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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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**Abstract**

New series of alumino-silicate glasses spanning a wide range of chemical compositions (basanites, tholeiitic basalts, calcalkaline andesites, peraluminous and peralkaline rhyolites) and with water contents from 0.02 to 6.70 wt % were used for improving the method of quantification of dissolved water with a highly confocal Raman micro-spectrometer. After reconsideration of previously proposed methods for spectra acquisition and post-analysis data treatment, we define the main critical steps that allow minimizing glass matrix effects. First, we carefully assess the variation of Raman band intensities, in both water ( $\sim 3000\text{-}3800\text{ cm}^{-1}$ ) and alumino-silicate vibration ( $\sim 200\text{-}1250\text{ cm}^{-1}$ ) regions with focus depth of the laser beam inside the sample. Our results indicate that in the first 2-10  $\mu\text{m}$  depth, the intensity increase in the alumino-silicate region is twice as high as that in the water region. Optimal focus depths, 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 the Raman spectrometer. This influences both external and internal calibration slopes. 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

calibration method. (a) We provide a procedure for correcting the effect of glass density on water internal calibration based on the observation that the integrated intensity (i.e. the area) of the alumino-silicate envelope generally drops with the increase of water content and decrease of glass density. (b) In CO<sub>2</sub>-bearing glasses, the intensity of the  $\nu_1$  Raman vibration of dissolved carbonate at  $\sim 1087\text{ cm}^{-1}$  has to be subtracted from the intensity of the alumino-silicate envelope before applying the density correction. (c) Using peak-fitting, the intensity of the  $850\text{-}1250\text{ cm}^{-1}$  envelope of peralkaline rhyolitic glasses is corrected for the effect of the presence of four-fold coordinated Fe<sup>3+</sup>, as revealed by the strong Raman scattering of the vibrational mode at  $\sim 980\text{ cm}^{-1}$ . Following this procedure, all the studied glasses define a 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 the external and internal calibrations reproduce the whole dataset within 0.13-0.11 wt % (high and standard confocality) and 0.17 wt %, respectively. The accuracy of the external calibration is evaluated based upon comparison with ion-probe measurements of water dissolved in natural glass inclusions: the relative standard deviation is  $\sim 4\%$  ( $1\sigma$ ) on average, and reaches  $\sim 12\%$  ( $1\sigma$ ) for water contents of  $\sim 0.1\text{ wt\%}$ .

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

## 1. INTRODUCTION

Concentration, speciation and distribution of volatile species dissolved in silicate melts are key factors that control the physico-chemical evolution of magmas from their genesis to their final emplacement and affect the dynamics, style, and intensity of volcanic eruptions (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 quantification of volatiles contained in a variety of materials, which are of interest in volcanological and petrological studies, in particular water (regardless of speciation) dissolved in natural glasses. With respect to the other micro-analytical techniques used for quantification of water in rock samples, such as Fourier transform infrared spectroscopy (FTIR), secondary ion mass spectrometry (SIMS), and elastic recoil detection analysis (ERDA), Raman spectroscopy has several advantages: (i) it requires minimal sample preparation, (ii) it is non-destructive, (iii) it allows rapid analysis with high spatial resolution, which is of utmost importance for characterization of small samples and samples with small-scale heterogeneity, and (iv) it allows analysis of unexposed glass, fluid and solid inclusions 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., 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

height, hereafter  $I_{OH}$ ) or the integrated intensity (i.e. the area, hereafter  $A_{OH}$ ) of the water band located around  $3570\text{ cm}^{-1}$  (Fig. 1) with water band intensities or integrated intensities of well-characterized standard glasses. The relationship between intensity of the water Raman band 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 glass composition is especially apparent when glasses belonging to alkaline and sub-alkaline series are compared (Behrens et al., 2006; Di Muro et al., 2006b; Mercier et al., 2010). According to Mercier et al. (2010), glass reflectance and density, as well as water environment, are the main parameters causing matrix effects on the external calibration. Thus, a set of glass standards spanning a wide range of compositions seems required for accurate quantification of water in natural glass samples.

The second calibration method is known as “internal calibration” because the intensity 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  $1250\text{ cm}^{-1}$  (Behrens et al., 2006; Le Losq et al., 2012; Di Genova et al., 2017), the band located at high wavenumbers between  $850$  and  $1250\text{ cm}^{-1}$  (Zajacz et al., 2005; Behrens et al., 2006; Severs et al., 2007; Mercier et al., 2009), or the band at low wavenumbers ranging from  $200$  to  $650\text{ cm}^{-1}$  (Thomas, 2000; Chabiron et al., 2004; Behrens et al., 2006; Mercier et al., 2009) (Fig. 1). Intensity versus content relationships obtained with an internal calibration procedure are expected to be less affected by instrumental and analytical conditions, such as laser power fluctuations, focusing errors, and differences in confocal volume size, light absorption and reflectance that depend on glass structure and composition. In reality, internal calibrations also depend on glass chemical composition, because both bands in the alumino-silicate region and the average Raman scattering cross section of all the different alumino-silicate structural units ( $Q^n$ ) depend on glass composition (Franz and Mysen, 1995).

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

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

## 2. METHODOLOGY

### *2.1 Starting materials*

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

Two distinct sets of rhyolitic glasses were synthesized from the Güney Dag obsidian (Turkey; Druitt et al., 1995) and from a peralkaline rhyolite (labeled as NSL) from New Zealand, whose exact provenance is unknown (Behrens and Jantos, 2001) (Table 1). Both rhyolites are very poor in microlites. The Güney Dag rhyolite is mildly peraluminous, SiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-rich (~77 and 12.5 wt %, respectively), FeO- and CaO-poor (0.8 and 0.25 wt %, respectively) and contains 1.39 wt % H<sub>2</sub>O (Mourtada-Bonnefoi and Laporte, 2002). This relatively large H<sub>2</sub>O content is due to the water contained in the glass phase of the obsidian (1.05 ± 0.05 wt %; Mourtada-Bonnefoi and Laporte, 2002) and to the presence of biotite and amphibole microlites (Cluzel et al., 2008). The rhyolite from New Zealand has lower SiO<sub>2</sub> (~75 wt %) and Al<sub>2</sub>O<sub>3</sub> (~10 wt %), higher Fe (as total FeO ~4 wt %) and Na<sub>2</sub>O (~5.5 wt %) contents, and contains 0.1-0.4 wt % H<sub>2</sub>O.

Two sets of basaltic glasses were synthesized starting from a primitive high-alumina basalt erupted from the Giant Crater Lava Field (Medicine Lake volcano, California; Médard and Grove, 2008; Malfait et al., 2011) and from tephra erupted from Holuhraun volcano (Iceland) in 2014 (Haddadi, 2016). The composition of the Medicine Lake volcano basalt (labeled as 82-72f) is very close to that of primitive mid-ocean ridge basalts, with a higher Al<sub>2</sub>O<sub>3</sub> content (~18.5 wt %). The composition of the basalt from Holuhraun is richer in FeO (~12.5 wt %) and poorer in Al<sub>2</sub>O<sub>3</sub> (~14 wt %) and is typical of lavas erupted from the Bárðarbunga magmatic system (Sigmarsson and Halldorsson, 2015).

A set of reference glasses with basaltic composition and bearing different amounts of H<sub>2</sub>O and CO<sub>2</sub> were synthesized from a natural basaltic tephra sampled at Thueyts volcano (Ardèche, France). The tephra composition is characterized by low SiO<sub>2</sub> (~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 Na<sub>2</sub>O concentration. The details of the syntheses are presented below.

## ***2.2 Experimental Procedures***

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

For the synthesis of the andesitic glasses, we used a decarbonated mixture of oxide (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MnO and MgO), silicate (CaSiO<sub>3</sub>) and carbonate (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>) reagent powders. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO powders were dried in platinum crucibles in air at 1000-1100 °C overnight. CaSiO<sub>3</sub> and carbonate powders were dried in air at 250-400 °C overnight. These dried powders were weighed and ground altogether in an agate mortar to ensure a homogeneous starting mixture. For decarbonation and fusion, the mixture was held in a platinum crucible and heated by a gas-mixing furnace at one bar; as temperature changed, the gas mixture was adjusted to maintain *f*O<sub>2</sub> near FMQ buffering conditions. Temperature



was increased to 1000 °C in 6 hours, kept constant overnight, then increased and held for 30 min at 1400 °C before quenching the glass in water. In order to obtain a homogeneous glass, grinding and fusion were repeated a second time. Finally, the glass was ground for two more 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.

Anhydrous glasses were synthesized by re-melting the starting materials in a gas-mixing furnace at one bar, 1300 °C and  $fO_2$  ~FMQ (Table 1). The starting materials were loaded into Au<sub>80</sub>-Pd<sub>20</sub> capsules whose upper side was left open to allow degassing, held at high temperature for several hours, and finally drop-quenched in water.

The hydrous glasses were synthesized in a piston-cylinder apparatus using a Pyrex-MgO assembly, a graphite heater, an outer NaCl cell, and Au<sub>80</sub>-Pd<sub>20</sub> capsules (5 and 4 mm outer diameter for 3/4" and 1/2" assemblies, 0.2 mm wall thickness, 4-5 mm length). First, deionized water was added at the bottom of the capsule using a micro-syringe; after loading and compacting ~100 mg of glass powders (or cylinders), the capsule was welded shut. We checked for leaks during capsule preparation by weighing the welded capsules before and after 1-hour heating at 120 °C in an oven. For the synthesis of H<sub>2</sub>O and CO<sub>2</sub>-bearing glasses with andesitic and basanitic compositions (Table 1), we added a mixture of water and oxalic acid dihydrate (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) to glass powders. After welding, the capsules were placed in an oven first at 350 °C for 1 hour to decompose the oxalic acid, and then at 120 °C overnight to ensure homogenous distribution of the volatiles. In all experiments, the *P-T* conditions

were chosen to be well above the volatile saturation curve (Duan, 2014). The temperature was measured very close to the capsule by a W<sub>95</sub>Re<sub>5</sub>-W<sub>74</sub>Re<sub>26</sub> thermocouple. Hydration experiments were ended by switching off the heating power, quenching the samples at cooling rate > 80 °C/s. Experimental conditions are reported in Table 1.

The glasses recovered from the experiments were cut and polished on one or both sides for major element characterization by electron microprobe and water and CO<sub>2</sub> concentration measurements by infrared and Raman spectroscopies. Homogeneity of the glasses was first checked under the microscope. All analyzed glasses were bubble- and crystal-free, except for one andesitic water-rich glass (A011215) that contains microlites crystallized upon quenching. The microlite-bearing glass is not suitable as standard; however, since the percentage of microlites is small and glass composition is homogeneous, it was used for comparison in Raman measurements.

### **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 µm (10 µm for basaltic glasses) defocused beam in order to reduce Na loss. The acquisition time was 20 s for Al (and for Mg and Ca in basaltic 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.

