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Densification mechanisms of haplogranite glasses as a function of water content and pressure based on density and Raman data

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ABSTRACT

This study investigates the effect of pressure (1 atm – 2.5 GPa) and water (0.15, 2.7, 3.6 and 5.2 wt% H₂O) on the network structure of alkali-rich aluminosilicate glasses synthesized at 1000 °C. Density increases linearly with pressure in the water-poor composition, while in the water-rich glasses and above 1.5 GPa densification decreases with pressure. Raman data suggest that several structural changes follow one upon another with increasing pressure and water content. The almost dry glasses undergo large modifications of the network ring structure with pressure, namely a decrease in average T-O-T angle, change in ring size statistics and possibly an increasingly homogeneous distribution of Al- and Si-rich domains at high pressure. Water dissolution favors a homogenization of ring sizes at low pressures. Pressure essentially induces a decrease in the average intertetrahedral angle and, above 1.5 GPa, a possible redistribution of Al/Si-rich regions. Pressure induces an increase in O-H bonding but decreases the O-H bond strength. The observed structural modifications are consistent with the decreasing net effect of pressure on viscosity as temperature and water increase through variation of the activation volume of viscosity.

1. INTRODUCTION

The structural evolution of alkali and silica rich melts and glasses with pressure and dissolved total water contents (H₂O_T) is crucial for understanding the physical-chemical properties of silicic (rhyolitic, phonolitic or trachytic) magmas at crustal depths and, eventually, for modelling intrusive and eruptive processes. Considerable effort has been devoted to interpreting changes of bulk properties such as density and viscosity in Si-rich aluminosilicate melts in terms of short- and medium-range structural variations (Mysen et al., 1980a; Mysen and Virgo 1986; Matson et al.,

38 1986; Lange and Carmichael, 1987, 1989; Okuno et al, 1996; Zotov and Keppler, 1998; Zotov, 2003;
39 Allwardt et al., 2007). Pressure, temperature and dissolved water content play contrasting roles on
40 liquid structural rearrangement and physico-chemical properties. Density decreases with increasing
41 temperature and bulk water content due to thermal expansivity and to the large molar volume of
42 "water" (sum of hydroxyl OH and molecular water H₂O; Ochs and Lange, 1999; Richet et al., 2000).
43 In haplogranite melts, water has a major effect on melt and glass properties and its solubility is a
44 positive function of pressure, alkali ratio (Na/K) and, subordinately, of temperature (Holtz et al.,
45 1992; Acosta-Virgil et al., 2005; Ardia et al., 2008). Conversely, compression results in network
46 densification and a linear increase in bulk density (1 atm to 2 GPa, Kushiro, 1978; 2.6 to 5.3 GPa,
47 Suzuki et al., 2002). Similarly, the viscosity of silicic melts is drastically affected by temperature,
48 water-content and pressure (Shaw, 1963; Hess and Dingwell, 1996; Dingwell et al., 1996, Ardia et
49 al., 2008; Giordano et al., 2008a, del Gaudio and Behrens, 2009; Hui et al., 2009). At high
50 temperature, both the first compression applied to haplogranite melts and the first dissolution of H₂O
51 induces a stronger decrease in viscosity than subsequent increments (Kushiro, 1978; Behrens and
52 Schulze, 2003; Ardia et al., 2008). On the other hand, pressure increases the viscosity of hydrous
53 rhyolites at low temperatures (Hui et al., 2009). Structural models designed to interpret the effect of
54 pressure on the properties of alkali-bearing alumino-silicate melts must therefore explain the
55 simultaneous linear density increase and the non-linear evolution of viscosity with increasing
56 pressure at varying water content.

57 Kushiro (1978) interpreted the structural evolution of albitic and silica-rich melts with increasing
58 pressure by analogy to the structural changes observed in crystals. In this model, a gradual change of
59 Al-coordination from IV to VI is proposed at pressures below 1.0 GPa. Alternatively, Sharma et al.
60 (1979) suggested that the observed decrease in melt viscosity with pressure relates to ordering or
61 reorganization of the three-dimensional network. More specifically, Seifert et al. (1982) and Mysen
62 et al. (1983) proposed that the decrease in average T-O-T angles with pressure determines the
63 counterintuitive decrease in viscosity with increasing density. Hochella and Brown (1985)
64 summarized the investigations on albitic to jadeitic compositions and only report minor changes in
65 Raman spectra up to 4.0 GPa thus discarding the possibility that Al-coordination changes would be
66 responsible for the observed melt densification and viscosity changes. This has been further
67 confirmed by more recent Raman spectroscopy studies (Okuno et al., 1999; Reynard et al., 1999;
68 Shimoda et al., 2004; Champagnon et al., 2008), which investigate the effect of pressure on water-
69 poor natural obsidians and dry synthetic glass analogues (silica, anorthite and albite glass
70 compositions) between 1 atm and 25 GPa. Spectral analysis suggests that the densification process
71 operates through two main mechanisms, a decrease in the intertetrahedral angles (T-O-T), and a re-
72 organization of the connected rings forming the alumino-silicate network.

