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

3 Federica Schiavi<sup>\*1</sup>, Nathalie Bolfan-Casanova<sup>1</sup>, Anthony C. Withers<sup>2</sup>, Etienne Médard<sup>1,3</sup>,  
4 Mickaël Laumonier<sup>1</sup>, Didier Laporte<sup>1</sup>, Taya Flaherty<sup>1</sup>, Alejandra Gómez-Ulla<sup>1</sup>

5 <sup>1</sup>Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-  
6 Ferrand, France

7 <sup>2</sup>Department of Earth Sciences and Centre for Planetary Science and Exploration, University of Western Ontario,  
8 1151 Richmond Street, London, Ontario, Canada

9 <sup>3</sup>Universities Space Research Association, Lunar and Planetary Institute, Houston, TX, United States

10  
11 \*Corresponding author e-mail: [f.schiavi@opgc.univ-bpclermont.fr](mailto:f.schiavi@opgc.univ-bpclermont.fr)

12 **Abstract**

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

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

44

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

## 47 1. INTRODUCTION

48 Concentration, speciation and distribution of volatile species dissolved in silicate melts  
49 are key factors that control the physico-chemical evolution of magmas from their genesis to  
50 their final emplacement and affect the dynamics, style, and intensity of volcanic eruptions  
51 (e.g., [Carroll and Holloway, 1994](#); [Cashman 2004](#); [Sanchez-Valle et al., 2015](#)). Volatiles are

52 also important in mantle processes as they control melting and mantle rheology. Crucial  
53 information about volatile contents of magmas and behavior of volatiles at depth is usually  
54 recorded in small objects, such as phenocryst-hosted melt and fluid inclusions and tiny  
55 pockets of glassy matrix (e.g., [Andersen and Neumann, 2001](#); [Métrich and Wallace, 2008](#)).

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

69 Since the work by [Thomas \(2000\)](#), several studies have shown that accurate  
70 quantification of water dissolved in natural glasses can be achieved after proper calibration of  
71 Raman spectrometers ([Chabiron et al., 2004](#); [Zajacz et al., 2005](#); [Behrens et al., 2006](#); [Di  
72 Muro et al., 2006a, 2006b](#); [Thomas et al., 2006](#); [Mercier et al., 2009, 2010](#); [Le Losq et al.,  
73 2012](#); [Di Genova et al., 2017](#)). These studies investigated the advantages and limitations of  
74 distinct calibration methods. The first method is called “external calibration”, as  
75 quantification of water in the unknown sample is obtained by comparing the intensity (i.e. the

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

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

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

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

## 123 **2. METHODOLOGY**

### 124 ***2.1 Starting materials***

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

130 Two distinct sets of rhyolitic glasses were synthesized from the Güney Dag obsidian  
131 (Turkey; Druitt et al., 1995) and from a peralkaline rhyolite (labeled as NSL) from New  
132 Zealand, whose exact provenance is unknown (Behrens and Jantos, 2001) (Table 1). Both  
133 rhyolites are very poor in microlites. The Güney Dag rhyolite is mildly peraluminous, SiO<sub>2</sub>-  
134 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 %,   
135 respectively) and contains 1.39 wt % H<sub>2</sub>O (Mourtada-Bonnefoi and Laporte, 2002). This  
136 relatively large H<sub>2</sub>O content is due to the water contained in the glass phase of the obsidian  
137 (1.05 ± 0.05 wt %; Mourtada-Bonnefoi and Laporte, 2002) and to the presence of biotite and  
138 amphibole microlites (Cluzel et al., 2008). The rhyolite from New Zealand has lower SiO<sub>2</sub>  
139 (~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 %)   
140 contents, and contains 0.1-0.4 wt % H<sub>2</sub>O.

141 Two sets of basaltic glasses were synthesized starting from a primitive high-alumina  
142 basalt erupted from the Giant Crater Lava Field (Medicine Lake volcano, California; Médard  
143 and Grove, 2008; Malfait et al., 2011) and from tephra erupted from Holuhraun volcano  
144 (Iceland) in 2014 (Haddadi, 2016). The composition of the Medicine Lake volcano basalt  
145 (labeled as 82-72f) is very close to that of primitive mid-ocean ridge basalts, with a higher  
146 Al<sub>2</sub>O<sub>3</sub> content (~18.5 wt %). The composition of the basalt from Holuhraun is richer in FeO  
147 (~12.5 wt %) and poorer in Al<sub>2</sub>O<sub>3</sub> (~14 wt %) and is typical of lavas erupted from the  
148 Bárðarbunga magmatic system (Sigmarsson and Halldorsson, 2015).

149 A set of reference glasses with basaltic composition and bearing different amounts of  
150 H<sub>2</sub>O and CO<sub>2</sub> were synthesized from a natural basaltic tephra sampled at Thueyts volcano  
151 (Ardèche, France). The tephra composition is characterized by low SiO<sub>2</sub> (~45 wt %) and high  
152 total alkali (~6 wt %).

153 We also synthesized an intermediate (andesitic) composition closely reproducing the  
154 andesites erupted at Mt. Shasta (California, [Grove et al., 2002](#)) with a slight difference in  
155 Na<sub>2</sub>O concentration. The details of the syntheses are presented below.

## 156 **2.2 Experimental Procedures**

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

165 For the synthesis of the andesitic glasses, we used a decarbonated mixture of oxide  
166 (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>)  
167 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  
168 1000-1100 °C overnight. CaSiO<sub>3</sub> and carbonate powders were dried in air at 250-400 °C  
169 overnight. These dried powders were weighed and ground altogether in an agate mortar to  
170 ensure a homogeneous starting mixture. For decarbonation and fusion, the mixture was held  
171 in a platinum crucible and heated by a gas-mixing furnace at one bar; as temperature changed,  
172 the gas mixture was adjusted to maintain  $fO_2$  near FMQ buffering conditions. Temperature



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

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

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

186 The hydrous glasses were synthesized in a piston-cylinder apparatus using a Pyrex-  
187 MgO assembly, a graphite heater, an outer NaCl cell, and Au<sub>80</sub>-Pd<sub>20</sub> capsules (5 and 4 mm  
188 outer diameter for 3/4" and 1/2" assemblies, 0.2 mm wall thickness, 4-5 mm length). First,  
189 deionized water was added at the bottom of the capsule using a micro-syringe; after loading  
190 and compacting ~100 mg of glass powders (or cylinders), the capsule was welded shut. We  
191 checked for leaks during capsule preparation by weighing the welded capsules before and  
192 after 1-hour heating at 120 °C in an oven. For the synthesis of H<sub>2</sub>O and CO<sub>2</sub>-bearing glasses  
193 with andesitic and basanitic compositions (Table 1), we added a mixture of water and oxalic  
194 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  
195 an oven first at 350 °C for 1 hour to decompose the oxalic acid, and then at 120 °C overnight  
196 to ensure homogenous distribution of the volatiles. In all experiments, the *P-T* conditions

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

201 The glasses recovered from the experiments were cut and polished on one or both sides  
202 for major element characterization by electron microprobe and water and  $CO_2$  concentration  
203 measurements by infrared and Raman spectroscopies. Homogeneity of the glasses was first  
204 checked under the microscope. All analyzed glasses were bubble- and crystal-free, except for  
205 one andesitic water-rich glass (A011215) that contains microlites crystallized upon  
206 quenching. The microlite-bearing glass is not suitable as standard; however, since the  
207 percentage of microlites is small and glass composition is homogeneous, it was used for  
208 comparison in Raman measurements.

### 209 ***2.3 Electron microprobe***

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

### 217 ***2.4 Infrared Spectroscopy***

218 Total water content of reference glasses was determined by Fourier Transform Infrared  
219 Spectroscopy, using a Bruker Vertex 70 spectrometer coupled with a Hyperion microscope  
220 system, housed at LMV. Spectra were recorded using a Globar light source, a KBr

221 beamsplitter and a MCT (Mercury-Cadmium-Tellurium alloy) detector. Plane parallel, double  
222 polished glass samples were placed on a CaF<sub>2</sub> window. Absorbance and background spectra  
223 of the glasses were obtained by acquisition of 300 and 100 scans, respectively. Beam size was  
224 70 × 70 μm and spectral resolution was 4 cm<sup>-1</sup>. Concentrations of OH groups and molecular  
225 H<sub>2</sub>O were determined from the height of the absorbance bands at 4500 and 5240 cm<sup>-1</sup>,  
226 respectively, using the Beer-Lambert law (e.g. [Stolper, 1982](#)). The 4500 and 5240 cm<sup>-1</sup> bands  
227 are commonly assigned to a combination of the stretching vibrations of OH groups attached to  
228 Si and the combination of the stretching and bending vibrations of the H<sub>2</sub>O molecule,  
229 respectively. Total water contents of the basaltic glasses belonging to the Holuhraun set, the  
230 basaltic glasses and two water-poor andesitic glasses (A030417 and A040417) were derived  
231 from the height of the broad asymmetric band at 3570 cm<sup>-1</sup>, which contains the fundamental  
232 OH stretching vibrations of both molecular H<sub>2</sub>O and Si-OH (and Al-OH) structural groups  
233 (e.g. [Stolper, 1982](#)). Baseline correction (see below) and peak integration were performed  
234 using OPUS software. On each sample, we carried out several measurements in order to  
235 verify compositional homogeneity. Homogeneity was confirmed by small relative standard  
236 deviations (RSD < 5 %) associated with water measurements on each sample.