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

beamsplitter and a MCT (Mercury-Cadmium-Tellurium alloy) detector. Plane parallel, double polished glass samples were placed on a CaF<sub>2</sub> window. Absorbance and background spectra of the glasses were obtained by acquisition of 300 and 100 scans, respectively. Beam size was 70 × 70 μm and spectral resolution was 4 cm<sup>-1</sup>. Concentrations of OH groups and molecular H<sub>2</sub>O were determined from the height of the absorbance bands at 4500 and 5240 cm<sup>-1</sup>, respectively, using the Beer-Lambert law (e.g. [Stolper, 1982](#)). The 4500 and 5240 cm<sup>-1</sup> bands are commonly assigned to a combination of the stretching vibrations of OH groups attached to Si and the combination of the stretching and bending vibrations of the H<sub>2</sub>O molecule, respectively. Total water contents of the basaltic glasses belonging to the Holuhraun set, the basanitic glasses and two water-poor andesitic glasses (A030417 and A040417) were derived from the height of the broad asymmetric band at 3570 cm<sup>-1</sup>, which contains the fundamental OH stretching vibrations of both molecular H<sub>2</sub>O and Si-OH (and Al-OH) structural groups (e.g. [Stolper, 1982](#)). Baseline correction (see below) and peak integration were performed using OPUS software. On each sample, we carried out several measurements in order to verify compositional homogeneity. Homogeneity was confirmed by small relative standard 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 ± 1 μm and < 1 μm, respectively. Thicknesses (and associated standard deviations) reported in [Table 1](#) are average values of 4-8 measurements.

Glass density ( $\rho$ ) 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 studied reference glasses are reported in [Table 1](#) and [Figure 2](#).

The largest uncertainty in water contents determined by FTIR analysis is due to the uncertainty on the molar absorptivity (i.e. extinction coefficient) for the absorbance bands at 4500 and 5240  $\text{cm}^{-1}$ . As estimated absorptivity coefficients depend on the baseline subtraction method (e.g. [Ohlhorst et al., 2001](#)), we followed guidelines provided by [Ohlhorst et al. \(2001\)](#) and [Mandeville et al. \(2002\)](#) for proper choice of baseline fitting procedure and molar absorptivity values.

In rhyolitic glass spectra, a linear baseline was fitted as tangent through the minima on both sides of the 5240  $\text{cm}^{-1}$  band and then extrapolated below the 4500  $\text{cm}^{-1}$  band (GG 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  $\epsilon_{4500}$  (OH) and  $1.72 \pm 0.06 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{5240}$  ( $\text{H}_2\text{O}$ ). Measured water concentrations in rhyolitic glasses match with target compositions (i.e. the amount of water loaded into the capsule) and are close to the difference of EMP analyses total from 100 wt %.

For andesitic glasses, we used the average values of the extinction coefficients determined by [King et al. \(2002\)](#) and [Mandeville et al. \(2002\)](#):  $0.97 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{4500}$  (OH),  $1.08 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{5240}$  ( $\text{H}_2\text{O}$ ), and  $66.32 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{3570}$  (total water). [Mandeville et al. \(2002\)](#) showed that  $\epsilon_{4500}$  and  $\epsilon_{5240}$  molar absorptivities have significant compositional dependency and can be predicted if the tetrahedral ( $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ) cation /total cation fraction of the glass is known. Molar absorptivity values calculated for the andesitic glasses using the regression line equations provided by [Mandeville et al. \(2002\)](#) are  $\sim 1.00$  and  $1.19 \text{ (L mol}^{-1} \text{ cm}^{-1})$  for  $\epsilon_{4500}$  and  $\epsilon_{5240}$ , respectively, which are very close to the adopted values. The baseline of andesitic glass spectra was fitted as tangent through three points: the minima on both sides of the 4500  $\text{cm}^{-1}$  band and the minimum on the low wavenumber side of

the 5240  $\text{cm}^{-1}$  band. On its high wavenumber side (at  $\sim 5400 \text{ cm}^{-1}$ ), 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.

We determined water contents in the basanitic and Holuhraun basaltic glasses based on the height of the absorbance band at  $\sim 3570 \text{ cm}^{-1}$ . This choice was driven by the observation that the spectrum background around the 4500 and 5240  $\text{cm}^{-1}$  bands is strongly affected by the absorption of near infrared and visible electronic transitions or crystal field bands of iron ([Ohlhorst et al., 2001](#)). Consequently, baseline fitting around these bands becomes more laborious and the choice of  $\epsilon_{4500}$  and  $\epsilon_{5240}$  for basanites and iron-rich basalts may be less accurate. In contrast, the linear baseline under the large band at 3570  $\text{cm}^{-1}$  is unambiguously defined. For basanites, we used the molar absorption coefficient provided by [Shishkina et al. \(2014\)](#),  $57.3 \pm 1.8 \text{ L mol}^{-1} \text{ cm}^{-1}$ . For basalts, we adopted the molar absorption coefficient provided by [Mercier et al. \(2010\)](#),  $62.8 \pm 0.8 \text{ L mol}^{-1} \text{ cm}^{-1}$ , which is very close to the 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  $\text{cm}^{-1}$ , 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. \(2014\)](#) ( $306 \pm 32 \text{ L mol}^{-1} \text{ cm}^{-1}$  for 1430 and  $349 \pm 25 \text{ L mol}^{-1} \text{ cm}^{-1}$  for 1520) and those given by [King et al. \(2002\)](#) ( $269$  and  $271 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the 1430 and 1520 bands, respectively).

Water and CO<sub>2</sub> 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 %.

## ***2.5 Raman Spectroscopy***

Raman spectra were collected at LMV using an InVia confocal Raman micro-spectrometer 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<sup>-1</sup> that had been reflected by the sample surface.

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

observed that the Raman signal intensity of the dark H<sub>2</sub>O- 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.

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

Analytical precision calculated based on repeated daily measurements of reference glasses is generally better than 6 % and 2 % relative, respectively, in water-poor and water-rich glasses in highly confocal setting. This difference is mainly related to degradation of the signal-to-noise ratio in spectra of water-poor glasses. Performing measurements under standard confocality conditions yields better analytical precision because the analyzed volume is larger, so Raman signal is more intense and small differences in focusing depth are less 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 sample surface, in fact, small variations of the excited sample volume are more likely to occur because the beam is not entirely inside the sample and reflectance at the sample surface has a 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.

### 3. GLASS DENSITY

Figure 2 shows the relationship between glass densities,  $\rho$  (kg/m<sup>3</sup>), and water contents,  $C_{H_2O}$  (wt %), determined by FTIR spectroscopy or SIMS (Table 1). A linear relationship  $\rho = \rho_0 + b C_{H_2O}$ , where  $\rho_0$  is the density of the anhydrous glass and  $b$  the slope of the line, is observed. Density diminishes with increasing water content. The slope for mafic glasses is more important than the ones for intermediate and felsic glasses. The slopes defined by the rhyolitic and andesitic sample sets are in agreement with those found by Ohlhorst et al. (2001) and Behrens et al. (2006) for similar glass compositions. Moreover, the measured rhyolitic and andesitic glass densities are very close to densities measured by Withers and Behrens (1999) and Mandeville et al. (2002). The slope obtained for the 82-72f basaltic set is slightly more pronounced than the slope reported by Ohlhorst et al. (2001) for basaltic composition. As expected, the Fe-richer sets of basaltic and rhyolitic glasses are characterized by higher densities than the Fe-poorer sets. The measured basaltic glass densities fall within the range of values calculated by Iacovino et al. (2016). Density of the A011215 sample is aligned with that of the other andesitic glasses, even though it contains microlites.

### 4. RAMAN SPECTRAL TREATMENT

#### 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<sup>-1</sup>.

In previous studies, different approaches were adopted for defining the baseline shape and the choice of anchor points (e.g., Zajacz et al., 2005; Behrens et al., 2006; Severs et al., 2007; Di Muro et al., 2009; Mercier et al., 2009, 2010; Le Losq et al., 2012). A first approach consisted in fitting the baseline of raw spectra using either a combination of linear baselines (Severs et al., 2007), a cubic baseline (Mercier et al., 2009) or a cubic spline baseline (Behrens et al., 2006) with three/four anchor points in the alumino-silicate vibration region 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<sup>-1</sup> spectral region towards low wavenumbers (Fig. 1). Such an extrapolation is possible only if the spectral background between 1250 and 1850 cm<sup>-1</sup> is not too steep. In a second approach, the baseline was subtracted from spectra that had been previously corrected for Long's correction (Long, 1977). Behrens et al. (2006) and Di Muro et al. (2009) adopted, respectively, a cubic spline and a cubic baseline anchored only at the extremities of the alumino-silicate and water domains, whereas Le Losq et al. (2012) anchored the spline to a limited number of intermediate minima. In general, we observe that discrepancies between different spectral corrections arise from unconstrained concavity of the spline baseline.

Difficulties are encountered in fitting the baseline in the alumino-silicate vibration region, because there is no simple *a priori* way to relate the shape of broad Raman bands to specific network vibrations and structures, although statistical analysis and peak fitting

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).

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

several short linear segments are necessary to fit the curve. A second intermediate anchor point was set around 800-830  $\text{cm}^{-1}$  in basalts, 825-840  $\text{cm}^{-1}$  in andesites, and  $\sim 840 \text{ cm}^{-1}$  in rhyolites. We did not fix an anchor near 820  $\text{cm}^{-1}$  in basanites because the corresponding minimum tends to disappear in  $\text{H}_2\text{O}$  and  $\text{CO}_2$ -bearing basanites. The defined anchors correspond to minima regions, and in some cases are defined by tangent lines to the spectra. We note that the positions of the intermediate anchor points and that of the anchor at the high wavenumber end of the spectrum shift to higher frequency as the polymerization increases, in agreement with previous observations (Le Losq et al., 2012).

In the water domain of the spectra, linear baselines were anchored ( $\sim 2980$  and  $3780 \text{ cm}^{-1}$ ) and cubic baselines were fit (from 2980 to 3000-3008 and from 3725 to  $3780 \text{ cm}^{-1}$ ) 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.

## ***4.2 Alumino-silicate band topology and assignment***

### ***4.2.1 Topology of Raman spectra***

In the alumino-silicate region of the Raman spectrum (200 to  $1250 \text{ cm}^{-1}$ ), 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

bands as High-Frequency (HF) and Low-Frequency (LF) bands. Increasing water content in basanitic and basaltic glasses has several effects: a) the maximum peak position of the LF bands shifts from 556 to 510  $\text{cm}^{-1}$  and from 532 to 512  $\text{cm}^{-1}$  in basanites and basalts, respectively; b) the maximum peak position of the HF bands shifts from 968 to 975  $\text{cm}^{-1}$  in basanites, and from 966 to 990  $\text{cm}^{-1}$  in basalts. c) The FWHM of the HF band slightly decreases from 181 to 164  $\text{cm}^{-1}$  and from 184 to 177  $\text{cm}^{-1}$  in the Fe-rich (Holuhruan) and high-Al (82-72f) basaltic sets, respectively (Fig. 2S b). d) In basalts, the ratio of LF band (integrated) intensity to HF band (integrated) intensity increases due to apparent decrease of 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  $\sim 580 \text{ cm}^{-1}$  characterizes the LF bands. A broad weak band centered at  $\sim 710 \text{ cm}^{-1}$  defines the spectrum topology in the intermediate wavenumber range (650-800  $\text{cm}^{-1}$ ). In basanites, the relative 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  $\text{CO}_3^{2-}$  molecules in basanites produce a peak near 1083  $\text{cm}^{-1}$ , whose intensity increases with the  $\text{CO}_2$  content, in agreement 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  $\sim 1013\text{-}1022 \text{ cm}^{-1}$  (with the only exception of the A071215 glass whose maximum peak is at 970  $\text{cm}^{-1}$ ). 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  $\text{cm}^{-1}$  (Fig. 2S f). As in basalts, the LF band exhibits a shoulder at  $\sim 580 \text{ cm}^{-1}$ . A small asymmetric band centered at  $795 \text{ cm}^{-1}$  is present in all andesitic glasses (Fig. 4). Dissolved  $\text{CO}_3^{2-}$  molecules in A310317 and A030417 glass samples produce a peak near  $1078 \text{ cm}^{-1}$ , which is more pronounced in A310317.