73 In this study, we investigate the effect of pressure on the structure of water-poor (H_2O_T : 0.15 wt%)
74 and water-rich (H_2O_T : 2.7-5.2 wt%) haplogranite glasses ($\text{Qz}_{36}\text{Ab}_{37}\text{Or}_{27}$) combining density
75 measurements and Raman spectroscopy on isobarically quenched glasses from 1000 °C at five
76 different pressures (0.5, 1.0, 1.5, 2.0 and 2.5 GPa). High pressure glasses are compared to a reference
77 water-poor glass relaxed at 1 atm. Because of similarities in composition, our vibrational data are
78 interpreted by comparison with the extensively investigated (Na,K)AlO₂-SiO₂ system (Mysen et al.,
79 1980a; Seifert et al., 1983) with special reference to silica (Champagnon et al., 1996; Okuno et al.,
80 1999; Champagnon et al., 2008) and albite composition glasses (Kushiro, 1978; Romano et al., 2001;
81 Suzuki et al., 2002; Behrens and Schulze, 2003; Poe et al., 2006) whose structure and physical
82 properties are known over a broad range of pressures and temperatures.
83 Quenching is presumed to freeze the densest configuration attained at high pressure and the water-
84 speciation ($\text{OH}/\text{H}_2\text{O}_m$ ratio) (Hui et al., 2008) at the glass transition (T_g), while the purely elastic part
85 of the deformation is eventually released during decompression. In glasses, it has been proposed that
86 water speciation does not depend on pressure (Richet et al., 2000). This conclusion has been recently
87 questioned for rhyolites by Hui et al. (2008), who observed a variation of water speciation with
88 quench pressure and employed the speciation to calculate viscosities at various pressures (Hui et al.,
89 2009). As we will show, our data suggest that densification involves a set of mechanisms, which
90 change with increasing pressure and water content and affect the molar volume of H₂O, at least at
91 pressures above 1.5 GPa.

92 93 **2. GLASS SYNTHESIS AND QUENCH CONDITIONS**

94 95 **2.1. Synthesis**

96
97 *HGG* haplogranite glasses ($\text{Na}_{0.56}\text{K}_{0.38}\text{Al}_{0.95}\text{Si}_{5.19}\text{O}_{12.2}$) are silica-rich ($\text{Si}/(\text{Si}+\text{Al}) = 0.85$) and slightly
98 peralkaline ($(\text{Na}+\text{K})/\text{Al} = 1.04$; $\text{Na}/\text{K} = 1.5$). The starting glasses with different water contents were
99 synthesized in a hot isostatic press (HIP) and one of those was dehydrated using a concentric
100 cylinder technique (Ardia et al., 2008). The resulting four compositions are from the same batches
101 used for viscosity measurements at high pressure and temperature (Ardia et al., 2008), for elasticity
102 measurements using Brillouin spectroscopy and for ²⁷Al NMR studies (Malfait et al., 2011, 2012).
103 Samples HGG0, HGG3, HGG4 and HGG5 correspond to haplogranite glasses with total dissolved
104 water contents of 0.15, 2.7, 3.6 and 5.2 wt%, respectively. Water contents of the bulk glasses were
105 determined by Karl-Fischer titration at ETH Zurich (KFT, Behrens and Stuke, 2003). Glass
106 homogeneity was confirmed by micro-FTIR and micro-Raman analyses in Paris (Di Muro et al.,
107 2006a) for water content, and with electron microprobe (JEOL JXA 8200) analyses of bulk

108 compositions at ETH Zurich (Ardia et al., 2008). The glass samples for spectroscopic investigation
109 were prepared in an end-loaded piston cylinder by melting the starting glasses from a previous
110 synthesis (Ardia et al., 2008) in Pt capsules at various pressures (0.5-2.5 GPa) and a constant
111 temperature of 1000 °C. Complete homogenization and relaxation were assured by keeping the melts
112 at run condition for 12 h for water-rich samples (HGG 3, 4, 5) and for 2 h for the nearly anhydrous
113 synthesis HGG0, because the synthesis using concentric cylinder already ensures homogenization
114 (Ardia et al., 2008). Samples were isobarically quenched by manually maintaining pressure.
115 Although small pressure drops cannot be excluded, they cannot be precisely evaluated and are
116 assumed to be similar for each run. The cooling rate of the end-loaded piston cylinder is 150-200
117 °C/s and is assumed to be constant for each experiment. Recovered glasses were optically examined
118 and minor quench crystallization was identified at the rims of some water-rich glasses close to the
119 glass-capsule interface. Thin glass chips were double side polished with parallel faces for micro-
120 Raman studies. Only crystal-free glassy areas not affected by cracks or bubbles were analyzed.

121

122 **2.2. Influence of pressure on glass transition temperature**

123

124 The glass transition (T_g) is a kinetic boundary between the mechanical response to an applied stress
125 of a liquid-like viscous and solid-like elastic material, and corresponds to the temperature of
126 quenching of the liquid structure upon cooling (Dingwell and Webb, 1990; Gottsmann et al., 2002).
127 The glass transition temperature is associated to specific viscosity values at fixed cooling rate, but is
128 compositional dependent (Morizet et al., 2007; Giordano et al., 2008b). The temperature interval
129 across the glass transition depends on composition, thermal history (cooling rate) and
130 experimentally, upon the timescale of the investigation method (Moynihan et al., 1976; Dingwell and
131 Webb, 1990; Moynihan, 1995; Giordano et al., 2005, 2008b). The structural relaxation depends on
132 processes affecting both the viscous and elastic components (Maxwell, 1867) and, as a consequence,
133 its mechanical and thermodynamic properties.