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

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

245 each glass sample gave reproducibility better than 2 % relative. Densities of the studied  
246 reference glasses are reported in [Table 1](#) and [Figure 2](#).

247 The largest uncertainty in water contents determined by FTIR analysis is due to the  
248 uncertainty on the molar absorptivity (i.e. extinction coefficient) for the absorbance bands at  
249 4500 and 5240  $\text{cm}^{-1}$ . As estimated absorptivity coefficients depend on the baseline  
250 subtraction method (e.g. [Ohlhorst et al., 2001](#)), we followed guidelines provided by [Ohlhorst](#)  
251 [et al. \(2001\)](#) and [Mandeville et al. \(2002\)](#) for proper choice of baseline fitting procedure and  
252 molar absorptivity values.

253 In rhyolitic glass spectra, a linear baseline was fitted as tangent through the minima on  
254 both sides of the 5240  $\text{cm}^{-1}$  band and then extrapolated below the 4500  $\text{cm}^{-1}$  band (GG  
255 baseline of [Withers and Behrens, 1999](#)). For peraluminous rhyolites, we used the absorption  
256 coefficients provided by [Withers and Behrens \(1999\)](#):  $1.52 \pm 0.08 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{4500}$  (OH)  
257 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  
258 glasses match with target compositions (i.e. the amount of water loaded into the capsule) and  
259 are close to the difference of EMP analyses total from 100 wt %.

260 For andesitic glasses, we used the average values of the extinction coefficients  
261 determined by [King et al. \(2002\)](#) and [Mandeville et al. \(2002\)](#):  $0.97 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{4500}$   
262 (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).  
263 [Mandeville et al. \(2002\)](#) showed that  $\epsilon_{4500}$  and  $\epsilon_{5240}$  molar absorptivities have significant  
264 compositional dependency and can be predicted if the tetrahedral ( $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ) cation /total  
265 cation fraction of the glass is known. Molar absorptivity values calculated for the andesitic  
266 glasses using the regression line equations provided by [Mandeville et al. \(2002\)](#) are  $\sim 1.00$   
267 and  $1.19 \text{ (L mol}^{-1} \text{ cm}^{-1})$  for  $\epsilon_{4500}$  and  $\epsilon_{5240}$ , respectively, which are very close to the adopted  
268 values. The baseline of andesitic glass spectra was fitted as tangent through three points: the  
269 minima on both sides of the 4500  $\text{cm}^{-1}$  band and the minimum on the low wavenumber side of

270 the 5240  $\text{cm}^{-1}$  band. On its high wavenumber side (at  $\sim 5400 \text{ cm}^{-1}$ ), the linear baseline  
271 intersects the absorbance curve. This baseline fitting procedure is analogous to the one  
272 performed by [Mandeville et al. \(2002\)](#). Measured water concentrations in andesitic glasses are  
273 slightly lower than target amounts loaded into the capsule due to minor loss either during  
274 capsule preparation or upon the synthesis experiments.

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

286 Carbon dioxide concentrations in four basanitic and two andesitic glasses were  
287 determined from the heights of the absorbance bands at 1430 and 1520  $\text{cm}^{-1}$ , which  
288 correspond to antisymmetric stretching of distorted carbonate groups ([Dixon et al., 1995](#)). For  
289 basanitic and andesitic glasses, we adopted respectively the molar absorption coefficients  
290 provided by [Shishkina et al. \(2014\)](#) ( $306 \pm 32 \text{ L mol}^{-1} \text{ cm}^{-1}$  for 1430 and  $349 \pm 25 \text{ L mol}^{-1} \text{ cm}^{-1}$   
291 for 1520) and those given by [King et al. \(2002\)](#) ( $269$  and  $271 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the 1430 and  
292 1520 bands, respectively).

293 Water and CO<sub>2</sub> contents of a few andesitic and basaltic samples measured both by  
294 FTIR and elemental analyzer (Flash 2000 CHNS Thermo Electron housed at LMV) match  
295 within 5 %.

## 296 ***2.5 Raman Spectroscopy***

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

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

318 observed that the Raman signal intensity of the dark H<sub>2</sub>O- and Fe-rich basalt from the  
319 Holuhraun set was unstable at the highest laser power we used, possibly due to glass heating  
320 by the laser beam.

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

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

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

341

### 342 3. GLASS DENSITY

343 [Figure 2](#) shows the relationship between glass densities,  $\rho$  (kg/m<sup>3</sup>), and water contents,  
344  $C_{\text{H}_2\text{O}}$  (wt %), determined by FTIR spectroscopy or SIMS ([Table 1](#)). A linear relationship  $\rho =$   
345  $\rho_0 + b C_{\text{H}_2\text{O}}$ , where  $\rho_0$  is the density of the anhydrous glass and  $b$  the slope of the line, is  
346 observed. Density diminishes with increasing water content. The slope for mafic glasses is  
347 more important than the ones for intermediate and felsic glasses. The slopes defined by the  
348 rhyolitic and andesitic sample sets are in agreement with those found by [Ohlhorst et al. \(2001\)](#)  
349 and [Behrens et al. \(2006\)](#) for similar glass compositions. Moreover, the measured rhyolitic  
350 and andesitic glass densities are very close to densities measured by [Withers and Behrens](#)  
351 [\(1999\)](#) and [Mandeville et al. \(2002\)](#). The slope obtained for the 82-72f basaltic set is slightly  
352 more pronounced than the slope reported by [Ohlhorst et al. \(2001\)](#) for basaltic composition.  
353 As expected, the Fe-richer sets of basaltic and rhyolitic glasses are characterized by higher  
354 densities than the Fe-poorer sets. The measured basaltic glass densities fall within the range  
355 of values calculated by [Iacovino et al. \(2016\)](#). Density of the A011215 sample is aligned with  
356 that of the other andesitic glasses, even though it contains microlites.

### 357 4. RAMAN SPECTRAL TREATMENT

#### 358 *4.1 Baseline fitting*

359 Raman spectra of glass samples required baseline correction before being used for  
360 quantification of volatile species. In fact, a high signal intensity characterizes glass spectra at  
361 low wavenumbers (i.e. small Raman shifts, [Fig. 3](#)) due to the influence of the intense  
362 Rayleigh diffusion tail superimposed by the boson peak (e.g. [Le Losq et al., 2012](#)). [Long](#)  
363 [\(1977\)](#) was the first to highlight the need for correcting the raw spectra for the dependence of  
364 Raman scattering on frequency and temperature. Glasses, in particular rhyolitic ones, can be  
365 affected by fluorescence, which modifies the shape and intensity of the spectrum background.



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

372 In previous studies, different approaches were adopted for defining the baseline shape  
373 and the choice of anchor points (e.g., Zajacz et al., 2005; Behrens et al., 2006; Severs et al.,  
374 2007; Di Muro et al., 2009; Mercier et al., 2009, 2010; Le Losq et al., 2012). A first approach  
375 consisted in fitting the baseline of raw spectra using either a combination of linear baselines  
376 (Severs et al., 2007), a cubic baseline (Mercier et al., 2009) or a cubic spline baseline  
377 (Behrens et al., 2006) with three/four anchor points in the alumino-silicate vibration region  
378 and two anchor points in the water domain (Fig. 1). Zajacz et al. (2005) used a linear  
379 extrapolation of the flat signal from the  $1250\text{--}1850\text{ cm}^{-1}$  spectral region towards low  
380 wavenumbers (Fig. 1). Such an extrapolation is possible only if the spectral background  
381 between  $1250$  and  $1850\text{ cm}^{-1}$  is not too steep. In a second approach, the baseline was  
382 subtracted from spectra that had been previously corrected for Long's correction (Long,  
383 1977). Behrens et al. (2006) and Di Muro et al. (2009) adopted, respectively, a cubic spline  
384 and a cubic baseline anchored only at the extremities of the alumino-silicate and water  
385 domains, whereas Le Losq et al. (2012) anchored the spline to a limited number of  
386 intermediate minima. In general, we observe that discrepancies between different spectral  
387 corrections arise from unconstrained concavity of the spline baseline.

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

391 algorithms provided interesting results in this direction (e.g., Herzog and Zakaznova-Herzog,  
392 2011; Woelffel et al., 2015). Moreover, overlapping of bending and stretching bands occurs in  
393 the alumino-silicate region (e.g. Mysen et al., 1980), resulting in substantial uncertainty in  
394 selecting physically meaningful anchor points. The observed minima between the bands, in  
395 fact, may include contributions of the vibration bands (e.g. Le Losq et al., 2012).

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

416 several short linear segments are necessary to fit the curve. A second intermediate anchor  
417 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  
418 rhyolites. We did not fix an anchor near 820  $\text{cm}^{-1}$  in basanites because the corresponding  
419 minimum tends to disappear in  $\text{H}_2\text{O}$  and  $\text{CO}_2$ -bearing basanites. The defined anchors  
420 correspond to minima regions, and in some cases are defined by tangent lines to the spectra.  
421 We note that the positions of the intermediate anchor points and that of the anchor at the high  
422 wavenumber end of the spectrum shift to higher frequency as the polymerization increases, in  
423 agreement with previous observations (Le Losq et al., 2012).