Rhyolitic glasses are characterized by a main asymmetric band centered at 467-484  $\text{cm}^{-1}$ . Maximum LF peak position shifts to higher frequency with increase of water content dissolved in the glass, contrary to what is observed in basalts. Its FWHM varies from 122 to 130  $\text{cm}^{-1}$  and from 134 to 145  $\text{cm}^{-1}$  in the peraluminous (Güney Dag obsidian) and peralkaline (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 band has a shoulder at  $\sim 580 \text{ cm}^{-1}$ . A small band centered at  $795 \text{ cm}^{-1}$  is present in all rhyolitic spectra; its intensity slightly decreases with increased water content of peraluminous glasses. Major differences between the two glass sets and within each set are principally observed in the high wavenumber range (850 to  $1200 \text{ cm}^{-1}$ ). In this range, the spectra are defined by several sub-bands, whose position, shape and relative intensities are strongly affected by glass composition and degree of polymerization (Fig. 4). Peraluminous rhyolites spectra show a less intense band centered at  $\sim 930 \text{ cm}^{-1}$  and a more intense band centered at  $\sim 1135 \text{ cm}^{-1}$ . The intensity of the band near  $930 \text{ cm}^{-1}$  slightly increases with water content. In the peralkaline rhyolites, instead, the band occurring at  $1135 \text{ cm}^{-1}$  is much smaller than the band located around  $980 \text{ cm}^{-1}$ . Compared to the glasses of the same set, the water-poor NSL-N1 glass differs in that its spectrum has a more pronounced band near  $1050 \text{ cm}^{-1}$ .

#### 4.2.2 Review of the interpretation of bands

In the 200-1300  $\text{cm}^{-1}$  region of the Raman spectrum, bands correspond to different bridging and non-bridging T-O vibrations in the glass structure (e.g., [Brawer and White, 1977](#); [Matson et al., 1983](#); [McMillan, 1984](#); [McMillan et al., 1992](#)). The LF band near 400-500  $\text{cm}^{-1}$ , which is dominant in polymerized glasses, is traditionally assigned to: a) rocking motion in fully polymerized  $Q^4$  units (where  $Q^4$  denotes a tetrahedron linked by bridging O atoms to 4 adjacent tetrahedra), b) breathing modes of four- and six-membered rings of  $\text{TO}_4$  tetrahedra in polymerized glasses ([Sharma et al., 1981](#); [Matson et al., 1983](#); [Rossano and Mysen, 2012](#)), but also c) T-O-T symmetric stretching vibrations involving bridging oxygens and four-fold coordinated cations ([Zotov et al., 1992](#)) and d) T-O-T bending vibrations in glasses containing non-bridging oxygens ([McMillan, 1984](#); [Rossano and Mysen, 2012](#) and references therein). In rhyolitic glasses, decreasing FWHM of the LF band ([Fig. 2S j](#)) and its shift to higher frequency with increasing water content have been explained by a possible decrease in the average T-O-T angle ([McMillan and Remmele, 1986](#)).

The vibrational mode at 570-580  $\text{cm}^{-1}$  has been attributed to either structural defects (i.e. broken oxygen bridges, [Stolen and Walrafen, 1976](#); [Seifert et al., 1981](#); [McMillan and Remmele, 1986](#)) or a mixed stretch-bend vibration in  $Q^2$  structural units ([Furukawa et al. 1981](#)). The bands near 700 and 800  $\text{cm}^{-1}$  have been respectively ascribed to T-O-T bending motions ([Mysen et al., 1980](#); [Furukawa et al. 1981](#); [McMillan, 1984](#); [Rossano and Mysen, 2012](#)) and to cage-like vibrations of Si atoms mainly in  $Q^4$  tetrahedra ([Zotov and Keppler, 1998](#)).

The main HF envelope at 900-1200  $\text{cm}^{-1}$  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  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  for  $\text{Si}^{4+}$  as network-forming cations strongly

influences the spectral composition of this band; in particular, increasing the Al content of the glass results in the shifting of Raman bands to lower frequencies (Brawer and White, 1977; Mysen et al., 1980; Neuville et al., 2004). The intensity ratio between the bands near 950 and 1135  $\text{cm}^{-1}$  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 Keppler, 1998). The band near 1050  $\text{cm}^{-1}$  that characterizes the water-poor NSL-N1 glass is tentatively assigned to T-O stretching vibrations in distinct  $Q^3$  or  $Q^4$  units (Mysen et al., 1980; Zotov and Keppler, 1998). In the peraluminous rhyolites, the increased intensity of the band at ~930  $\text{cm}^{-1}$  with increasing water content can be attributed to the formation of T-OH units (Zotov and Keppler, 1998). In peralkaline glasses, the sharp increase of the band at 970-980  $\text{cm}^{-1}$  is attributed to progressive entry of four-fold  $\text{Fe}^{3+}$  in alkali-bonded  $Q^3$  units (Wang et al., 1995; Di Muro et al., 2009; Di Genova et al., 2016).

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

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  $Q^3$  units. In the high-Al basaltic set, both water content and polymerization degree correlate negatively with the FWHM of the HF band (Fig. 2S a, b) and positively with the intensity ratio of LF band to HF band (Fig. 2S c, d). This seems to be contradictory as water dissolution is expected to enhance depolymerization. Although investigation of dissolution mechanisms of water in basaltic melts is beyond the scope of this study, it is worth noting that the described spectral features likely suggest dissolution mechanisms other than those occurring in more polymerized glasses. In depolymerized CaO-MgO-SiO<sub>2</sub> glasses, Xue and Kanzaki (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.

### ***4.3 Water band topology***

The topology of the water stretching vibration band depends on glass matrix composition and water concentration (Fig. 5), but also on water speciation (e.g., Mysen and Virgo, 1986) and strength of H-bonding (e.g., Zajacz et al., 2005; Behrens et al., 2006; Di Muro et al., 2006). Different water species (metal-hydroxyl and molecular H<sub>2</sub>O) contribute to the intensity of the broad water band-envelope (e.g., Mysen and Virgo, 1986). The latter is asymmetric in shape with a long tail on the lower wavenumber side, and is characterized by two shoulders near 3250 cm<sup>-1</sup> and 3640 cm<sup>-1</sup> that are readily observed in rhyolitic glasses (Fig. 5). The exact position of the maximum peak of the water band shifts to lower frequency with increase of polymerization degree and water content (Fig. 5), in agreement with previous studies. The maximum is located within the 3565-3582 cm<sup>-1</sup> range in basaltic glasses and at 3552-3570 cm<sup>-1</sup> in basaltic, andesitic and rhyolitic glasses. In the basaltic, basaltic and andesitic glass sets, the FWHM of the band increases by 15-25 % relative with increasing water content.

The H<sub>2</sub>O bending vibration at ca. 1630 cm<sup>-1</sup> (not shown) can be clearly distinguished from the background in spectra of water-rich glasses.

### ***4.4 Peak fitting of the HF and water bands***

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



basaltic and rhyolitic glasses (Tables 1S, 2S and 3S). Spectra were fitted with a finite number of Gaussian components using the Multiple Peak Fit tool and following a procedure analogous to the one described by Morizet et al. (2013). This procedure consists of: i) locating a certain number of peaks based on results of previous studies (e.g., Di Muro et al., 2009; 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  $\chi^2$ ) does not change; and iii) performing a second set of iterations in which peak position and areas are left free to evolve, until the best fit possible (i.e., the lowest  $\chi^2$ ) is obtained. Fitting parameters were iterated until the fit converged using both Simplex method and Levenberg-Marquardt algorithm available in OriginPro, and the two algorithms provided comparable results. In our simulations, the  $\chi^2$  tolerance value of  $10^{-9}$  was always reached. The errors associated with the simulations are reported in Tables 1S, 2S and 3S. The proposed simulations may represent one of several possible fits; however, consistency in fitting parameters within each glass series and general agreement with deconvolutions reported in the literature (e.g., Di Muro et al., 2009; Rossano and Mysen, 2012; Morizet et al., 2013) ensure the reproducibility of the calibrations established in the next sections. In fact, we verified that the small changes in the constrained parameters had a negligible effect on the ratios between the areas of different 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  $\text{cm}^{-1}$ , II) 975-1000  $\text{cm}^{-1}$  (with the highest frequencies in peraluminous rhyolites), III) 1047-1060  $\text{cm}^{-1}$ , IV) 1113-1126  $\text{cm}^{-1}$ , and V) 1174-1182  $\text{cm}^{-1}$ . 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 CO<sub>2</sub>-bearing basanitic glasses, best fitting in the 630-1200 cm<sup>-1</sup> spectral range was achieved with six to seven components, whose positions are: I) 707-715 cm<sup>-1</sup>, II) 779-789 cm<sup>-1</sup>, III) 864-891 cm<sup>-1</sup>, IV) 930-963 cm<sup>-1</sup>, V) 990-1021 cm<sup>-1</sup>, VI) 1061-1077 cm<sup>-1</sup> and VII) 1084-1088 cm<sup>-1</sup> (Fig. 3S, Table 2S). The last component refers to the  $\nu_1$  Raman vibration of dissolved carbonate (Morizet et al., 2013).

Peak fitting of the total water band requires a minimum of four Gaussian components (Table 3S, Fig. 4S), in agreement with previous studies (e.g., Chabiron et al., 2004; Behrens et al., 2006; Di Muro et al., 2006). The positions of these components are: I) 3080-3098 cm<sup>-1</sup>, II) 3250-3298 cm<sup>-1</sup>, III) 3420-3487 cm<sup>-1</sup> (with the highest frequencies in rhyolites), IV) 3540-3575 cm<sup>-1</sup>, and V) 3600-3645 cm<sup>-1</sup> (with the lowest frequencies in basanites and basalts); these positions match those determined by Di Muro et al. (2006). The small component I is only present in water-rich glasses (Fig. 5), as observed by Behrens et al. (2006). In general, the intensity of the low frequency components increases with total dissolved water, in agreement with the expected increase of molecular water (e.g. Mysen and Virgo, 1986).