134 The glass transition depends on the cooling rate (q) applied to a system, and can be inferred from the
135 apparent equilibrium temperature (T_{ae}) for hydrous rhyolite melts using the relationship (Scherer,
136 1984; Stevenson et al., 1995; Toplis et al., 2001; Gottsmann et al., 2002; Sipp and Richet, 2002;
137 Zhang et al., 2003):

$$138 \quad \log \eta_{r_g} \approx \log \eta_{r_{ae}} = 11.45 - \log q \quad (1)$$

139 where η is the viscosity in Pa·s (Hui et al., 2009). Using a quench rate of $q = 150$ °/s we obtain a
140 viscosity of $10^{9.3}$ Pa·s. This viscosity is then used to recalculate T_{ae} applying available models for the
141 effect of pressure on the viscosity of rhyolitic liquids (Ardia et al., 2008 and Hui et al., 2009). The
142 model of Ardia et al. (2008) is derived from measured viscosities of $< 10^7$ Pa·s for hydrous and of $<$

143 10^8 Pa·s for low water content rhyolitic liquids. The model of Hui et al. (2009) applies to high
144 viscosities (10^{10} - 10^{12} Pa·s) but is not accurate at low water contents (< 0.80 wt% H_2O). The viscosity
145 corresponding to the glass transition of the HGG glasses ($10^{9.3}$ Pa·s) is intermediate between the
146 calibration ranges of both Ardia's (2008) and Hui's (2009) models. The temperature of freezing upon
147 constant cooling (quench temperature) (Table 1) calculated with the two models differ significantly
148 for high water contents. This discrepancy occurs because the Ardia et al. (2008) model predicts a
149 decrease in quenching temperature with pressure, following the trend derived from low water content
150 glasses, whereas the Hui et al. (2009) model suggests a modest increase in quench temperature with
151 pressure (Table 1). In this study, we retain the quench temperatures for the low water content glass as
152 predicted by Ardia et al. (2009) and for the high water content glasses as calculated from Hui et al.
153 (2009). For comparison, we have evaluated T_{ae} for a viscosity of $\eta=10^{12}$ Pa·s conventionally
154 assumed as the viscosity of the glass transition for dry glasses at 1 atm (Dingwell and Webb, 1990)
155 (Table 1). In summary, T_{ae} decreases with increasing pressure for nearly anhydrous compositions
156 (Ardia's model), whereas at increasing water contents T_{ae} increases with pressure (Hui's model). In
157 both models, T_{ae} decreases with water addition at a given pressure (Table 1).

158

159

3. METHODS

160

3.1 Density measurements

162

163 Density measurements were performed in a pyrex pycnometer by immersion of small glass chips of
164 cylindrical shape and ca. 1 mm diameter in a heavy liquid (Na-polytungstate solution). This method
165 requires a dilution of the solution with distilled water until neutral buoyancy of the immersed glass
166 chip is attained at room temperature. Care was taken to verify that no bubbles adhere to floating
167 glasses that could produce erroneous density measurements. The duration of the measurements
168 (minutes to tens of minutes) was optimized to prevent the evaporation of distilled water and to attain
169 neutral buoyancy. Density is then determined by calculating that of the diluted heavy liquid. The
170 accuracy of this method is estimated to ± 0.001 - 0.002 g/cm³ for 0.5 mg of sample (Popel et al.,
171 2011). Table 2 reports average errors (1σ standard deviation) of all measurements.

172

3.2 Raman spectroscopy

174

175 Raman spectra of HGG glasses (average of 3 full spectra for each glass) were obtained at room
176 conditions in confocal configuration using two micro-Raman apparatus: a LabRam HR 800
177 dispersive spectrometer (Jobin-Yvon®) at LADIR laboratory (UPMC Paris VI, France) and an inVia

178 Reflex dispersive spectrometer (Renishaw[®]) at Pierre-Süe laboratory (CEA, France). Non-polarized
179 spectra of all glass samples were acquired with the Renishaw system using a diode laser ($\lambda = 488.0$
180 nm) as excitation source. A sub-set of non-polarized and polarized spectra was collected with the
181 LabRam HR800 system using the 488.0 nm line of an argon ion laser. Both systems are equipped
182 with a Peltier-cooled multichannel CCD detector and a microscope that allows observation of the
183 sample, focusing of the laser beam at the surface of the sample, and collection of the Raman signal in
184 backscattering geometry. All spectra were collected using 1800 grooves/mm grating and edge filters
185 were used to suppress the dominant Rayleigh scattering. These conditions permitted to optimize the
186 intensity yield and provide the spatial resolution (ca. 1 μm) necessary to minimize the influence of
187 physical heterogeneities such as crystals, cracks, and bubbles. The LabRam setup provides a spectral
188 resolution of 0.6 $\text{cm}^{-1}/\text{pixel}$ in the 150-1400 cm^{-1} range due to the long focal length (800 mm)
189 whereas a resolution of 1.5 $\text{cm}^{-1}/\text{pixel}$ is achieved with the Renishaw spectrometer (250 mm focal).
190 The spectral resolution slightly decreases at higher frequencies (3000 - 3800 cm^{-1}) to 1.0 and 2.0 cm^{-1}
191 $^1/\text{pixel}$ for the LabRam and Renishaw systems, respectively. With the LabRam system, acquisition
192 times per spectrum at a power of 7.5 mW were 1000 s for the nearly anhydrous glasses and 250 s for
193 the water-rich glasses to avoid damage and instability of the sample. Measurements with the
194 Renishaw system were conducted using about 3 mW power at the sample surface and reduced
195 exposure times to 30 s for the high frequency domain (2800-4100 cm^{-1}) and to 40 s for the low
196 frequency domain (150-1400 cm^{-1}).