424 In the water domain of the spectra, linear baselines were anchored ( $\sim 2980$  and  $3780 \text{ cm}^{-1}$ )  
425 <sup>1)</sup> and cubic baselines were fit (from 2980 to 3000-3008 and from 3725 to  $3780 \text{ cm}^{-1}$ ) at both  
426 band extremities without any distinction between glasses of different composition. As the  
427 shape of cubic baseline is more sensitive to the topology and length of the fitted background,  
428 the more adequate cubic fitting was considered the one with the closest match of the baseline  
429 on the background on both sides of the band.

## 430 ***4.2 Alumino-silicate band topology and assignment***

### 431 *4.2.1 Topology of Raman spectra*

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

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

440 bands as High-Frequency (HF) and Low-Frequency (LF) bands. Increasing water content in  
441 basanitic and basaltic glasses has several effects: a) the maximum peak position of the LF  
442 bands shifts from 556 to 510  $\text{cm}^{-1}$  and from 532 to 512  $\text{cm}^{-1}$  in basanites and basalts,  
443 respectively; b) the maximum peak position of the HF bands shifts from 968 to 975  $\text{cm}^{-1}$  in  
444 basanites, and from 966 to 990  $\text{cm}^{-1}$  in basalts. c) The FWHM of the HF band slightly  
445 decreases from 181 to 164  $\text{cm}^{-1}$  and from 184 to 177  $\text{cm}^{-1}$  in the Fe-rich (Holuhruan) and  
446 high-Al (82-72f) basaltic sets, respectively (Fig. 2S b). d) In basalts, the ratio of LF band  
447 (integrated) intensity to HF band (integrated) intensity increases due to apparent decrease of  
448 the HF band height (Fig. 2S d). The latter observation is in agreement with previous  
449 observations on different basaltic glasses (Mercier et al., 2009). A shoulder at  $\sim 580 \text{ cm}^{-1}$   
450 characterizes the LF bands. A broad weak band centered at  $\sim 710 \text{ cm}^{-1}$  defines the spectrum  
451 topology in the intermediate wavenumber range ( $650\text{-}800 \text{ cm}^{-1}$ ). In basanites, the relative  
452 intensity of this middle-region band with respect to LF and HF bands is higher than in the  
453 other glasses, and increases with the volatile content. Dissolved  $\text{CO}_3^{2-}$  molecules in basanites  
454 produce a peak near  $1083 \text{ cm}^{-1}$ , whose intensity increases with the  $\text{CO}_2$  content, in agreement  
455 with Morizet et al. (2013).

456         With increasing polymerization, the relative intensity of the two main silicate bands  
457 inverts and the LF and HF maximum peaks shift, respectively, to lower and higher  
458 frequencies, in agreement with previous studies (e.g., Matson et al., 1983; Mercier et al.,  
459 2009). Moreover, the FWHM of the LF band diminishes with increasing degree of  
460 polymerization (Figs. 2S e,i).

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

464 band (integrated) intensity increases with increasing degree of polymerization (Fig. 2S g).  
465 With increasing water content, the FWHM of the LF band decreases from 137 to 114 cm<sup>-1</sup>  
466 (Fig. 2S f). As in basalts, the LF band exhibits a shoulder at ~580 cm<sup>-1</sup>. A small asymmetric  
467 band centered at 795 cm<sup>-1</sup> is present in all andesitic glasses (Fig. 4). Dissolved CO<sub>3</sub><sup>2-</sup>  
468 molecules in A310317 and A030417 glass samples produce a peak near 1078 cm<sup>-1</sup>, which is  
469 more pronounced in A310317.

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

487 *4.2.2 Review of the interpretation of bands*

488 In the 200-1300  $\text{cm}^{-1}$  region of the Raman spectrum, bands correspond to different  
489 bridging and non-bridging T-O vibrations in the glass structure (e.g., [Brawer and White,](#)  
490 [1977; Matson et al., 1983; McMillan, 1984; McMillan et al., 1992](#)). The LF band near 400-  
491 500  $\text{cm}^{-1}$ , which is dominant in polymerized glasses, is traditionally assigned to: a) rocking  
492 motion in fully polymerized  $Q^4$  units (where  $Q^4$  denotes a tetrahedron linked by bridging O  
493 atoms to 4 adjacent tetrahedra), b) breathing modes of four- and six-membered rings of  $\text{TO}_4$   
494 tetrahedra in polymerized glasses ([Sharma et al., 1981; Matson et al., 1983; Rossano and](#)  
495 [Mysen, 2012](#)), but also c) T-O-T symmetric stretching vibrations involving bridging oxygens  
496 and four-fold coordinated cations ([Zotov et al., 1992](#)) and d) T-O-T bending vibrations in  
497 glasses containing non-bridging oxygens ([McMillan, 1984; Rossano and Mysen, 2012](#) and  
498 references therein). In rhyolitic glasses, decreasing FWHM of the LF band ([Fig. 2S j](#)) and its  
499 shift to higher frequency with increasing water content have been explained by a possible  
500 decrease in the average T-O-T angle ([McMillan and Remmele, 1986](#)).

501 The vibrational mode at 570-580  $\text{cm}^{-1}$  has been attributed to either structural defects  
502 (i.e. broken oxygen bridges, [Stolen and Walrafen, 1976; Seifert et al., 1981; McMillan and](#)  
503 [Remmele, 1986](#)) or a mixed stretch-bend vibration in  $Q^2$  structural units ([Furukawa et al.](#)  
504 [1981](#)). The bands near 700 and 800  $\text{cm}^{-1}$  have been respectively ascribed to T-O-T bending  
505 motions ([Mysen et al., 1980; Furukawa et al. 1981; McMillan, 1984; Rossano and Mysen,](#)  
506 [2012](#)) and to cage-like vibrations of Si atoms mainly in  $Q^4$  tetrahedra ([Zotov and Keppler,](#)  
507 [1998](#)).

508 The main HF envelope at 900-1200  $\text{cm}^{-1}$  can be decomposed into several bands  
509 associated with localized symmetric and asymmetric T-O and T-O-T stretching modes of  
510 distinct structural species, i.e.  $Q^2$ ,  $Q^3$ ,  $Q^4$  (2, 3, 4 being the number of bridging oxygens;  
511 [Mysen et al., 1980; Matson et al., 1983; McMillan 1984; Zotov and Keppler, 1998; Rossano](#)  
512 [and Mysen, 2012](#)). Substitution of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  for  $\text{Si}^{4+}$  as network-forming cations strongly

513 influences the spectral composition of this band; in particular, increasing the Al content of the  
514 glass results in the shifting of Raman bands to lower frequencies (Brawer and White, 1977;  
515 Mysen et al., 1980; Neuville et al., 2004). The intensity ratio between the bands near 950 and  
516 1135  $\text{cm}^{-1}$  in rhyolitic glasses is indicative of relative proportions of structural units, which are  
517 likely  $Q^2$  and a combination of  $Q^3$  and  $Q^4$  units, respectively (Mysen et al., 1980; Zotov and  
518 Keppler, 1998). The band near 1050  $\text{cm}^{-1}$  that characterizes the water-poor NSL-N1 glass is  
519 tentatively assigned to T-O stretching vibrations in distinct  $Q^3$  or  $Q^4$  units (Mysen et al., 1980;  
520 Zotov and Keppler, 1998). In the peraluminous rhyolites, the increased intensity of the band  
521 at  $\sim 930 \text{ cm}^{-1}$  with increasing water content can be attributed to the formation of T-OH units  
522 (Zotov and Keppler, 1998). In peralkaline glasses, the sharp increase of the band at 970-980  
523  $\text{cm}^{-1}$  is attributed to progressive entry of four-fold  $\text{Fe}^{3+}$  in alkali-bonded  $Q^3$  units (Wang et al.,  
524 1995; Di Muro et al., 2009; Di Genova et al., 2016).

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

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

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

### 543 ***4.3 Water band topology***

544 The topology of the water stretching vibration band depends on glass matrix  
545 composition and water concentration (Fig. 5), but also on water speciation (e.g., Mysen and  
546 Virgo, 1986) and strength of H-bonding (e.g., Zajacz et al., 2005; Behrens et al., 2006; Di  
547 Muro et al., 2006). Different water species (metal-hydroxyl and molecular H<sub>2</sub>O) contribute to  
548 the intensity of the broad water band-envelope (e.g., Mysen and Virgo, 1986). The latter is  
549 asymmetric in shape with a long tail on the lower wavenumber side, and is characterized by  
550 two shoulders near 3250 cm<sup>-1</sup> and 3640 cm<sup>-1</sup> that are readily observed in rhyolitic glasses  
551 (Fig. 5). The exact position of the maximum peak of the water band shifts to lower frequency  
552 with increase of polymerization degree and water content (Fig. 5), in agreement with previous  
553 studies. The maximum is located within the 3565-3582 cm<sup>-1</sup> range in basaltic glasses and at  
554 3552-3570 cm<sup>-1</sup> in basaltic, andesitic and rhyolitic glasses. In the basaltic, basaltic and  
555 andesitic glass sets, the FWHM of the band increases by 15-25 % relative with increasing  
556 water content.