## 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.

In the alumino-silicate domain of basanitic and basaltic glass spectra, signal intensity increases from the surface to a depth of 2-3  $\mu\text{m}$  and 3-4  $\mu\text{m}$  in high and standard confocality, 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  $\mu\text{m}$   
613 depth, is 50 % higher than the signal at the surface. Below the maximum normalized intensity,  
614 the intensity decreases with depth by 3 %/ $\mu\text{m}$  in the first 30  $\mu\text{m}$  in basanitic glasses and by  
615 2 %/ $\mu\text{m}$  in both basaltic and andesitic glasses (Fig. 7). Maximum alumino-silicate signal  
616 intensity in rhyolitic glasses is attained at ~5  $\mu\text{m}$  depth in a highly confocal setting, but at 7-  
617 10  $\mu\text{m}$  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 %/ $\mu\text{m}$  (high confocality) and 0.5 %/ $\mu\text{m}$  (standard  
620 confocality) for the remainder of the first 30  $\mu\text{m}$ .

621 Maximum signal intensity of the water band is attained at the same depths as for the  
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 %/ $\mu\text{m}$  in basanites, by  
632 1.5 %/ $\mu\text{m}$  in basaltic and andesitic compositions, whereas it remains almost constant over 12  
633  $\mu\text{m}$  in rhyolitic glasses before dropping by 0.7 %/ $\mu\text{m}$ . The evolution with depth of the OH/Si  
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

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

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, the signal intensities of both alumino-silicate and water bands drop faster with depth when the laser power on the sample is about 75 mW. This is especially relevant for basaltic glasses, in which maximum signal intensity occurs at the glass surface at these high laser-power conditions. These observations are consistent with more intense self-absorption expected in basaltic glasses compared to more silica-rich glasses (e.g., [Behrens et al., 2006](#); [Mercier et al., 2009](#)). Excitation of (iron-bearing) basaltic samples, in fact, results in attenuation of both the 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  $\mu\text{m}$  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.

## 6. CALIBRATION

### *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  $\sim 3570\text{ cm}^{-1}$  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).

When spectra are treated using the described procedure for focus depth selection and 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 measurements, however, are affected by a larger scatter than correlations based on peak area (Fig. 5S), therefore, only calibrations based on area measurements are considered hereafter. Such a difference is explained by the observation that varying amounts of water dissolved in glasses with different compositions produce not only variations in peak height, but also in total band width and distribution of spectral components (as summarized in the previous 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:

$$C_{H_2O} \text{ (wt\%)} = 2.403 (\pm 0.033) \cdot A_{OH} - 0.058 (\pm 0.046) \quad (R^2 = 0.995), \quad (1)$$

and standard confocality setting:

$$C_{H_2O} \text{ (wt\%)} = 2.057(\pm 0.025) \cdot A_{OH} + 0.072 (\pm 0.039) \quad (R^2 = 0.996). \quad (2)$$

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  $H_2O$  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 several months.

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. \(2010\)](#).

## **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](#)).

OH/Si increases with water content and the increase is generally higher for mafic than for felsic glasses ([Fig. 9a](#)). Between the two felsic compositions, the increase of the OH/Si ratio with water of the peraluminous rhyolite is noticeably more important than the peralkaline one. More precisely, calcalkaline and tholeiitic glasses bearing less than 3 wt % H<sub>2</sub>O and the peraluminous rhyolite with various water contents fit on a single trend, whereas the other glasses diverge from the general trend to higher OH/Si ratios (the water-rich basalts) or lower OH/Si ratios (the basanites and peralkaline rhyolites) ([Fig. 9a](#)). Similar trends are obtained when subtracting a linear/cubic baseline from raw or Long-corrected data. Measurements performed in a standard confocality setting (not shown) yield a ~50 % steeper calibration line than measurements done under high confocality conditions.

The divergence of water-rich basalts and peralkaline rhyolites from the main trend in 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  $980\text{ cm}^{-1}$ , respectively. Careful inspection of spectra in the alumino-silicate vibration region reveals that the integrated intensity (hereafter  $A_{\text{Al-Si}}$ ) of this region generally decreases with increasing water content and decreasing density (Fig. 10), regardless of analytical conditions (i.e. laser power on sample and confocality) and baseline treatment, except for the peralkaline and basanitic glasses. The effect of water in lowering  $A_{\text{Al-Si}}$  is maximum in basaltic glasses, in particular in the 82-72f set with 30 % intensity reduction for 15 mol %  $\text{H}_2\text{O}$  (Fig. 10 c), and becomes smaller in andesitic and rhyolitic glasses characterized by < 12 % and 10 % reduction for 18 mol %  $\text{H}_2\text{O}$  and 25 mol %  $\text{H}_2\text{O}$ , respectively (Fig. 10 e, g). In  $\text{CO}_2$ -bearing basanitic glasses, the observed increase of  $A_{\text{Al-Si}}$  with decreasing density (Fig. 10 b) is due to the presence of  $\text{CO}_3^{2-}$  dissolved in these glasses; the intensity of the  $\nu_1$  Raman vibration of dissolved carbonate at  $\sim 1087\text{ cm}^{-1}$  (Fig. 3S) has to be subtracted from the intensity of the alumino-silicate envelope (Table 2S). Adjustments of the internal calibration method to take into account the effect of water content on  $A_{\text{Al-Si}}$ , the behavior of the band at  $980\text{ cm}^{-1}$  in peralkaline rhyolites and the presence of  $\text{CO}_3^{2-}$  in basanites are presented in the Discussion section.

Small deviations from the general trends of Fig. 10 in a given set of glasses reflect differences in glass structure. For instance, the higher  $A_{\text{Al-Si}}$  measured in the A071215 sample is probably due to a different iron oxidation state compared to the other andesitic glasses (see spectra of Fig. 4c). The HF band in A310317 and A030417 glass spectra contains an additional contribution from the vibration of  $\text{CO}_3^{2-}$  molecules (Fig. 10 e). The basaltic sample 82-72f#10 is characterized by a larger  $A_{\text{Al-Si}}$  than expected from the general trend of the 82-72f basaltic set (Fig. 10 c). This may be due to the slightly higher density of this sample 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 significantly larger  $A_{\text{Al-Si}}$  (Fig. 10 a, b).

## 7. DISCUSSION

### 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:

$$N = N_{V0}/A \cdot d\sigma/d\Omega \cdot \Delta\Omega \cdot N_m \quad (3)$$

where  $N$  is the total number of Raman photons for a specific vibrational mode,  $N_m$  is the number of molecules contained in the scattering volume  $V$  that are responsible for that vibrational mode (i.e.  $N_m = \rho V$  if  $\rho$  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.

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

## 7.2. External versus internal calibration

Concerning the external calibration, the linear relationship between water contents (as determined by FTIR or SIMS) and  $A_{OH}$  (Fig. 8) can be explained in two ways: either the scattering cross-section of the water stretching vibration mode is independent of the glass matrix composition, or the procedure established for spectra acquisition and baseline treatment minimizes the differences in Raman cross-section and the effects related with size of the confocal volume, self-absorption and reflectance at the sample surface. Taking into account the findings of previous studies (e.g. Mercier et al., 2010), we believe this second hypothesis is more likely. Small differences in shape and componentry between the water bands of the studied glasses (Fig. 5 and Fig. 4S) are consistent with differences in water bonding environments and speciation, as previously discussed by Behrens et al. (2006), Di Muro et al. (2006b) and Mercier et al. (2010). The external calibration method proposed here yields a single calibration line allowing analysis of all alumino-silicate glasses with the same level of accuracy as previous studies (e.g., Behrens et al., 2006). This suggests that measurements performed following the procedure established in this study (i.e., measurements performed at optimal focus depths rather than on sample surface, and based on quantification of the water band area instead of band height) provide the best conditions for correction of differences in Raman scattering efficiency between glasses with variable 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  $CO_2$ -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

$A_{\text{Al-Si}}$  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  $\text{CO}_3^{2-}$  is proportional to the total  $\text{CO}_2$  content.

The observed relationships between  $A_{\text{Al-Si}}$ , 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:

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

where  $\alpha_1 = 1 - (A_{\text{Al-Si}}^{\text{hydrous}}/A_{\text{Al-Si}}^{\text{anhydrous}})$ ,  $p$  is the laser power, and  $t_1$  and  $t_2$  are the acquisition times in the water and alumino-silicate regions, respectively. In other words, the correction factor ( $\alpha_1$ , Table 4S) is proportional to the difference between the  $A_{\text{Al-Si}}$  of the anhydrous glass and that of the hydrous glasses of each set (Fig. 10). The correction factor depends on both glass composition and water content (see Fig. 2); either density or mol%  $\text{H}_2\text{O}$  estimated with the external calibration method can be used to estimate  $\alpha_1$  (Fig. 10). Up to ~7 wt %  $\text{H}_2\text{O}$  contents, rhyolitic, andesitic and basanitic glasses require a minor correction (< 10-12 % in the studied range of water contents). In contrast, water-rich (> 3 wt %  $\text{H}_2\text{O}$ ) basaltic glasses 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

peralkaline ones, whereas the opposite behavior is observed for the components II and III. The sum of the components III, IV and V represents approximately 50 % of the total area in both glass sets ( $51 \pm 6$ ,  $1\sigma$ ). In contrast, the sum of the areas of the components I, II and III varies significantly from peraluminous (~50 % of the total area) to peralkaline (70-75 % of the total area) glasses, with a 20-25 % difference. This difference can be explained by the higher Fe content and oxidation state of peralkaline glasses, as revealed by the sharp increase of the component (II) at  $\sim 980 \text{ cm}^{-1}$ , which is attributed to the presence of four-fold coordinated  $\text{Fe}^{3+}$  in alkali-bonded  $Q^3$  units (e.g., Wang et al., 1995; Di Muro et al., 2009; Di Genova et al., 2016). The internal calibration procedure can be improved by taking into account the high Raman scattering of the  $980 \text{ cm}^{-1}$  band in peralkaline rhyolites, and this can be performed by calculating a correction factor:

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

where (I-II-III) represent the sum of the areas of the components I, II and III (Table 1S). Once the  $A_{\text{Al-Si}}$  of peralkaline glasses is corrected for the difference in componentry compared to peraluminous glasses, all rhyolitic glasses follow the same calibration line defined by all other compositions (Fig. 9c). This observation suggests that  $\text{Fe}^{3+}$  has an important effect on the Raman scattering efficiency of alumino-silicate glasses; in rhyolitic glasses the vibrational mode at  $970\text{-}980 \text{ cm}^{-1}$  has an important Raman scattering cross-section.

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

$$C_{\text{H}_2\text{O}} (\text{wt}\%) = 2.179 (\pm 0.037) \cdot A_{\text{OH}}/A_{\text{Al-Si corr}} + 0.060 (\pm 0.055) \quad (R^2 = 0.992), \quad (6)$$

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

### 7.3. Application to natural glass inclusions

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

The studied inclusions have variable composition spanning from basanitic to basaltic and andesitic, and contain different amounts of water ranging from 0.1 to 3.3 wt% (Table 3). They contain less than 0.13 wt% CO<sub>2</sub>, except for two basanitic inclusions, TAO-ol1 and TGN-ol18 bearing, respectively,  $0.43 \pm 0.09$  and  $0.21 \pm 0.09$  wt% CO<sub>2</sub>. As CO<sub>2</sub> contents < 0.2 wt% are not detected using Raman spectroscopy ([Morizet et al., 2013](#)), only the two basanitic inclusions were corrected for the presence of dissolved carbonate. The relatively large size of the analyzed glass inclusions and the very weak or absent scattering from the embedding olivine crystals allowed focusing the laser beam at depths where the intensity of the water signal was maximum (-2 or -3  $\mu\text{m}$ ). These correspond to the optimal depths reported in [Figure 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<sup>-1</sup> ([Frezzotti et al., 2012](#)). In line with the findings by [Di Genova et al. \(2017\)](#), we observed that presence of Fe-oxides

dispersed in the glass causes underestimation of the water content of the inclusion, most likely due to light absorbance and possible heating and oxidation of the oxide phases.