197

198 3.2.1. Data treatment

199

200 High resolution polarized spectra were collected to identify the main Raman features and to
201 accurately determine band positions and widths, and the depolarization ratios ($\rho_{dr}=I_{VH}/I_{VV}$). A
202 polarized band is associated with a totally symmetric vibration ($\rho_{dr}=0$), while a slightly asymmetric
203 vibration results in depolarized bands. Conversely, the analysis of non-polarized data allows
204 assessing and correlating the general evolution of spectra with the synthesis conditions of the
205 samples. Raw scattered intensities $I(\nu)(I_{obs}^{Stokes}$ in equation 2) in Raman spectra (Fig. 1a) are frequency-
206 and temperature-dependent, with the intensities of low-frequency bands being enhanced relative to
207 those at high-frequencies. Therefore the raw Raman intensities I_{obs}^{Stokes} were corrected to obtain the
208 reduced spectra I_{corr}^{Stokes} (Long, 1977; Brooker et al., 1988; McMillan and Wolf, 1995; Long, 2002)
209 that provide representative intensities for all vibrational modes (Fig1b). A linear baseline (Fig. 1a)
210 was first fitted to the high-frequency domain ($>1200 \text{ cm}^{-1}$) and subtracted from all spectra before
211 correcting them according to the relation:

$$I_{\text{cor}}^{\text{Stokes}} = I_{\text{obs}}^{\text{Stokes}} \cdot \nu^*{}^3 \cdot (1 - e^{-\frac{h\nu}{kT}}) \cdot \frac{\nu}{(\nu^* - \nu)^4} \quad (2)$$

212
 213 where $I_{\text{obs}}^{\text{Stokes}}$ is the measured intensity, ν^* the wavenumber of the incident laser light, ν the measured
 214 wavenumber, both in cm^{-1} , T temperature in K, c the speed of light (ms^{-1}) and k ($1.38 \cdot 10^{-23} \text{ JK}^{-1}$) and
 215 h ($6.63 \cdot 10^{-34} \text{ Js}$) the Boltzmann and Planck constants, respectively (Fig. 1b). In the analysis of the
 216 OH-stretching domain ($2900\text{-}4000 \text{ cm}^{-1}$), a cubic baseline was subtracted (Fig. 2) (Zajacz et al.,
 217 2005; Behrens et al., 2006; Di Muro et al., 2006a). All spectra were normalized to the intensity of the
 218 most intense observed band at ca. 490 cm^{-1} and smoothed using the Loess algorithm (3%) (Figs. 1c,
 219 2) before performing spectral deconvolution using the software PeakFit^(R). All intensities and
 220 intensity changes reported in the following are normalized intensities (N.I.).

221

222

4. RESULTS

223

4.1. Density

224

225
 226 Figure 3a reports the measured densities of HGG glasses (Table 2), compared with that of dry albitic
 227 glasses (Kushiro, 1978), and calculated densities of rhyolitic glasses following Withers and Behrens
 228 (1999). Densities increase linearly with quench pressure for the dry albitic and almost dry
 229 haplogranitic (HGG0) compositions, following parallel trends. The density of HGG0 is 1.4-2.5 %
 230 lower than that of dry albitic glass in the investigated pressure range. The densities of hydrous
 231 haplogranitic glasses also increase linearly with pressure up to 1.5 GPa for HGG3 and HGG4, and to
 232 1.0 GPa for HGG5, respectively. Above these pressures, density increase levels off.

233 Figure 3b shows the evolution of glass densities as a function of water content. Density decreases
 234 linearly with increasing dissolved H_2O at a given pressure, and with a rate that is similar over the
 235 whole explored pressure range. Withers and Behrens (1999) suggested that quench rate, together
 236 with water content, influence glass densities. In fact, lower densities in rhyolites are found for high
 237 quench rates ($>100 \text{ }^\circ/\text{s}$; at 0.3 GPa), while slower cooling (ca. $100\text{-}150 \text{ }^\circ/\text{min}$; at 0.5 GPa) results in
 238 slightly higher glass densities. Our density data on HGG glasses from 0.5 GPa are very close to those
 239 of Withers and Behrens (1999) for fast quenched rhyolites from 0.3 GPa, in agreement with the
 240 finding that fast quench glasses have lower densities. The almost constant difference between our
 241 glasses quenched at various pressures and the rhyolitic glasses obtained by slow cooling (Withers
 242 and Behrens, 1999) indicates that our glasses retained the effect at high pressure upon cooling.

243 Pressure increases the density of glasses with the exception of one hydrous glass of the HGG4 set,
 244 where the glass synthesized at 2.5 GPa has a lower density than that at 1.5 GPa (Fig. 3a). This

245 behavior may be related to partial crystallization and cracking upon quench and therefore the
246 spectroscopic properties of the HGG4/2.5 GPa sample will not be discussed further.