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

### 559 ***4.4 Peak fitting of the HF and water bands***

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



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

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

587 Concerning CO<sub>2</sub>-bearing basanitic glasses, best fitting in the 630-1200 cm<sup>-1</sup> spectral  
588 range was achieved with six to seven components, whose positions are: I) 707-715 cm<sup>-1</sup>, II)  
589 779-789 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>  
590 and VII) 1084-1088 cm<sup>-1</sup> (Fig. 3S, Table 2S). The last component refers to the  $\nu_1$  Raman  
591 vibration of dissolved carbonate (Morizet et al., 2013).

592 Peak fitting of the total water band requires a minimum of four Gaussian components  
593 (Table 3S, Fig. 4S), in agreement with previous studies (e.g., Chabiron et al., 2004; Behrens  
594 et al., 2006; Di Muro et al., 2006). The positions of these components are: I) 3080-3098 cm<sup>-1</sup>,  
595 II) 3250-3298 cm<sup>-1</sup>, III) 3420-3487 cm<sup>-1</sup> (with the highest frequencies in rhyolites), IV) 3540-  
596 3575 cm<sup>-1</sup>, and V) 3600-3645 cm<sup>-1</sup> (with the lowest frequencies in basanites and basalts);  
597 these positions match those determined by Di Muro et al. (2006). The small component I is  
598 only present in water-rich glasses (Fig. 5), as observed by Behrens et al. (2006). In general,  
599 the intensity of the low frequency components increases with total dissolved water, in  
600 agreement with the expected increase of molecular water (e.g. Mysen and Virgo, 1986).

## 601 5. DEPTH PROFILES

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

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

611 signal intensity at the surface in high confocality, whereas it increases by ~45 % in standard  
612 confocality (Fig. 7). In andesitic glasses, maximum intensity, which is attained at 3-4  $\mu\text{m}$   
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 basaltic 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 basaltic 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 basaltic 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 basaltic, 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

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

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

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

## 655 **6. CALIBRATION**

### 656 ***6.1 External calibration method***

657 In the external calibration method, water concentration in an unknown glass sample is  
658 derived from the absolute (integrated) intensity of the band at  $\sim 3570\text{ cm}^{-1}$  compared to band

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

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

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

$$675 \quad C_{H_2O} (\text{wt}\%) = 2.403 (\pm 0.033) \cdot A_{OH} - 0.058 (\pm 0.046) \quad (R^2 = 0.995), \quad (1)$$

676 and standard confocality setting:

$$677 \quad C_{H_2O} (\text{wt}\%) = 2.057 (\pm 0.025) \cdot A_{OH} + 0.072 (\pm 0.039) \quad (R^2 = 0.996). \quad (2)$$

678 The data are reproduced with a root-mean-square error of ~0.13 and ~0.11 wt% in high and  
679 standard confocality, respectively (Fig. 8, Table 4S). The linear regressions do not take into  
680 account the uncertainties on H<sub>2</sub>O content of the reference glasses. Their intercepts pass very  
681 close to the origin. Linear calibrations with similar slopes (within 15 % difference) were

682 reproduced using a range (1-16 mW) of laser powers in different sessions over several  
683 months.

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

## 688 ***6.2 Internal calibration method***

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

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

706 The divergence of water-rich basalts and peralkaline rhyolites from the main trend in  
707 Fig. 9a is due to the effect of water content on the integrated intensity of the alumino-silicate  
708 region and to the behavior of the band at  $980\text{ cm}^{-1}$ , respectively. Careful inspection of spectra  
709 in the alumino-silicate vibration region reveals that the integrated intensity (hereafter  $A_{\text{Al-Si}}$ )  
710 of this region generally decreases with increasing water content and decreasing density (Fig.  
711 10), regardless of analytical conditions (i.e. laser power on sample and confocality) and  
712 baseline treatment, except for the peralkaline and basanitic glasses. The effect of water in  
713 lowering  $A_{\text{Al-Si}}$  is maximum in basaltic glasses, in particular in the 82-72f set with 30 %  
714 intensity reduction for 15 mol %  $\text{H}_2\text{O}$  (Fig. 10 c), and becomes smaller in andesitic and  
715 rhyolitic glasses characterized by < 12 % and 10 % reduction for 18 mol %  $\text{H}_2\text{O}$  and 25  
716 mol %  $\text{H}_2\text{O}$ , respectively (Fig. 10 e, g). In  $\text{CO}_2$ -bearing basanitic glasses, the observed  
717 increase of  $A_{\text{Al-Si}}$  with decreasing density (Fig. 10 b) is due to the presence of  $\text{CO}_3^{2-}$  dissolved  
718 in these glasses; the intensity of the  $\nu_1$  Raman vibration of dissolved carbonate at  $\sim 1087\text{ cm}^{-1}$   
719 (Fig. 3S) has to be subtracted from the intensity of the alumino-silicate envelope (Table 2S).  
720 Adjustments of the internal calibration method to take into account the effect of water content  
721 on  $A_{\text{Al-Si}}$ , the behavior of the band at  $980\text{ cm}^{-1}$  in peralkaline rhyolites and the presence of  
722  $\text{CO}_3^{2-}$  in basanites are presented in the Discussion section.

723 Small deviations from the general trends of Fig. 10 in a given set of glasses reflect  
724 differences in glass structure. For instance, the higher  $A_{\text{Al-Si}}$  measured in the A071215 sample  
725 is probably due to a different iron oxidation state compared to the other andesitic glasses (see  
726 spectra of Fig. 4c). The HF band in A310317 and A030417 glass spectra contains an  
727 additional contribution from the vibration of  $\text{CO}_3^{2-}$  molecules (Fig. 10 e). The basaltic sample  
728 82-72f#10 is characterized by a larger  $A_{\text{Al-Si}}$  than expected from the general trend of the 82-  
729 72f basaltic set (Fig. 10 c). This may be due to the slightly higher density of this sample  
730 compared to the other glasses of the same basaltic set (Fig. 2). Analogously, the higher

731 synthesis pressure (and thus the relatively higher density) of the basanite BSN101117-2  
732 compared to the other basanitic glasses (Table 1) may be partly responsible for its  
733 significantly larger  $A_{\text{Al-Si}}$  (Fig. 10 a, b).

## 734 7. DISCUSSION

### 735 7.1. Parameters controlling the Raman signal

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

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

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

750 Previous studies showed that the Raman scattering cross-section of different  $Q^n$  species  
751 and dissolved hydrous species depends on glass composition and structure (Fukumi et al.,  
752 1990; Zotov 2001; Zajacz et al., 2005; Behrens et al., 2006; Mercier et al., 2010). Mercier et  
753 al. (2010) highlighted that the matrix effect on the total water band is related to differences in



754 glass reflectance and water bonding environment. Moreover, they reported positive  
755 correlations between the slope of the calibration line and both reflectance and density of the  
756 glass.

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

778 **7.2. External versus internal calibration**

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

797 In the case of internal calibration, the intensity of the water band is scaled to the  
798 alumino-silicate band intensity, resulting in a stronger dependence on glass composition (Fig.  
799 9a), in agreement with previous works (e.g., Zajacz et al. 2005, Mercier et al. 2009). To better  
800 compare all the glass sets, the  $CO_2$ -bearing glasses need to be corrected for the contribution of  
801 the  $CO_3^{2-}$ -related spectral component (Fig. 3S). This is simply achieved by multiplying the

802  $A_{\text{Al-Si}}$  by a factor that takes into account the contribution of the component VII relative to the  
803 sum of the areas of all spectral components (Table 2S). In line with the results of Morizet et  
804 al. (2013), we found that the relative contribution of the  $\text{CO}_3^{2-}$  is proportional to the total  $\text{CO}_2$   
805 content.

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

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

813 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  
814 times in the water and alumino-silicate regions, respectively. In other words, the correction  
815 factor ( $\alpha_1$ , Table 4S) is proportional to the difference between the  $A_{\text{Al-Si}}$  of the anhydrous glass  
816 and that of the hydrous glasses of each set (Fig. 10). The correction factor depends on both  
817 glass composition and water content (see Fig. 2); either density or mol%  $\text{H}_2\text{O}$  estimated with  
818 the external calibration method can be used to estimate  $\alpha_1$  (Fig. 10). Up to ~7 wt %  $\text{H}_2\text{O}$   
819 contents, rhyolitic, andesitic and basaltic glasses require a minor correction (< 10-12 % in  
820 the studied range of water contents). In contrast, water-rich (> 3 wt %  $\text{H}_2\text{O}$ ) basaltic glasses  
821 need more important corrections.

822 Peralkaline glasses are well aligned below the calibration line defined by peraluminous  
823 rhyolites (Fig. 9a). In order to understand their distinct behavior, we performed peak fitting of  
824 the alumino-silicate HF envelope of both peralkaline and peraluminous glasses (Fig. 6). The  
825 spectral components I, IV and V are more important in peraluminous rhyolites than in

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

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

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

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

$$845 \quad C_{\text{H}_2\text{O}} (\text{wt}\%) = 2.179 (\pm 0.037) \cdot A_{\text{OH}}/A_{\text{Al-Si corr}} + 0.060 (\pm 0.055) \quad (R^2 = 0.992), \quad (6)$$

846 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.,  
 847 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  
 848 within 0.17 wt % (root-mean-square error).