[Figure 8d](#) shows the results of the external calibration procedure applied to glass inclusions. The estimated water contents are in very good agreement with SIMS measurements and provide information about the accuracy of the method. The average relative standard deviations (RSD) between Raman and SIMS analyses are ~3 % and 5 % ( $1\sigma$ ) when using a cubic or a linear baseline correction, respectively. It is worth noting that SIMS measurements were carried out first, so we cannot exclude that some water loss occurred from the inclusion before Raman analyses. For glass inclusions bearing H<sub>2</sub>O contents close to the detection limit of the method (i.e. ~0.1 wt%), the RSD between FTIR and Raman measurements increases (4-22 %, with maximum values for cubic background subtraction), partly due to decreasing signal/noise intensity ratio.

When using the internal calibration approach without applying the corrections (for density and componentry) defined above, a first approximate estimate of the water dissolved in the glasses is obtained (inset in [Fig. 9a](#)). Basaltic and andesitic inclusions fall close to the main trend defined by the reference glasses, although some scatter is observed in inclusions bearing ~3 wt% H<sub>2</sub>O. The basaltic inclusions, instead, are aligned with the basaltic 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  $A_{\text{Al-Si}}$  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  $A_{\text{Al-Si}}$ . 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.

Attempts to estimate the density-related factor  $\alpha_1$  for the studied inclusions resulted in non-negligible uncertainties on the OH/Si ratio. This is mainly due to the small number of analyzed inclusions with similar composition that did not allow defining trends as in [Fig. 10](#) without uncertainty. For a qualitative analysis, the compositions of the inclusions, not corrected for density, are plotted on the main density-corrected trend defined by the reference glasses (inset in [Fig. 9c](#)). The observed distribution of the glass inclusions is in line with our expectations based on the behavior of the reference compositions ([Fig. 10](#)): the andesitic glass falls on the main trend as it is not expected to be strongly influenced by the density correction, several basaltic inclusions fall slightly above the main trend as observed for non-corrected reference basalts, while basanitic inclusions behave analogously to the reference basanites. Although this may be speculative, the strong similarities observed between reference samples and uncorrected glass inclusions probably suggest that differences of quench pressure in the studied inclusions has a minor influence on the established water quantification procedures.

## CONCLUDING REMARKS

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

We examined in detail how the Raman intensities of the water band and the alumino-silicate envelope change with confocality performance and focus depth of the laser beam, as previously investigated (e.g., [Behrens et al., 2006](#); [Mercier et al., 2009](#)). We found that the extent of increase of water band intensity with focus depth is lower than that measured in the alumino-silicate envelope. This results in a variable OH/Si band intensity ratio, and highlights the importance of measuring glasses at their optimal focus depth, which corresponds to the depth of maximum intensity of the water band and minimum OH/Si ratio. The optimal focus depth depends on glass composition and confocal performance of the Raman instrument, and is expected to change with laser wavelength as well. Maximum intensity in both water and alumino-silicate regions is attained at 2-3  $\mu\text{m}$ , 3-4  $\mu\text{m}$  and 5-10  $\mu\text{m}$  depth, respectively in basaltic-basaltic, andesitic and rhyolitic glasses under the instrumental and analytical conditions used in this study.

Thirty reference glasses belonging to both alkaline and subalkaline magmatic series and bearing up to ~7 wt %  $\text{H}_2\text{O}$  define a single external calibration line when they are analyzed at their optimal focus depth. In contrast, measurements performed on the sample surface did not yield a single calibration curve for glasses of different compositions. Our study suggests that water content of unknown samples can be determined based on a minimum of two reference glasses whose compositions do not need to match that of the unknown samples. However, using three or more reference glasses is recommended to improve the accuracy of water content quantification. In general, accurate water quantification using the external calibration



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

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

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 calibration method. We provide simple procedures for correcting and/or minimizing the effects of these parameters. Increasing water content lowers glass density and results in reduction of the area of the alumino-silicate envelope ( $A_{\text{Al-Si}}$ ); we measured up to 30% intensity reduction in a high-Al basaltic glass bearing 15 mol% water. The correction method that we propose is based on the relative difference between  $A_{\text{Al-Si}}$  of anhydrous and hydrous glasses with similar composition.

Peak fitting of the alumino-silicate high frequency envelope (approximately located between 800 and 1250  $\text{cm}^{-1}$ ) is required to quantify the intense scatterings around 980  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$  caused, respectively, by  $\text{Fe}^{3+}$  in four-fold coordination and  $\text{CO}_3^{2-}$  dissolved in glasses. Concerning the  $\text{Fe}^{3+}$ -related matrix effect, we must point out that, in principle, all  $\text{Fe}^{3+}$ -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

rhyolites is far more sensitive to changes in  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  than in mafic compositions (Di Muro et al., 2009; Di Genova et al., 2016). Once the proposed corrections are performed, all the studied glasses define a single internal calibration line in spite of their compositional variability. Alkaline glasses, specifically basanites, behave coherently with the other glass compositions when the analytical strategies and data treatment procedures (i.e., for baseline 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% ( $1\sigma$ ) for most samples, and increases to ~12% ( $1\sigma$ ) for glass inclusions with  $\text{H}_2\text{O}$  contents close to the detection limits (~0.1 wt%).

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

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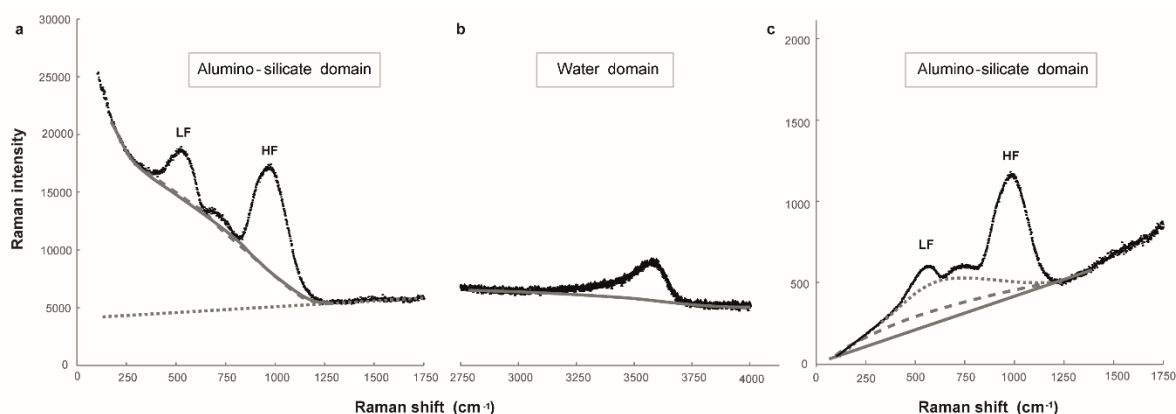
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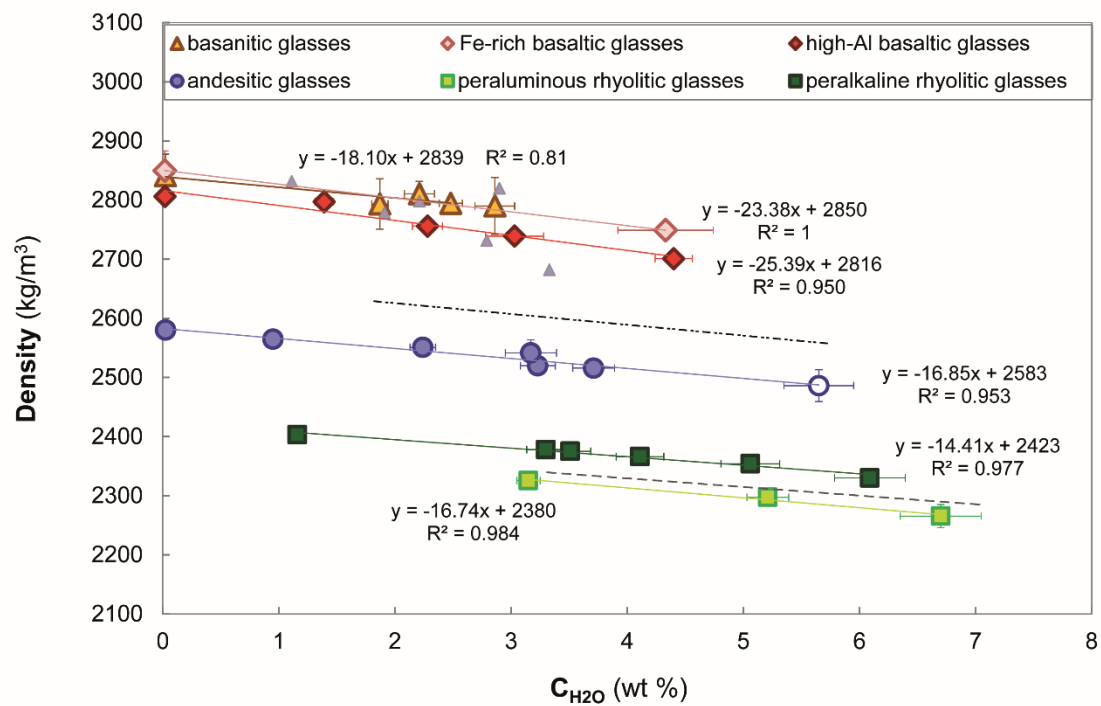
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## FIGURES

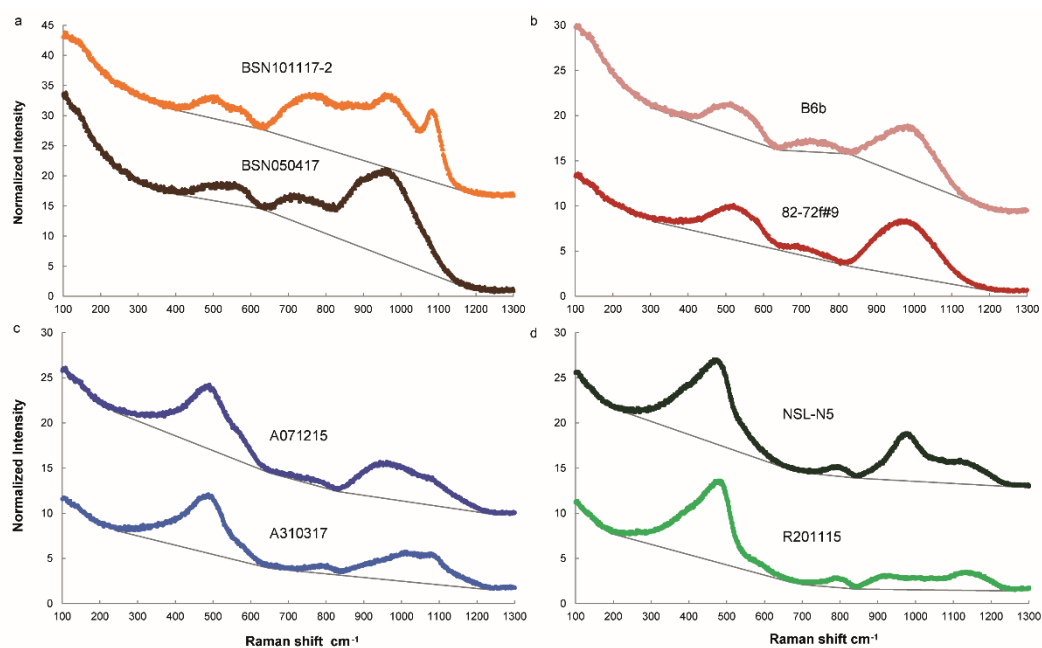


**Fig. 1.** Procedures for background subtraction used in previous studies. (a-b) Baseline fitting on raw Raman spectra. (a) In the alumino-silicate domain: cubic baseline (Mercier et al., 2009; dashed curve), cubic spline baseline (Behrens et al., 2006; continuous curve), and linear extrapolation method by Zajacz et al. (2005, dotted line); (b) cubic baseline in the water domain. (c) Baseline fitting on Long-corrected spectra in the alumino-silicate domain: cubic baseline (Di Muro et al., 2009; dashed curve) and cubic spline baseline (Behrens et al., 2006; continuous line) anchored at the extremities of the domain, or to a limited number of intermediate minima (Le Losq et al., 2012; dotted curve). LF and HF indicate low-frequency and high-frequency bands.