247

248 **4.2. Partial molar volumes of water**

249

250 Figure 4 and Table 3 show the calculated ambient molar volumes for HGG glasses synthesized at
251 various pressures, together with data for a set of albitic and rhyolitic compositions (Richet et al.,
252 2000). Molar volumes derived from high-pressure synthesis are up to 6.5 % lower than those derived
253 from low-pressure runs and are very similar for the albitic, most of the rhyolitic and HGG glasses
254 (Table 3). Only the rhyolitic glasses of Withers and Behrens (1999) have an opposite trend that
255 would result from the inverse relation of density as a function of synthesis pressure caused by
256 different quench rates. The linear variation of molar volume as a function of the molar fraction of
257 dissolved water (Fig. 4) indicates an almost constant partial molar volume of water ($V^*_{\text{H}_2\text{O}}$), within
258 experimental uncertainty (Table 3). This is in agreement with Richet et al. (2000) who reported a
259 constant $V^*_{\text{H}_2\text{O}}$ of $12.0 \pm 0.5 \text{ cm}^3/\text{mol}$ for albitic and rhyolitic compositions. In this study, a $V^*_{\text{H}_2\text{O}}$ of
260 $12.1 \pm 1.0 \text{ cm}^3/\text{mol}$ is obtained for pressures to 1.5 GPa, in agreement with Richet et al. (2000) (Fig.
261 4; Table 3). However, the $V^*_{\text{H}_2\text{O}}$ increases to $13.7 \pm 1.0 \text{ cm}^3/\text{mol}$ at 2.5 GPa and is associated with a
262 smoother increase in density at high pressure.

263

264 **4.3. Spectra analysis**

265

266 *4.3.1. Raman spectra general features and deconvolution strategy*

267

268 The unpolarized Raman raw spectra of HGG glasses display broad bands typical of amorphous
269 materials (Fig. 5). Three main envelopes can be identified in the low- ($150\text{-}650 \text{ cm}^{-1}$; LF intensity
270 envelope), intermediate- ($650\text{-}850 \text{ cm}^{-1}$; MF intensity envelope) and high- ($850\text{-}1250 \text{ cm}^{-1}$; HF
271 intensity envelope) frequency ranges, respectively. In the raw spectra of water-poor HGG0 glasses,
272 one narrow peak is observed at $490 \pm 5 \text{ cm}^{-1}$ (D1) superimposed on the major broad LF envelope
273 ($465 \pm 5 \text{ cm}^{-1}$) and an additional shoulder, which peaks at $600 \pm 5 \text{ cm}^{-1}$ (D2), is observed on the high
274 frequency part of the same envelope (Fig. 5a) (Pasquarello and Car, 1998; Ruiz et al., 2002, Thao To
275 et al., 2008). The water region $3000\text{-}3700 \text{ cm}^{-1}$ is characterized by a broad and asymmetric band in
276 all HGG glasses that is attributed to the stretching of OH units with variable degrees of hydrogen
277 bonding as will be discussed further (Behrens et al., 2006; Di Muro et al., 2006a) (Fig. 2).

278 Collected polarized spectra were used to guide the deconvolution of the HF envelope in unpolarized
279 spectra, in order to describe the spectral evolution with pressure and water increase. Inspection of

280 shoulders occurring in both parallel (VV) and perpendicular (VH) polarized spectra constrains the
281 adopted deconvolution strategy (Figs. 5, 6). Band positions, intensities and depolarization ratios were
282 obtained as follows: The polarized MF and HF envelopes of water-poor and water-rich glasses
283 quenched at low pressure were initially deconvoluted using 6 Gaussian bands, 5 bands corresponding
284 to the HF envelope (as Seifert et al., 1982; Mysen and Frantz, 1994), in addition to a band at 800 cm^{-1}
285 1 in the MF envelope taken as lower limit for the deconvolution. In a first step, all parameters were
286 free and unconstrained in the fitting of the polarized spectra. We observe that the resulting
287 frequencies of the deconvolution bands are very similar for water-poor and hydrous glasses.
288 Therefore, the HF envelope of the unpolarized spectra was deconvoluted by maintaining
289 deconvolution band position and width/intensity-ratio constant, only allowing for variation in the
290 band relative intensity (Fig. 6). This strategy was chosen to minimize the error associated with
291 deconvolution and to simplify comparison among spectra obtained at variable pressures and water
292 contents (Fig. 6).

293 Deconvolution demonstrates that the main LF envelope and the D1 and D2 bands are highly
294 polarized, whereas the band at 800 cm^{-1} in the MF spectral range is almost depolarized ($\rho_{dr}= 0.30-$
295 0.18 ; Table 3). The HF intensity envelope has a variable degree of polarization that evolves with
296 frequency and water content (Table 4). In the water-poor HGG0 glass, the high wavenumber region
297 of the HF envelope ($>1100\text{ cm}^{-1}$) is highly polarized ($\rho_{dr}=0.08$; Table 4), whereas the low
298 wavenumber region is only weakly polarized ($\rho_{dr}=0.15-0.23$) (Fig. 5a; Table 4). In the low
299 wavenumber tail of the HF envelope, the slightly polarized deconvolution band centered at about 905
300 $\pm 10\text{ cm}^{-1}$ ($\rho_{dr}=0.15$; Table 4) is barely visible in the VV spectrum of water-poor glass but its
301 intensity increases with water content (Fig. 5b). Depolarization ratios of deconvolution bands at 800
302 cm^{-1} and 905 cm^{-1} are similar in HGG0 and HGG3 glasses, but become 2-4 times higher for the other
303 bands with increasing water contents. In HGG3, the high-wavenumber side becomes faintly
304 polarized ($\rho_{dr}= 0.20-0.17$; Table 4), while the low-wavenumber side is depolarized ($\rho_{dr}=0.55-0.20$;
305 Table 4). With increasing water contents, the peak position of the LF envelope shifts from 465 to 490
306 $\pm 5\text{ cm}^{-1}$ and merges with the D1 peak, while the D2 peak decreases in intensity (Fig. 5b). The
307 observed evolution of the LF envelope could be produced by i) a decrease in D1 intensity and
308 concomitant positive shift of the LF envelope or ii) a pronounced increase in D1 intensity with
309 respect to the low frequency side of the main band. The LF envelope was not deconvoluted and only
310 the evolution of the frequency, intensity and width of the experimental features will be described.