### 849 **7.3. Application to natural glass inclusions**

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

860 The studied inclusions have variable composition spanning from basanitic to basaltic  
861 and andesitic, and contain different amounts of water ranging from 0.1 to 3.3 wt% (Table 3).  
862 They contain less than 0.13 wt% CO<sub>2</sub>, except for two basanitic inclusions, TAO-011 and  
863 TGN-0118 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  
864 wt% are not detected using Raman spectroscopy ([Morizet et al., 2013](#)), only the two basanitic  
865 inclusions were corrected for the presence of dissolved carbonate. The relatively large size of  
866 the analyzed glass inclusions and the very weak or absent scattering from the embedding  
867 olivine crystals allowed focusing the laser beam at depths where the intensity of the water  
868 signal was maximum (-2 or -3 μm). These correspond to the optimal depths reported in [Figure](#)  
869 [7](#) for the reference glasses.

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

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

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

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

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

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

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

919 **CONCLUDING REMARKS**

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

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

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



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

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

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

961 Peak fitting of the alumino-silicate high frequency envelope (approximately located  
962 between 800 and 1250  $\text{cm}^{-1}$ ) is required to quantify the intense scatterings around 980  $\text{cm}^{-1}$   
963 and 1080  $\text{cm}^{-1}$  caused, respectively, by  $\text{Fe}^{3+}$  in four-fold coordination and  $\text{CO}_3^{2-}$  dissolved in  
964 glasses. Concerning the  $\text{Fe}^{3+}$ -related matrix effect, we must point out that, in principle, all  
965  $\text{Fe}^{3+}$ -bearing glasses should be corrected for it. Nevertheless, only peralkaline rhyolites were  
966 corrected in this study because the area of the high frequency envelope in peralkaline

967 rhyolites is far more sensitive to changes in  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  than in mafic compositions (Di Muro et  
968 al., 2009; Di Genova et al., 2016). Once the proposed corrections are performed, all the  
969 studied glasses define a single internal calibration line in spite of their compositional  
970 variability. Alkaline glasses, specifically basanites, behave coherently with the other glass  
971 compositions when the analytical strategies and data treatment procedures (i.e., for baseline  
972 subtraction, peak fitting and density correction) established in the present study are used.

973 Accuracy of the external calibration in the high confocality setting was determined by  
974 testing our method on olivine-hosted glass inclusions whose water content was measured  
975 using SIMS or FTIR. The calculated average RSD is ~4% ( $1\sigma$ ) for most samples, and  
976 increases to ~12% ( $1\sigma$ ) for glass inclusions with  $\text{H}_2\text{O}$  contents close to the detection limits  
977 (~0.1 wt%).

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

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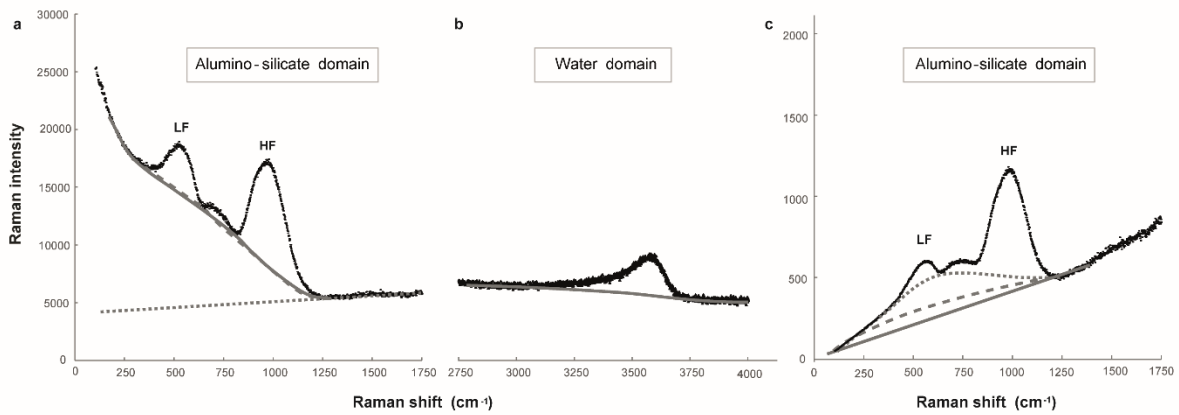
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1176 **FIGURES**

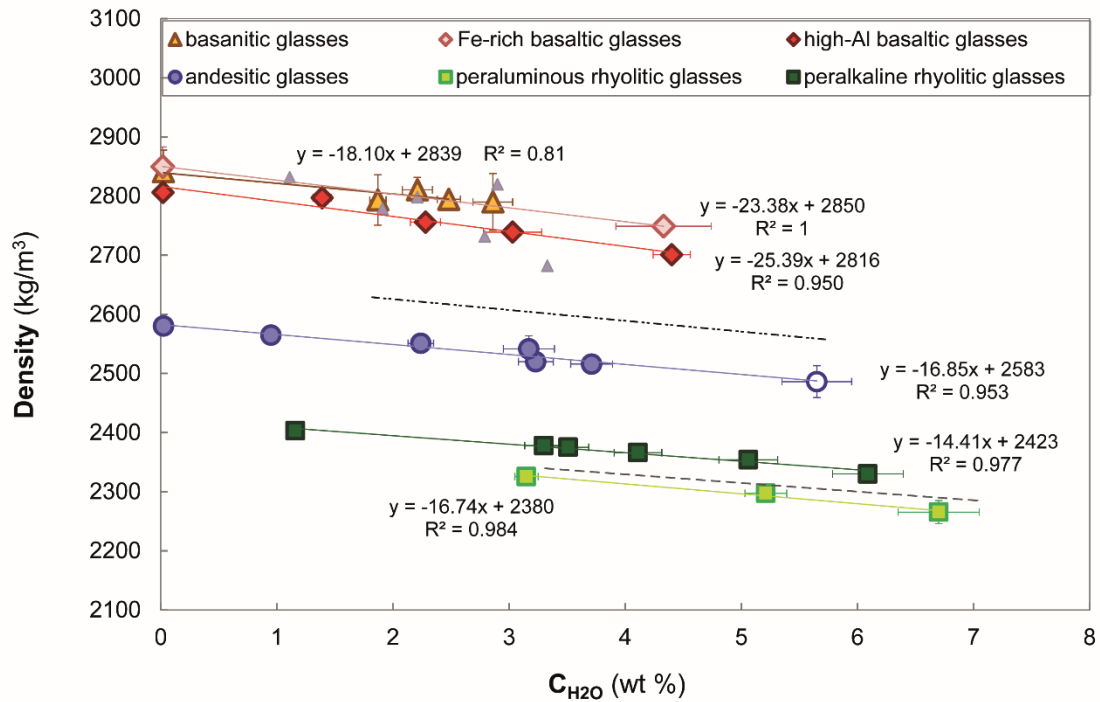
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1179 **Fig. 1.** Procedures for background subtraction used in previous studies. (a-b) Baseline  
1180 fitting on raw Raman spectra. (a) In the aluminosilicate domain: cubic baseline (Mercier et  
1181 al., 2009; dashed curve), cubic spline baseline (Behrens et al., 2006; continuous curve), and  
1182 linear extrapolation method by Zajacz et al. (2005, dotted line); (b) cubic baseline in the water  
1183 domain. (c) Baseline fitting on Long-corrected spectra in the aluminosilicate domain: cubic  
1184 baseline (Di Muro et al., 2009; dashed curve) and cubic spline baseline (Behrens et al., 2006;  
1185 continuous line) anchored at the extremities of the domain, or to a limited number of  
1186 intermediate minima (Le Losq et al., 2012; dotted curve). LF and HF indicate low-frequency  
1187 and high-frequency bands.