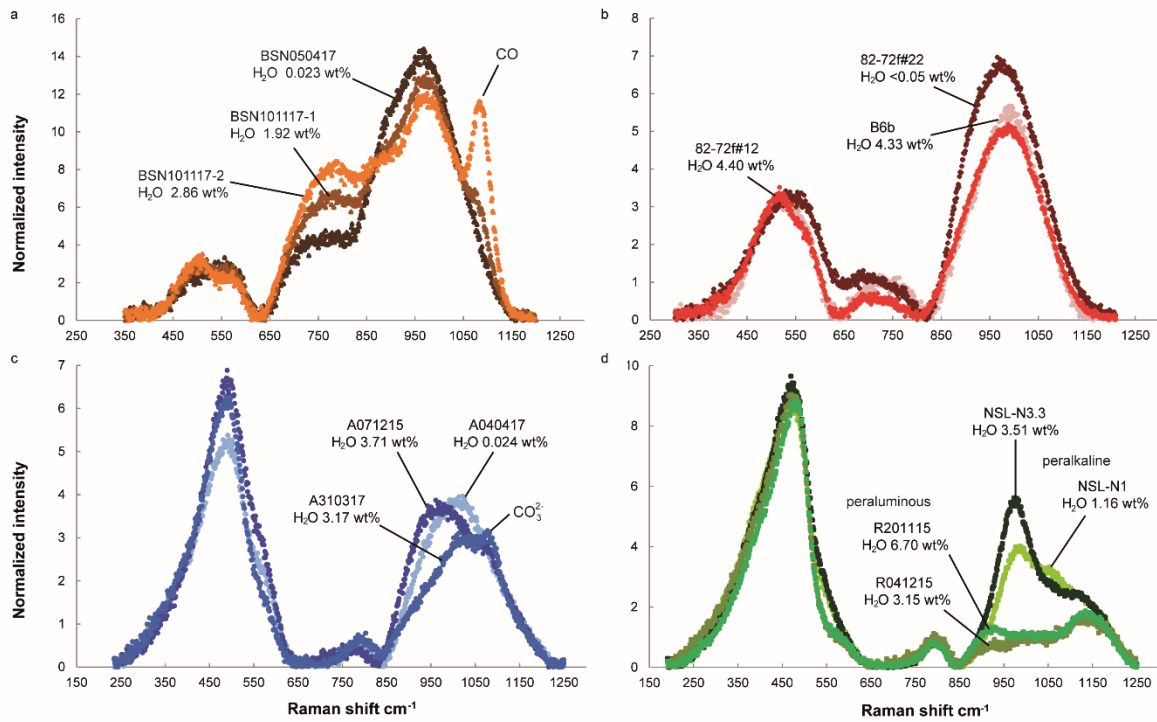


**Fig. 2.** Glass density versus glass water content determined by FTIR or SIMS

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

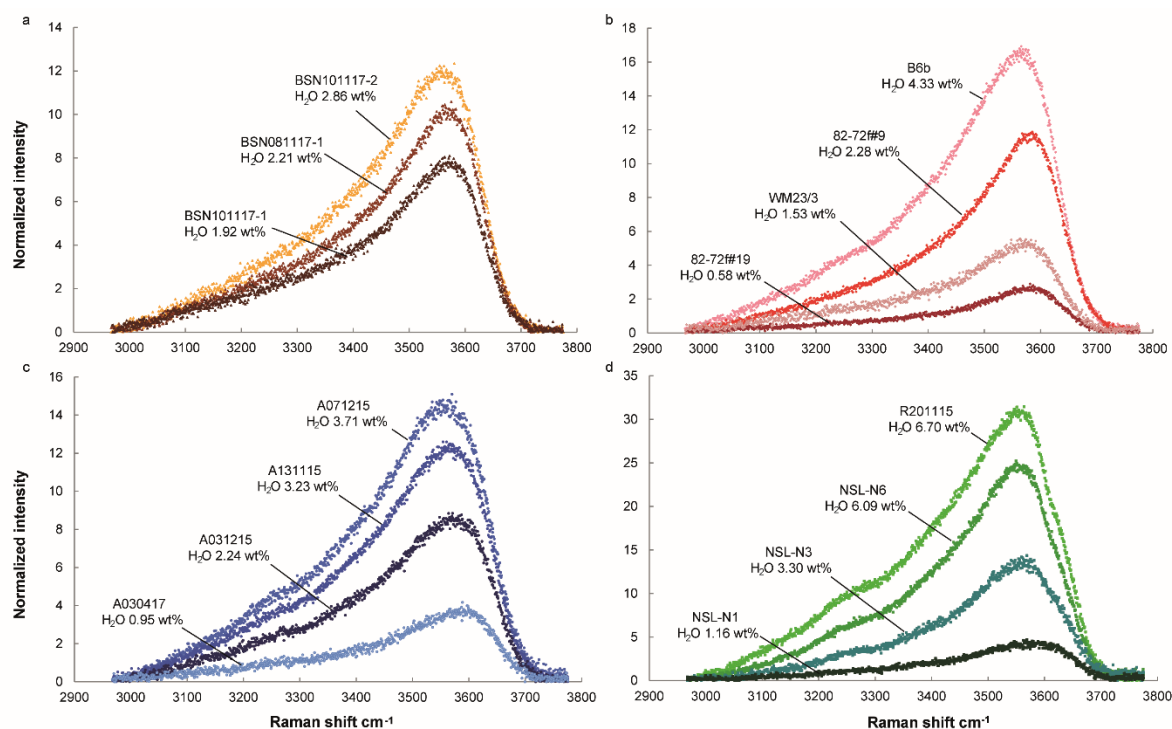


**Fig. 3.** Raw Raman spectra of the alumino-silicate vibration bands of the glasses with basanitic (a), basaltic (b), andesitic (c) and rhyolitic (d) compositions. Linear baselines adopted for background subtraction are shown with anchor points. Spectra are displaced vertically for clarity. Intensities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



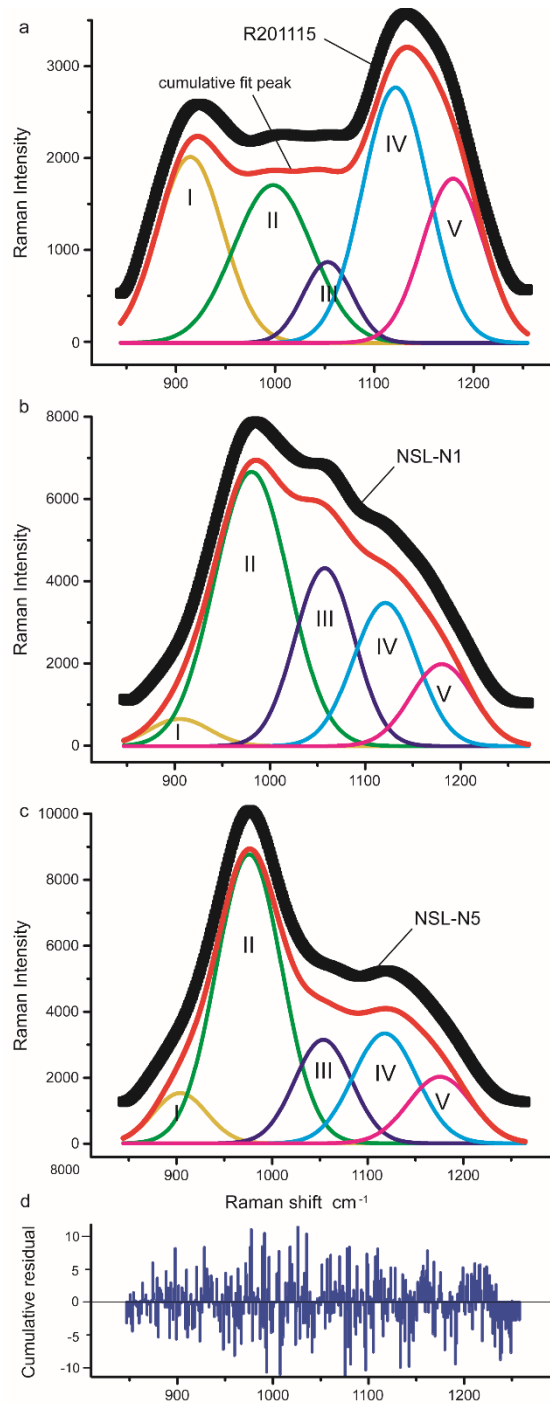
**Fig. 4.** Alumino-silicate region of raw Raman spectra of basanitic (a), basaltic (b),

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).