311

312 *4.3.2. Raman band assignments*

313

314 The structure of natural and synthetic aluminosilicate glasses can be schematically described as a
315 statistical distribution of interconnected n-fold rings. For instance, the structures of remelted rhyolitic
316 (Zotov et al. 1992) and alkali feldspar glasses (Taylor and Brown, 1979; Seifert et al., 1981, Seifert
317 et al., 1982), whose composition is close to that of our glasses, is dominated by interconnected 6-
318 membered rings. The sharp D1 and D2 defect bands observed in vitreous silica have been attributed
319 to embedded populations of highly localized (*i.e.*, non-propagating) vibrational modes of regular
320 rings with 3 and 4 members, respectively (Pasquarello and Car, 1998; Ruiz et al., 2002). Thao To et
321 al. (2008) later attributed D1 to 3- and 4-membered rings and D2 to 3-membered rings.

322 In the Raman spectra of HGG glasses, the main and broad asymmetric LF envelope ($150\text{-}650\text{ cm}^{-1}$) is
323 ascribed to delocalized vibrations of the aluminosilicate network that involve the displacement of
324 bridging oxygen in intertetrahedral T-O-T linkages (McMillan et al., 1982). Specifically, the
325 vibrations have been described either as symmetric oxygen stretching of the bent T-O-T linkages,
326 with oxygen motion perpendicular to the T-T line, or as symmetric O-T-O angular deformation of
327 the coupled TO_4 groups (Galeener and Geissberger, 1983; Sharma et al., 1984; McMillan and Hess,
328 1990; Ruiz et al., 2002). Spectral composition and width of the LF envelope are thus sensitive to
329 both the average T-O-T intertetrahedral angle and the ring distribution statistics (Ruiz et al., 2002). A
330 decrease in the average T-O-T bond angle and a change in ring statistics both concur in shifting to
331 higher frequency and narrowing the LF envelope. Significant increase in the proportion of 4-
332 membered rings at the expense of the largest ones is also a viable mechanism to produce the
333 observed spectral evolution. With increasing depolymerization of the glass network, the observed LF
334 envelope is expected to decrease in intensity relative to the HF envelope and to shift to higher
335 frequency irrespective of the network modifying cations (Matson et al., 1983). In both synthetic and
336 natural glasses, the LF/HF intensity ratio exponentially decreases with increasing glass
337 depolymerization and increases with total dissolved water content (Mysen et al., 1980b; Di Muro et
338 al., 2006b; 2009, Mercier et al., 2009).

339 The low intensity MF envelope ($650\text{-}850\text{ cm}^{-1}$) is attributed to the Si-O stretching mode
340 (Kalampounias, et al., 2006) with a dominant Si motion (Matson et al., 1983), its intensity correlating
341 with silica content (Seifert et al., 1982). The main feature of the envelope at 800 cm^{-1} contains two
342 bands and was initially assigned to the TO-LO splitting, similarly to that observed in crystalline
343 phases and glassy SiO_2 (Galeener, 1979), but later studies have challenged this interpretation
344 (Galeener and Geissberger, 1983; McMillan et al. 1994). Kalampounias et al. (2006) described the
345 network structure of potassium tetrasilicate glass/melt as a combination of tetrahedral units arranged
346 in open (cristobalite-like at 790 cm^{-1}) and cluster (supertetrahedra at 830 cm^{-1}) substructures. As this
347 feature appears insensitive to changes in pressure and water content (e.g., Fig.7), its behavior will not
348 be discussed further and we will refer to it uniquely as a feature for the sake of clarity.

349 Conversely, the HF envelope provides information about the covalently bonded units, in Si-rich
350 glasses, in terms of Q^n species, with n being the number of bridging oxygen: Q^4 at 1190 cm^{-1} , Q^3 at
351 1130 cm^{-1} , the band at 1045 cm^{-1} that may reflect the amount of Bridging Oxigens in the structure
352 (BO; Mysen et al., 1980a), and Q^2 at 970 cm^{-1} . The assignment of the 900 cm^{-1} band is still debated
353 (see discussion). In this frequency range, there are no Raman bands attributed to the vibration of
354 network-modifying or charge-balancing cations in silica or alumino-silicate glasses. The specific
355 effect of substituting Al for Si on the HF envelope is discussed in the section 5.1. The assignment of
356 Raman bands proposed here is based on the close resemblance of HGG spectra (Figs. 1, 5, 6) with
357 those of glasses and melts along the (Na,K)AlO₂-SiO₂ join, especially albitic glasses and the silica-
358 rich glass AS50 (Seifert et al., 1982; Mysen et al., 1982; McMillan, 1984; Mysen, 1988; McMillan
359 and Wolf, 1995; Poe et al., 2001; Shimoda et al., 2004).