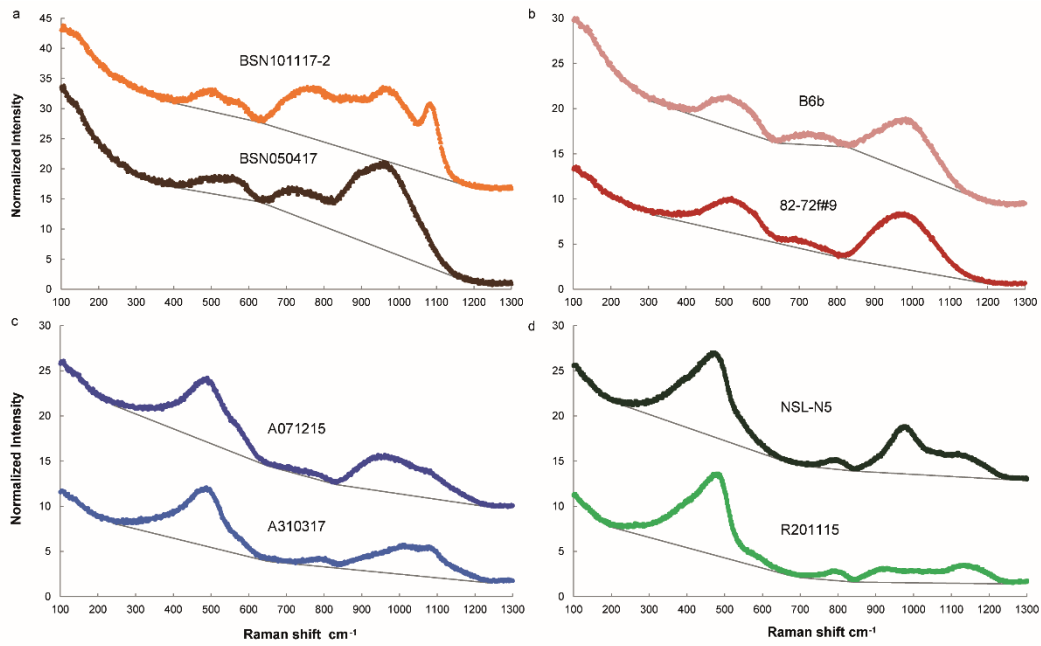
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1190 **Fig. 2.** Glass density versus glass water content determined by FTIR or SIMS  
 1191 measurements (see Table 1). A decrease of slope value from basaltic to rhyolitic glasses is  
 1192 observed. The dashed line represents the density of rhyolitic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

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**Fig. 3.** Raw Raman spectra of the alumino-silicate vibration bands of the glasses with

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basanitic (a), basaltic (b), andesitic (c) and rhyolitic (d) compositions. Linear baselines

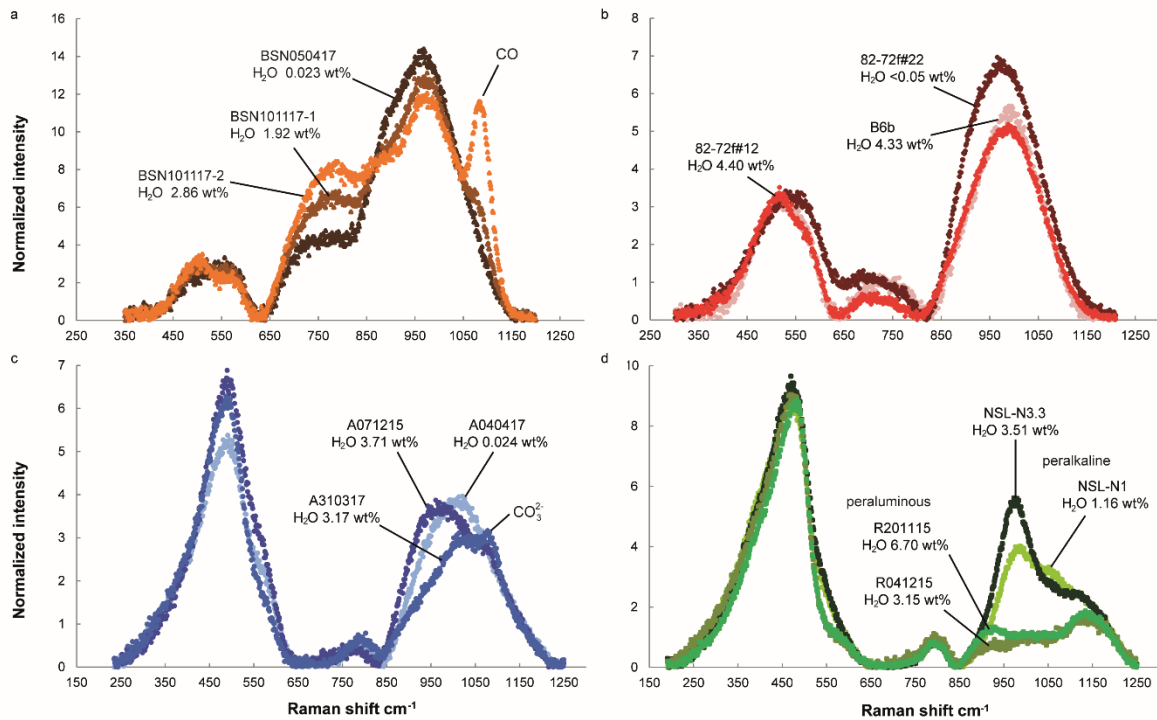
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adopted for background subtraction are shown with anchor points. Spectra are displaced

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vertically for clarity. Intensities were normalized to laser power and acquisition time.

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

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andesitic (c) and rhyolitic (d) glasses after subtraction of linear baselines. Spectra were

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measured under the same conditions of laser power and confocality. Intensities were

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normalized to acquisition time. Laser beam was focused at the optimal depth as defined in the

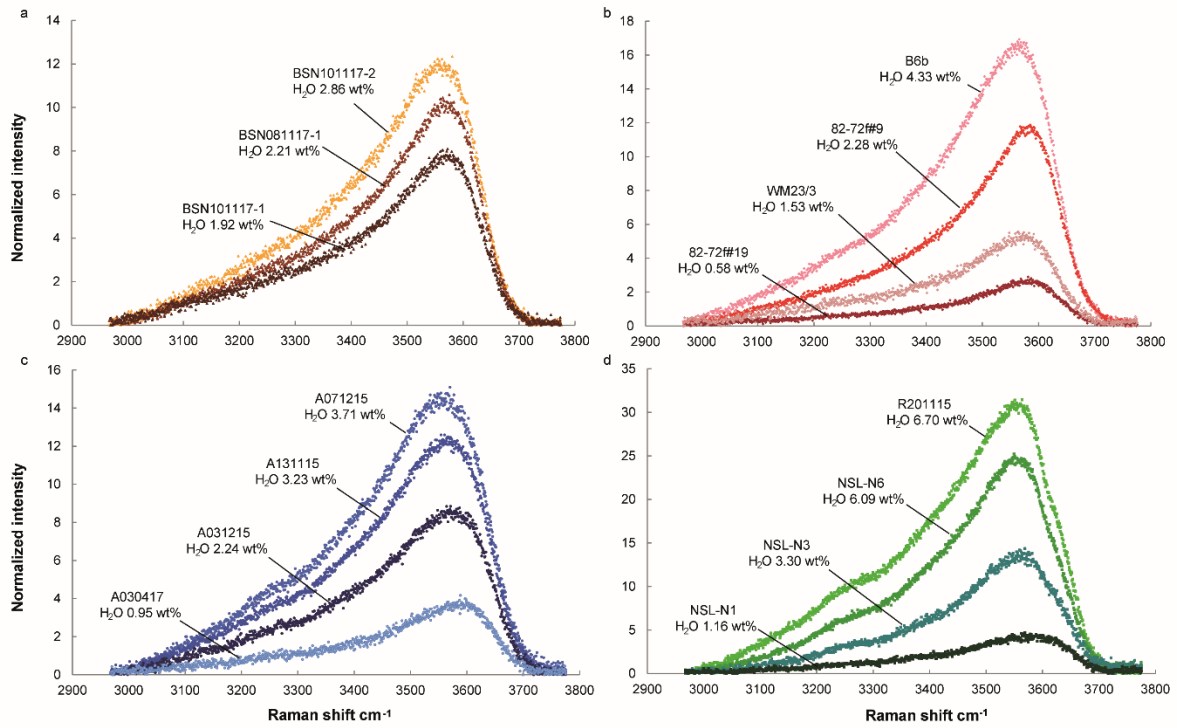
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text. Note differences in band topology associated with different major element compositions,

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water contents, degree of polymerization, and oxidation state (see text).

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

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basanites (a), basalts (b), andesites (c) and rhyolites (d) with different water contents. Spectra

1216

were measured under the same conditions of laser power and confocality. Intensities were

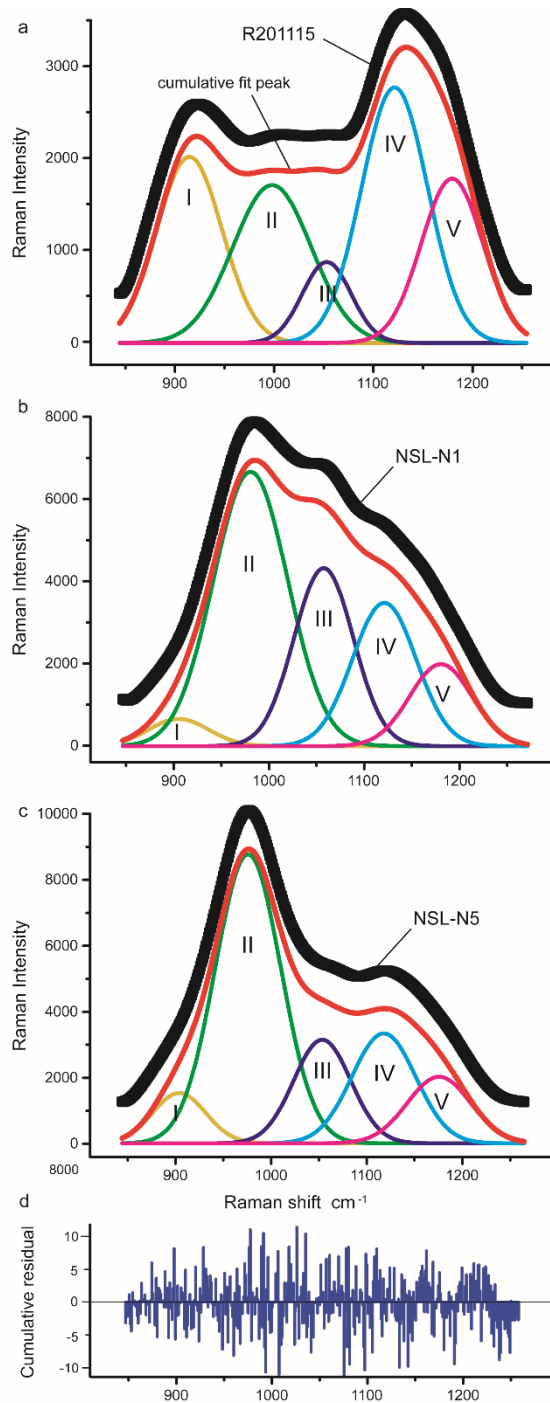
1217

normalized to acquisition time. Laser beam was focused at optimal depths as defined in the

1218

text.