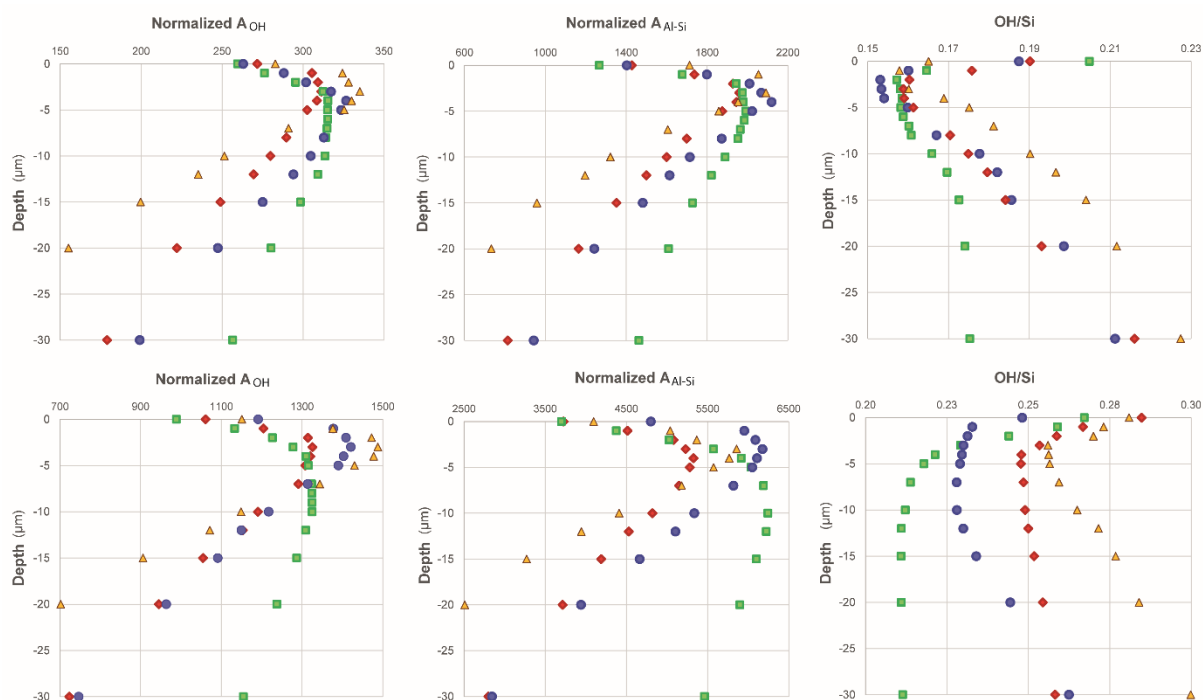
**Fig. 5.** Baseline-corrected Raman spectra in the water region of reference glasses:

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.

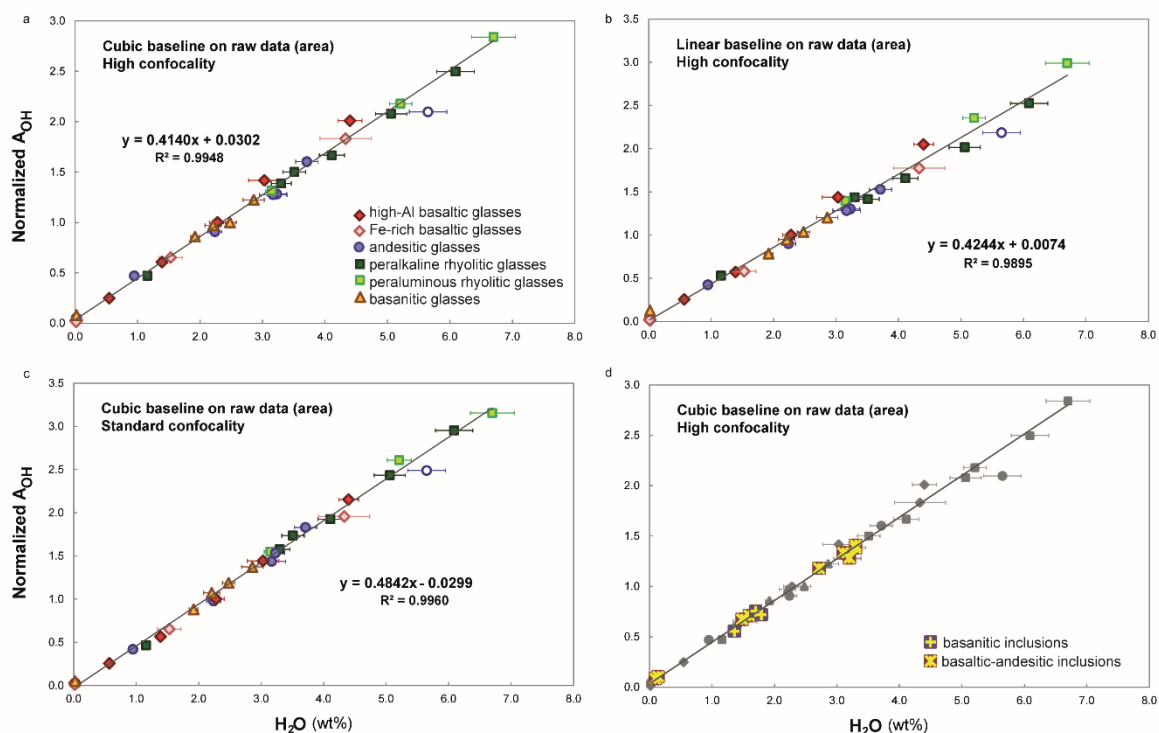


**Fig. 6.** Peak fitting of the HF aluminosilicate envelope of peraluminous (a), water-poor (b) and water-rich peralkaline (c) rhyolitic glasses with a finite number of Gaussian components performed with OriginPro software. The good quality of the fit is indicated by the randomness of the residuals (d).

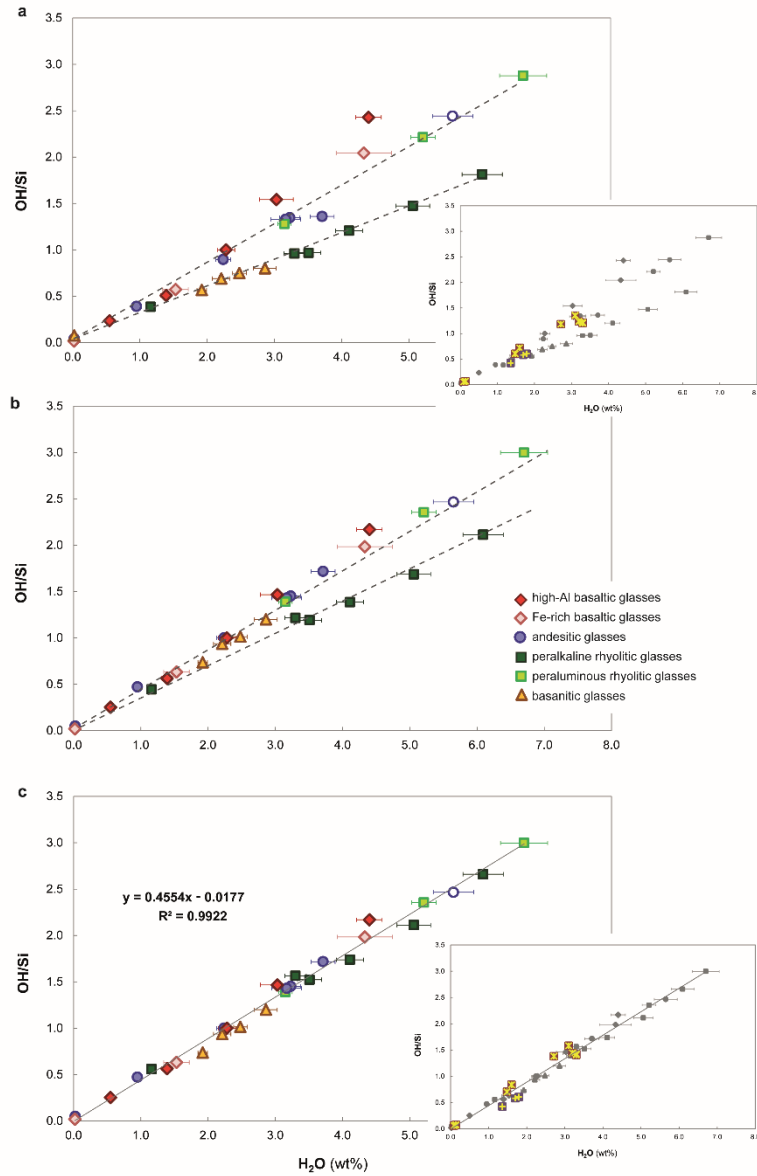




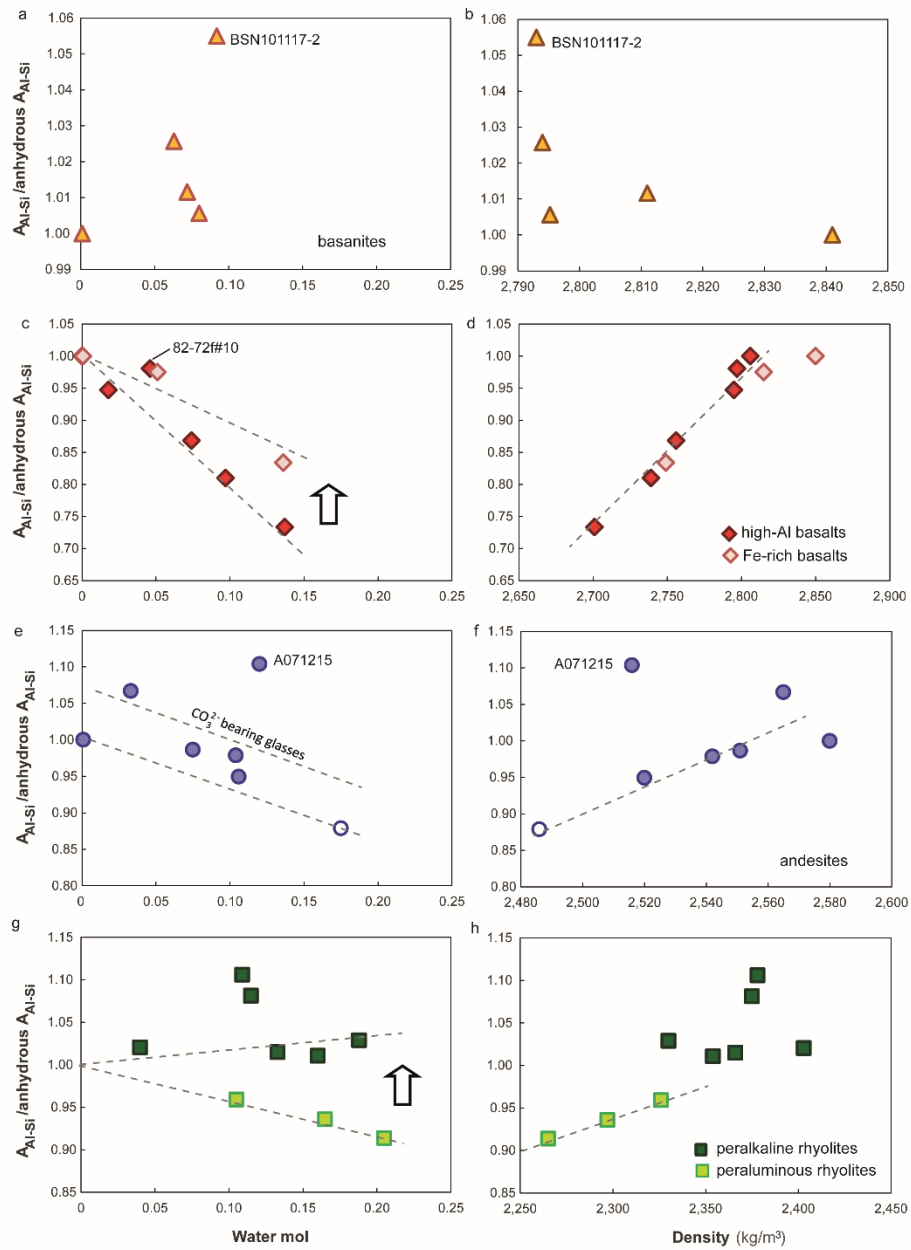
**Fig. 7.** Depth profiles measured in the water and alumino-silicate vibration regions of basanitic (yellow triangles), basaltic (red diamonds), andesitic (blue circles) and rhyolitic (green squares) glasses under high (upper row) and standard (lower row) confocality conditions. Integrated intensities 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.