360 The HGG0 glass was dehydrated and relaxed at 1 atm, but residual amounts of water are still
361 observed in the high frequency domain of the Raman spectra. In this glass, a Raman band attributed
362 to OH units peaks at $3506 \pm 10\text{ cm}^{-1}$ and has an asymmetric negative skewed shape with a shoulder
363 at $3740 \pm 10\text{ cm}^{-1}$ (Fig. 7). Di Muro et al. (2006a) interpreted this polymodality as evidence of the
364 presence of multiple OH sites with variable H-bonding. According to this interpretation the main
365 shoulder is attributed to H-bonded OH units (Aines and Rossman, 1984; Mysen and Virgo, 1986),
366 while the 3740 cm^{-1} shoulder can be ascribed to vibrations of “free” OH units (Di Muro et al., 2006a;
367 Le Losq et al., 2013). or weakly H-bonded hydroxyl species, a feature that has been reported only in
368 glasses with very low water contents (Di Muro et al., 2006a). In the hydrous glasses, an asymmetric
369 high frequency envelope peaks at ca. 3575 cm^{-1} (Fig. 2). The shape and the spectral distribution of
370 this broad envelope vary with the total dissolved water content and with the composition and
371 structure of the glass (Mysen and Virgo, 1986; Di Muro et al., 2006a). The broad envelope does not
372 allow a unique frequency identification for each species. Nevertheless, it is widely recognized that
373 the lowest frequency features of the envelope ($3300\text{-}3550\text{ cm}^{-1}$) reflects the molecular water
374 vibrations, whereas the higher frequency part ($>3550\text{ cm}^{-1}$) is related to the hydroxyl OH vibrations
375 (Aines and Rossman, 1984; Mysen and Virgo, 1986). No tail is observed at the higher frequency side
376 corresponding to the weakly free OH unit observed in natural glasses with less than 1 wt% dissolved
377 water (Muro et al., 2006a).

378

379 **4.4. Effect of pressure on water-poor glasses (HGG0)**

380

381 The previous description of the spectral features of the water poor glass (HGG0) synthesized at 1 atm
382 also applies to higher pressure syntheses (Fig. 7). The LF main envelope evolves with pressure,
383 whereas changes in the MF and HF envelopes are less prominent. The LF intensity envelope

384 becomes progressively narrower and peaks at higher frequencies with increasing pressure (Fig. 7;
385 Table 5). The FWHM* of the LF envelope was obtained as the width at half of the maximum height,
386 without any specific deconvolution of the envelope (Fig. 8). The width of the LF envelope remains
387 almost constant for the first pressure increment from 1 atm to 0.5 GPa but decreases by about 14%
388 between 0.5 and 2.0 GPa, levelling off in the last pressure step to 2.5 GPa (Fig. 8). The experimental
389 frequencies of the LF and HF envelopes (not deconvoluted) for all investigated compositions are
390 reported as a function of pressure in Figure 9. The experimental frequency of the main envelope LF
391 increases with pressure by $32 \pm 5 \text{ cm}^{-1}$ in our pressure range (1 atm to 2.5 GPa, Fig. 9a; Table 5). The
392 D1 defect band becomes embedded in the LF envelope at pressures higher than 2.0 GPa and then
393 cannot be unambiguously resolved from the main feature of the LF envelope (Fig. 7). In the pressure
394 range lower than 2.0 GPa, the frequency of the D1 defect band remains constant (Fig. 9a). In all
395 spectra, the D2 defect band remains visible as a shoulder whose intensity (normalized to that of the
396 LF band) decreases slightly (ca. 10%) with pressure.

397 The experimental frequency of the main feature of the MF envelope remains almost constant at $800 \pm$
398 10 cm^{-1} . Its normalized intensity is constant up to 1.0 GPa but drops by 14% and then remains
399 constant with further pressure increase (Fig. 7). Also the experimental frequency of the main feature
400 of the HF envelope remains mostly constant at $1132 \pm 3 \text{ cm}^{-1}$ (Fig. 9d; Table 5). The only exception
401 is for the glass synthesized at 0.5 GPa, in which the main feature of the HF envelope is located at
402 slightly higher frequency (+1 %). The normalized intensity of this feature decreases linearly with
403 pressure by about 15 % from 1 atm to 2.5 GPa (Fig. 9e). The spectral evolution of the HF envelope,
404 deconvoluted as illustrated in Figure 6, shows that nearly anhydrous glasses have, within error,
405 constant deconvoluted band areas up to 1.0 GPa (Fig. 10a). For the same composition, higher
406 pressures decrease the deconvoluted area of the high frequency band at 1190 cm^{-1} but increase that of
407 the 970 cm^{-1} band (Fig. 10a).

408

409 **4.5. Effect of water at a constant pressure of 0.5 GPa**

410

411 The spectra of HGG glasses with various water contents quenched at 0.5 GPa are compared in Fig.
412 11. This comparison is made initially for the low pressure range to discuss the effect of hydration
413 separately from that of pressure. The effect of water depends on the frequency range considered. The
414 main change in the spectra upon hydration is the appearance of a strong deconvolution band visible
415 near 900 cm^{-1} (Fig. 6) that progressively increases in intensity with water content, although its
416 experimental frequency remains constant within errors (Figs. 9c; 11). In addition, water dissolution
417 results in a 6-12 % narrower (Fig. 8) and positively shifted (from 469 ± 5 to $485 \pm 5 \text{ cm}^{-1}$) LF
418 envelope compared to the HGG0 glass (Fig. 9a; Table 5) and in a decrease of the normalized

419 intensity of the HF envelope (Fig. 9e; Table 5) whereas the MF envelope remains unaffected. In all
420 hydrous glasses, the position of the LF envelope is positively shifted by about $20 \pm 4 \text{ cm}^{-1}$ by the first
421 water addition compared to HGG0, but then remains constant with further water addition (Fig. 9a;
422 Table 5). The narrow defect band D1 cannot be resolved from the broad LF envelope of the water-
423 rich glasses (Fig. 9a). The position of the HF envelope does not change significantly with increasing
424 water content compared to the anhydrous samples (HGG0) while its normalized intensity decreases
425 with initial addition of water, and remains almost constant at high water contents (Fig. 9e).