1219

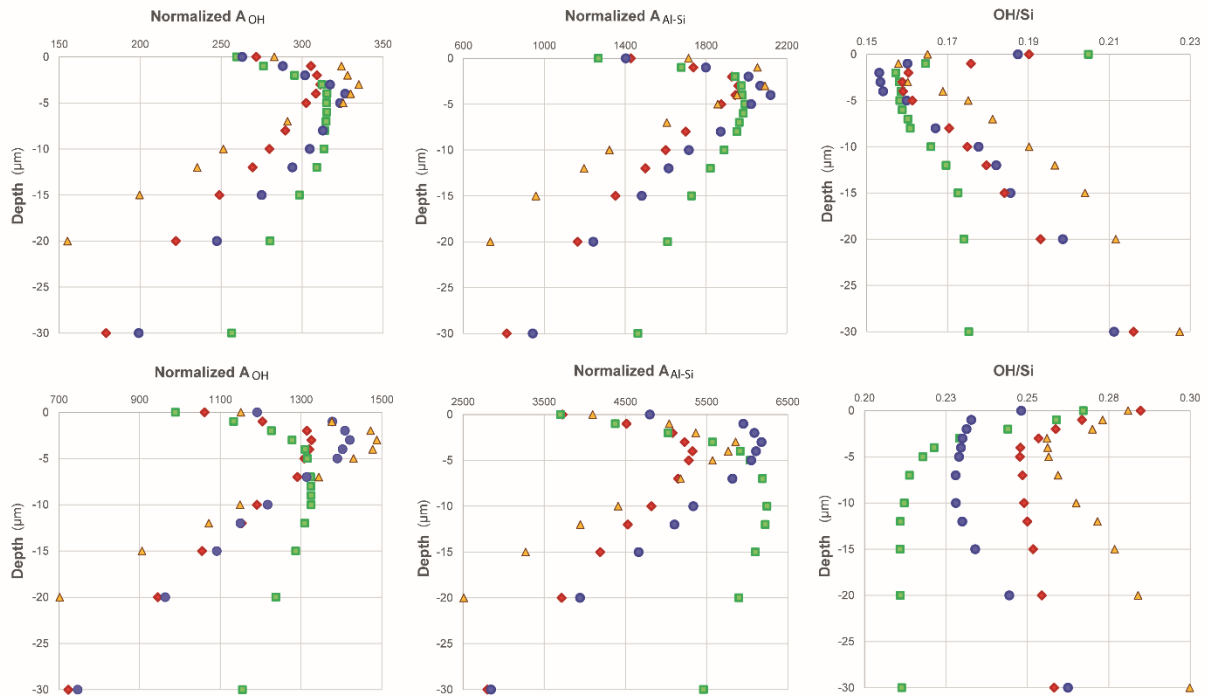


1220

1221 **Fig. 6.** Peak fitting of the HF aluminosilicate envelope of peraluminous (a), water-poor  
 1222 (b) and water-rich peralkaline (c) rhyolitic glasses with a finite number of Gaussian  
 1223 components performed with OriginPro software. The good quality of the fit is indicated by  
 1224 the randomness of the residuals (d).

1225





1226

1227

**Fig. 7.** Depth profiles measured in the water and aluminosilicate vibration regions of

1228

basaltic (yellow triangles), basaltic (red diamonds), andesitic (blue circles) and rhyolitic

1229

(green squares) glasses under high (upper row) and standard (lower row) confocality

1230

conditions. Integrated intensities of the water band ( $A_{OH}$ ) and the aluminosilicate envelope

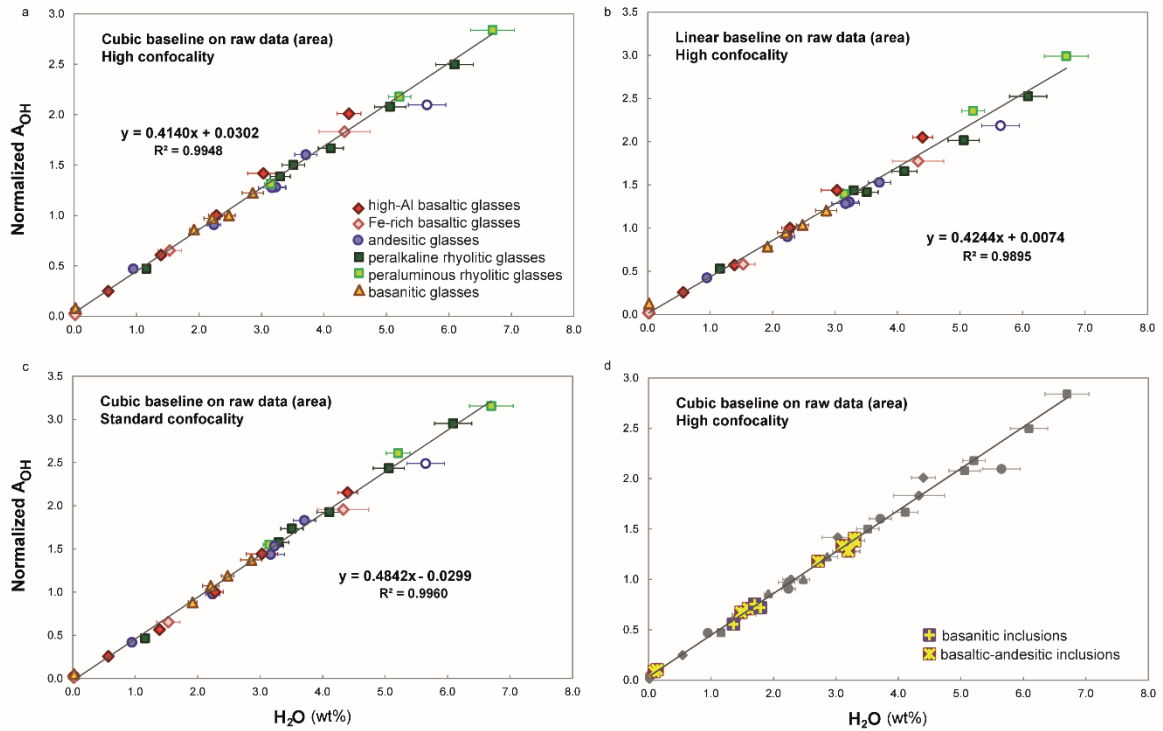
1231

( $A_{Al-Si}$ ) were normalized to laser power and acquisition time; water band intensities were also

1232

normalized to water content.

1233



1234

1235 **Fig. 8.** External calibration lines for quantification of water contents in glasses, obtained

1236 after subtracting a cubic or a linear baseline from raw data: areas in high confocalty setting

1237 (a-b, d), and in standard confocalty setting (c). Reference glasses define a composition-

1238 independent linear relationship. In (d) glass inclusions are plotted over the reference glasses.