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



**Fig. 9.** a) Internal calibration diagram showing variation of the “OH/Si” ratio (i.e. the area ratio between the total water band,  $A_{OH}$ , and the total aluminosilicate band region,  $A_{Al-Si}$ ) versus water content. b) Internal calibration lines after applying the density-related correction. c) Internal calibration line after correcting for the high Raman scattering of the  $980\text{ cm}^{-1}$  band in peralkaline rhyolites. All samples define a single calibration line passing through the origin. The insets show the non-corrected glass inclusion compositions (symbols as in Fig. 8). Signal intensities were normalized to laser power and acquisition time, and to the areas of the 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 (e-f) 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. Microlite-bearing andesitic glass A011215 is represented by an empty blue circle.

**Table 1**  
Synthesis conditions and volatile composition of reference glasses.

GLASSES	Series	Starting material	Synthesis method	Capsule material	P (GPa)	T (K)	Time (h)	Loaded H <sub>2</sub> O wt%	Analytical technique	Thickness (cm)	Density <sup>a</sup>	Water content			CO <sub>2</sub>	References
											(kg m <sup>-3</sup> )	wt%	1σ <sup>c</sup>	mol	wt%	
Basaltic																
BSN050417	Alkaline	Thueyts tephra	GMF	1/2"	Au <sub>80</sub> Pd <sub>20</sub>	0	1573	4	FTIR	0.0410(5)	2841(37)	0.023	0.001	0.001		This study
BSN081117-1	Alkaline	Thueyts tephra	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.5	1598	3	FTIR	0.0054(7)	2811(21)	2.21	0.13	0.072	0.48 ± 0.07	This study
BSN081117-2	Alkaline	Thueyts tephra	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.5	1598	3	FTIR/CHNS	0.0055(7)	2794(11)	2.48	0.10	0.080	1.76 ± 0.03	This study
BSN101117-1	Alkaline	Thueyts tephra	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.5	1598	3	FTIR/CHNS	0.0095(1)	2793(43)	1.92	0.07	0.063	0.82 ± 0.03	This study
BSN101117-2	Alkaline	Thueyts tephra	PC	1/2"	Au <sub>80</sub> Pd <sub>20</sub>	2.2	1598	3	FTIR/CHNS	0.0022(3)	2790(48)	2.86	0.17	0.092	2.35 ± 0.15	This study
Basaltic																
82-72f#22	Tholeiitic	Giant Crater Lava Field	GMF			0	1564	5.0			2806	< 0.05			[1],[2]	
82-72f#19	Tholeiitic	Giant Crater Lava Field	MHC		Au <sub>80</sub> Pd <sub>20</sub>	0.01	1503	2.1	SIMS/FTIR		2795 <sup>b</sup>	0.58	0.05	0.020		[1]
82-72f#10	Tholeiitic	Giant Crater Lava Field	MHC		Au <sub>80</sub> Pd <sub>20</sub>	0.025	1486	2.0	SIMS		2797	1.39	0.08	0.046		[1],[2]
82-72f#9	Tholeiitic	Giant Crater Lava Field	MHC		Au <sub>90</sub> Pd <sub>10</sub>	0.05	1472	2.0	SIMS		2756	2.28	0.13	0.074		[1],[2]
82-72f#7	Tholeiitic	Giant Crater Lava Field	MHC		Au <sub>90</sub> Pd <sub>10</sub>	0.10	1446	2.0	SIMS		2739	3.03	0.25	0.097		[1],[2]
82-72f#12	Tholeiitic	Giant Crater Lava Field	MHC		Au <sub>90</sub> Pd <sub>10</sub>	0.20	1443	3.1	SIMS		2701	4.40	0.16	0.137		[1],[2]
B250317	Tholeiitic	Holuhraun tephra	GMF	1/2"	Au <sub>80</sub> Pd <sub>20</sub>	0	1573	3.0	FTIR	0.0250(4)	2850(33)	0.017	0.001	0.001		This study
WM23/3	Tholeiitic	Holuhraun tephra	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	68	FTIR	0.0324(4)	2815 <sup>b</sup>	1.53	0.19	0.051		This study
B6b	Tholeiitic	Holuhraun tephra	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.0	1473	2.0	FTIR	0.0016(1)	2749(11)	4.33	0.41	0.136		This study
Andesitic																
A040417	Calcalikaline	Synthetic	GMF	1/2"	Au <sub>80</sub> Pd <sub>20</sub>	0	1573	20	FTIR	0.0181(6)	2580(1)	0.024	0.003	0.001		This study
A030417	Calcalikaline	Synthetic	PC		Au <sub>80</sub> Pd <sub>20</sub>	0.75	1573	24	FTIR	0.0120(2)	2565(4)	0.95	0.05	0.033	0.28 ± 0.02	This study
A310317	Calcalikaline	Synthetic	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.1	1573	24	FTIR/CHNS	0.0451(2)	2542(22)	3.17	0.22	0.104	0.59 ± 0.01	This study
A031215	Calcalikaline	Synthetic	PC		Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	17	FTIR	0.0357(2)	2551(5)	2.24	0.11	0.075		This study
A131115	Calcalikaline	Synthetic	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	18	FTIR/CHNS	0.0298(5)	2520(5)	3.23	0.15	0.106		This study
A071215	Calcalikaline	Synthetic	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	24	FTIR	0.0521(2)	2516(9)	3.71	0.18	0.120		This study
Rhyolitic																
NSL-N1	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2403	1.16	0.06	0.040		[3]
NSL-N3	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2378	3.30	0.16	0.109		[3]
NSL-N3.3	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2375	3.51	0.18	0.115		[3]
NSL-N4b	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2366	4.11	0.20	0.133		[3]
NSL-N5	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2354	5.06	0.25	0.160		[3]
NSL-N6	Peralkaline	obsidian from New Zealand	IHPV		Au		1273		FTIR		2330	6.09	0.30	0.188		[3]
R041215	Peraluminous	Güney Dag obsidian	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1373	64	FTIR	0.0371(2)	2326(7)	3.15	0.10	0.105		This study
R261115	Peraluminous	Güney Dag obsidian	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1373	70	FTIR	0.0434(3)	2297(2)	5.21	0.18	0.165		This study
R201115	Peraluminous	Güney Dag obsidian	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1323	63	FTIR	0.0228(3)	2265(20)	6.70	0.35	0.205		This study
Microlites-bearing																
A011215	Calcalikaline	Synthetic	PC	3/4"	Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	18	FTIR	0.0135(3)	2486(27)	5.65	0.30	0.175		This study

Notes  
GMF is gas-mixing furnace; MHC is Molybdenum-Hafnium-Carbide cold-seal pressure vessel; PC is non-endloaded piston cylinder; IHPV internally heated pressure vessel.  
The numbers in parentheses are 1σ 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).  
<sup>a</sup> The sink/float method was used to measure the density of the 82-72f series of basaltic glasses; Archimedes' method for the other glasses.  
<sup>b</sup> Density calculated using the regression line of Fig. 2.  
<sup>c</sup> Uncertainty resulting from error propagation in Beer-Lambert equation.  
<sup>d</sup> In addition to ~1.39 wt% H<sub>2</sub>O of Güney Dag obsidian starting material.

Table 2  
Major element composition of reference glasses.

GLASSES	n	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub> <sup>a</sup>	Total	NBO/T <sup>b</sup>
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%		
BASALTIC <sup>c</sup>													
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)	–	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)	–	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(16)	–	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)	–	96.63	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)	5.16(39)	4.22(13)	–	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 <sup>c</sup>		70.4	0.20	9.86	3.87	0.07	0.004	0.17	5.17	4.18	–	93.91	0.051
R041215 <sup>a</sup>	10	75.1(4)	0.04(5)	12.22(8)	0.74(10)	0.07(4)	0.03(2)	0.42(5)	4.09(14)	4.46(26)	–	97.20	0.004
R261115 <sup>a</sup>	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 <sup>a</sup>	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													
A011215	11	57.7(3)	0.71(5)	15.60(14)	4.49(10)	0.14(2)	3.74(10)	6.08(13)	3.59(11)	1.38(7)	–	93.39	0.192

Notes  
n is the number of measurements; the numbers in parentheses are 1σ standard deviations, given in terms of the last unit cited. All Fe is reported as FeO.  
<sup>a</sup> The P<sub>2</sub>O<sub>5</sub> content of reference glasses was only measured for basaltic compositions. The P<sub>2</sub>O<sub>5</sub> content of the basaltic starting material is equal to 0.7 wt%.  
<sup>b</sup> NBO/T (i.e., non-bridging oxygen per tetrahedrally coordinated cation) is calculated on an Fe- and H<sub>2</sub>O-free basis, following Behrens et al. (2006).  
<sup>c</sup> calculated based on the starting composition of the dry natural obsidian.

**Table 3**

Water quantification in glass inclusions.

Sample	Provenance	Host phase	Glass composition	2D size ( $\mu\text{m}$ )	H <sub>2</sub> O wt%					% host phase correct. <sup>d</sup>	
					SIMS/ FTIR <sup>a</sup>	$\pm 1 \sigma$	External cal. (cubic bas.) <sup>b</sup>	$\pm 1 \sigma^c$	External cal. (linear bas.) <sup>b</sup>	$\pm 1 \sigma^c$	
Vaggelli-3-1 <sup>c</sup>	Santorini	Olivine	Basalt	110 × 50	3.10	0.06	3.15	0.12	3.25	0.17	0.0
Vaggelli-4-1 <sup>c</sup>	Santorini	Olivine	Basalt	140 × 120	3.20	0.05	3.02	0.12	3.15	0.17	0.0
Vaggelli-6-1 <sup>c</sup>	Santorini	Olivine	Basaltic andesite	210 × 110	3.30	0.04	3.27	0.13	2.98	0.19	0.0
Vaggelli-2-1 <sup>c</sup>	Santorini	Olivine	Andesite	130 × 80	3.30	0.10	3.33	0.13	3.10	0.19	0.5
S12-371-3 <sup>c</sup>	Santorini	Olivine	Basalt	190 × 115	2.71	0.03	2.77	0.11	2.71	0.15	0.0
S12-43-7-1 <sup>c</sup>	Santorini	Olivine	Basalt	255 × 135	1.48	0.01	1.55	0.06	1.29	0.08	0.0
S12-43-1-1 <sup>c</sup>	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**<sup>a</sup> Water contents measured by SIMS, except for FZ OL37b and OL39 analyzed with FTIR (Schiavi et al., 2016).<sup>b</sup> Water contents estimated from the regression lines of Fig. 8 (high confocality setting).<sup>c</sup> Uncertainties calculated from the errors related to the linear regression (see Eq. 1 in the text) for 95% confidence interval.<sup>d</sup> Arithmetic subtraction of host phase spectrum from glass spectrum.<sup>e</sup> Reference: Druitt et al., 2016