 38(7)	-	93 30	0 192
		57.7(3)	21/10/	-0.00(14)	1.17(10)	0.1-1(2)	30 1(10)	5.00(10)	5.5 P(11)	1.00(7)		20.03	0.12-

Notes n is the number of measurements; the numbers in parentheses are 1 σ standard deviations, given in terms of the last unit cited. All Fe is reported as FeO. ^a The P₂O₅ content of reference glasses was only measured for bæaltic compositions. The P₂O₅ content of the basanitic starting material is equal to 0.7 wt%. ^b NBO/T (i.e., non-bridging oxygen per tetrahedrally coordinated cation) is calculated on an Fe- and H₂O-free basis, following Behrens et al. (2006). ^c calculated bæed on the starting composition of the dry natural obsidian.

Table 3

Water quantification in glass inclusions.

Sample	Provenance	Host phase	Glass composition	2D size	H ₂ O wt%						% host phase
				(µm)	SIMS/ FTIR ^a	$\pm 1 \sigma$	External cal. (cubic bas.) ^b	$\pm1\sigma^c$	External cal. (linear bas.) ^b	$\pm 1 \sigma^c$	-correct.
Vaggelli-3-1 ^e	Santorini	Olivine	Basalt	110 × 50	3.10	0.06	3.15	0.12	3.25	0.17	0.0
Vaggelli-4-1°	Santorini	Olivine	Basalt	140×120	3.20	0.05	3.02	0.12	3.15	0.17	0.0
Vaggelli-6-1°	Santorini	Olivine	Basaltic andesite	210×110	3.30	0.04	3.27	0.13	2.98	0.19	0.0
Vaggelli-2-1°	Santorini	Olivine	Andesite	130×80	3.30	0.10	3.33	0.13	3.10	0.19	0.5
\$12-371-3°	Santorini	Olivine	Basalt	190×115	2.71	0.03	2.77	0.11	2.71	0.15	0.0
S12-43-7-1"	Santorini	Olivine	Basalt	255×135	1.48	0.01	1.55	0.06	1.29	0.08	0.0
S12-43-1-1°	Santorini	Olivine	Basaltic andesite	65×50	1.60		1.64	0.06	1.62	0.09	1.0
TAO-ol1	Lanzarote	Olivine	Basanite	62×52	1.70	0.05	1.74	0.07	1.53	0.10	4.0
TAO-ol20	Lanzarote	Olivine	Basanite	101×25	1.36	0.05	1.26	0.06	1.14	0.08	1.5
TGN-ol18	Lanzarote	Olivine	Basanite	244×154	1.79	0.05	1.66	0.07	1.73	0.11	0.0
FZ OL37b	FAMOUS Zone	Olivine	Basalt	75×70	0.093	0.003	0.127	0.007	0.105	0.007	not embedded
FZ OL39	FAMOUS Zone	Olivine	Basalt	150×125	0.140	0.006	0.173	0.008	0.132	0.009	not embedded

Notes ^a Water contents measured by SIMS, except for FZ OL37b and OL39 analyzed with FTIR (Schiavi et al., 2016). ^b Water contents estimated from the regression lines of Fig. 8 (high confocality setting). ^c Uncertainties calculated from the errors related to the linear regression (see Eq. 1 in the text) for 95% confidence interval. ^d Arithmetic subtraction of host phase spectrum from glass spectrum. ^e Reference: Druitt et al., 2016