1239 Microlite-bearing A011215 glass (empty circle) is shown but is not considered for calibration

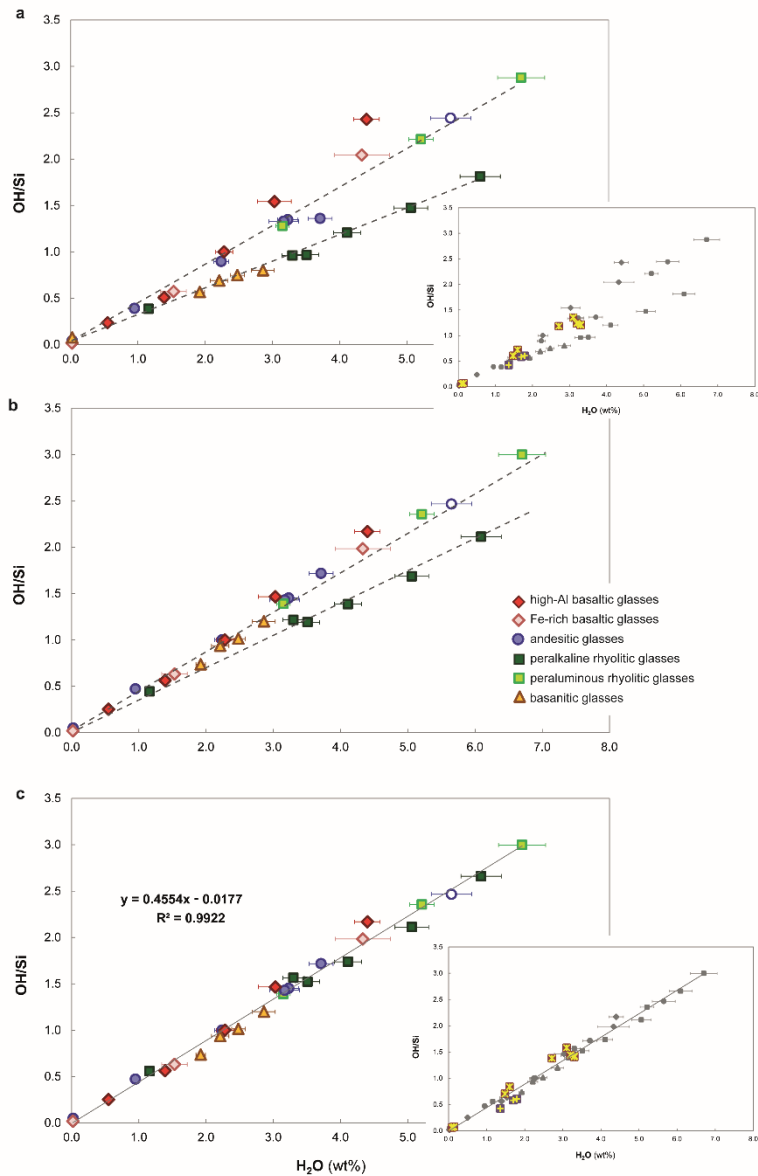
1240 line definition. Water band areas were normalized to the water band area of the 82-72f#9

1241 basaltic glass, which was used as internal standard to eliminate small variations in

1242 measurement conditions. For glass inclusions, errors associated with SIMS measurements are

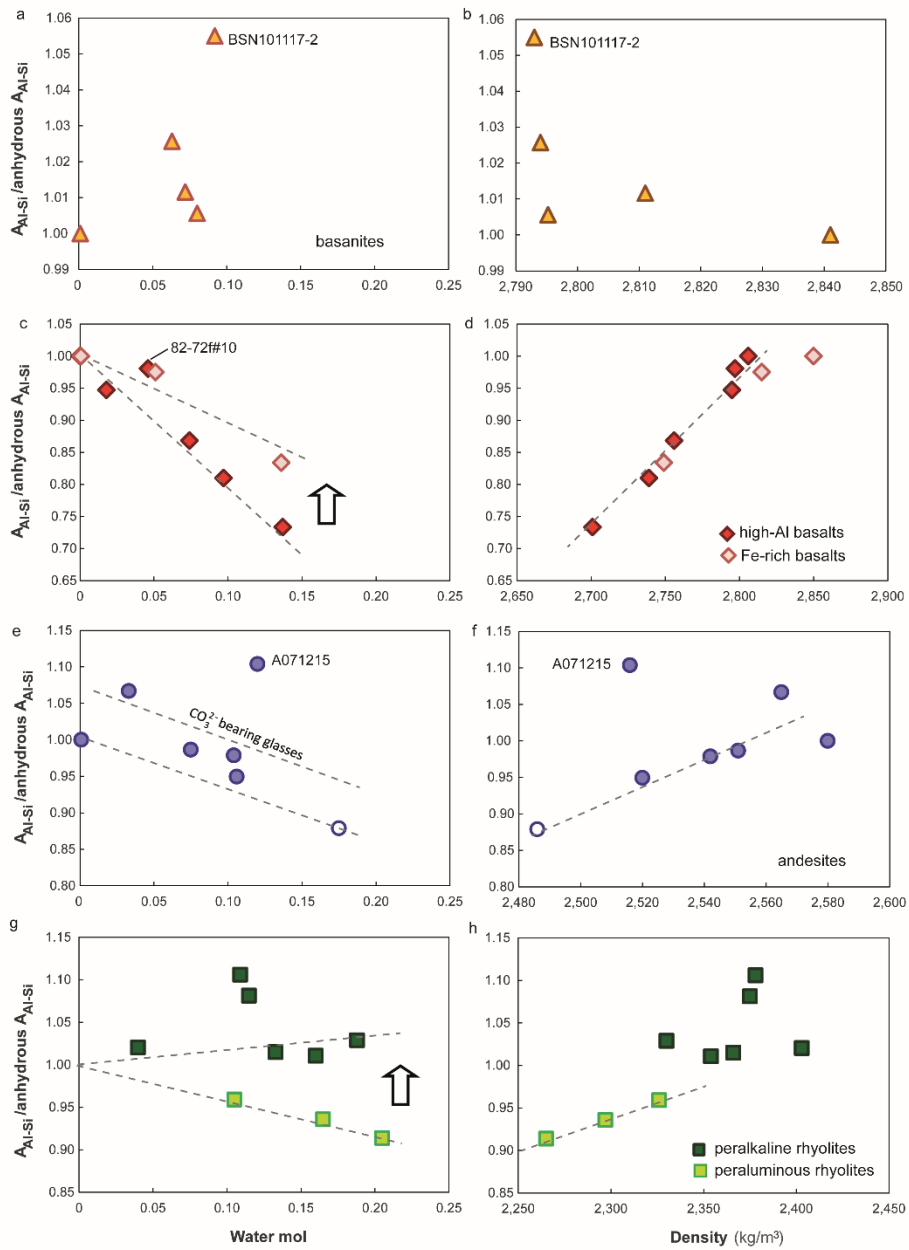
1243 smaller than symbols.

1244



1245

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



1254

1255 **Fig. 10.** Evolution of the area of the alumino-silicate band (expressed as ratio between  
 1256 the alumino-silicate band area of hydrous glasses and that of the anhydrous glass) with water  
 1257 content (left column) and density (right column) of basanitic (a-b), basaltic (c-d), andesitic (e-  
 1258 f) and rhyolitic (g-h) glasses. Grey dashed curves show the main trends. The arrows highlight  
 1259 the different behavior of Fe-rich and Fe-poor glasses with similar compositions. Microlite-  
 1260 bearing andesitic glass A011215 is represented by an empty blue circle.

1261

**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%	l <sup>c</sup>	mol	wt%		
<b>Basaltic</b>																	
BSN050417	Alkaline	Thueyts tephra	GMF	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	1/2* 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	1/2* 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	1/2* 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
<b>Basaltic</b>																	
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>80</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>80</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>80</sub> Pd <sub>10</sub>	0.20	1443	3.1		SIMS		2701	4.40	0.16	0.137			[1],[2]
B250317	Tholeiitic	Holuhran tephra	GMF	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	Holuhran tephra	PC	1/2* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	68	3.7	FTIR	0.0324(4)	2815 <sup>b</sup>	1.53	0.19	0.051			This study
B6b	Tholeiitic	Holuhran tephra	PC	1/2* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1473	2.0	5	FTIR	0.0016(1)	2749(11)	4.33	0.41	0.136			This study
<b>Andesitic</b>																	
A040417	Calcaline	Synthetic	GMF	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	Calcaline	Synthetic	PC	1/2* Au <sub>80</sub> Pd <sub>20</sub>	0.75	1573	24	1.0	FTIR	0.0120(2)	2565(4)	0.95	0.05	0.033	0.28 ± 0.02		This study
A310317	Calcaline	Synthetic	PC	1/2* Au <sub>80</sub> Pd <sub>20</sub>	1.1	1573	24	2.7	FTIR/CHNS	0.0451(2)	2542(22)	3.17	0.22	0.104	0.59 ± 0.01		This study
A031215	Calcaline	Synthetic	PC	3/4* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	17	2.5	FTIR	0.0357(2)	2551(5)	2.24	0.11	0.075			This study
A131115	Calcaline	Synthetic	PC	3/4* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	18	3.5	FTIR/CHNS	0.0298(5)	2520(5)	3.23	0.15	0.106			This study
A071215	Calcaline	Synthetic	PC	3/4* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	24	4.0	FTIR	0.0521(2)	2516(9)	3.71	0.18	0.120			This study
<b>Rhyolitic</b>																	
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	2 <sup>d</sup>	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	4 <sup>d</sup>	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	6 <sup>d</sup>	FTIR	0.0228(3)	2265(20)	6.70	0.35	0.205			This study
<b>Microlites-bearing</b>																	
A011215	Calcaline	Synthetic	PC	3/4* Au <sub>80</sub> Pd <sub>20</sub>	1.0	1573	18	6	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%		
<b>BASANITIC<sup>c</sup></b>													
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
<b>BASALTIC</b>													
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
<b>ANDESITIC</b>													
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
<b>RHYOLITIC</b>													
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
<b>Microlites-bearing</b>													
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>e</sup>	Santorini	Olivine	Basalt	110 × 50	3.10	0.06	3.15	0.12	3.25	0.17	0.0
Vaggelli-4-1 <sup>e</sup>	Santorini	Olivine	Basalt	140 × 120	3.20	0.05	3.02	0.12	3.15	0.17	0.0
Vaggelli-6-1 <sup>e</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>e</sup>	Santorini	Olivine	Andesite	130 × 80	3.30	0.10	3.33	0.13	3.10	0.19	0.5
S12-371-3 <sup>e</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>e</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>e</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