426

427 **4.6. Combined effect of water and pressure**

428

429 In comparison with HGG0 glasses, the spectra of hydrous glass sets (HGG3 - HGG5) display only
430 minor changes with increasing pressure in the spectral features of the LF and MF envelopes but
431 differences are more noticeable for the HF envelope (Fig. 12). In the HGG3 and HGG4 glass sets,
432 increasing pressure narrows the LF envelope (see the evolution of FHMW in Fig. 8). In hydrous
433 glasses, the weak D2 band decreases slightly (10% or less) in intensity, showing the most
434 pronounced decrease with the first pressure increment from 0.5 to 1.0 GPa (Fig. 12). At 2.0 GPa, the
435 frequency of the main feature of the LF envelope is similar in both water poor (HGG0) and water-
436 rich glasses (Fig. 9a). The MF envelope remains at a constant position of $800 \pm 10 \text{ cm}^{-1}$ in the spectra
437 of all hydrous glass (Figs. 7, 12).

438 In all series of hydrous glasses, the frequency of the peak observed in the HF envelope at ca. 1130
439 cm^{-1} displays a negative frequency shift with increasing pressure to 2.5 GPa (Fig. 12) that varies
440 from $17 \pm 10 \text{ cm}^{-1}$ for the HGG3 series to 6 and $17 \pm 10 \text{ cm}^{-1}$ for the HGG4 and HGG5 glass sets,
441 respectively (Figs. 9d, 12). In HGG3 glasses, the normalized intensity of the HF envelope decreases
442 with increasing pressure from 1 atm to 1.5 GPa and from 2.0 to 2.5 GPa, displaying a similar
443 behavior as the HGG0 set (Fig. 9e). Between 1.5 and 2.0 GPa an increase in the normalized
444 intensities, which is directly related to the positive shift of the band, is observed. A continuous
445 negative linear shift is observed only at $P > 1.0 \text{ GPa}$ in the HGG4 and HGG5 sets (Fig. 9e; Table 5).

446 Close inspection of the spectral evolution of the HF envelope prior to deconvolution reveals that the
447 evolution of the spectra with pressure is not continuous and that distinct processes occur below and
448 above 1.5 GPa, as already described for the water poor HGG0 set. The intensity of the slightly
449 polarized deconvolution band near 900 cm^{-1} shows a positive correlation with total dissolved water
450 content as reported by Sharma et al. (1997). In our HGG glasses the evolution of the 900 cm^{-1} band
451 intensity with pressure changes at 1.5 GPa, in particular for the lower water content glasses (*i.e.*,
452 HGG3, Fig. 9c). At $P > 1.5 \text{ GPa}$, a decrease in intensity with pressure is observed in the HGG3 and
453 HGG4 sets, while HGG5 intensities remain constant. Irrespective of the pressure dependence, the

454 900 cm^{-1} band is always most intense in the set with the highest water content. The spectral evolution
455 of the HF envelope, indicated by the variation of the deconvolution band at 1045 cm^{-1} (Fig. 10b),
456 shows small variations with pressure only above 1.0 GPa, suggesting that structural changes related
457 to NBO-bonding only occur above this pressure threshold. Nearly anhydrous glasses display, within
458 error, constant deconvoluted band areas to 1.0 GPa (Fig. 10a). Higher pressures decrease the area of
459 the high frequency 1190 cm^{-1} deconvolution band but increase that of the 970 cm^{-1} deconvolution
460 band (Fig. 10a). The HF envelope for the HGG3 glass displays a similar evolution with pressure, but
461 variations are within experimental errors. The glasses with higher water contents (HGG4 and HGG5)
462 show smaller variations with pressure that become apparent only above 1.5 GPa.

463

464 **4.7. Effect of pressure on OH stretching bands**

465

466 In the high-frequency range (3000-4000 cm^{-1}), HGG Raman spectra show a broad and asymmetric
467 envelope. As in spectra of both natural and synthetic glasses and melts, the intensity (relative to the
468 low-frequency envelopes) of this band envelope correlates positively with the total dissolved water
469 content (Di Muro et al., 2006). The bands convoluted to form this intensity envelope are assigned to
470 OH stretching vibrations in molecular water (H_2O_m) and hydroxyl groups (OH).

471 All investigated glass series display a shift of the envelope observed in the water stretching region
472 towards lower frequencies with increasing pressure. This shift increases with the amount of dissolved
473 water in the structure (Table 5, Fig. 7; 12). In the nearly anhydrous glasses, the envelope attributed to
474 OH stretching exhibits two peaks, the most intense at 3506 cm^{-1} and a second one at 3740 cm^{-1} . The
475 main shoulder shifts rapidly to $3447 \pm 10 \text{ cm}^{-1}$ as pressure increases from 1 atm to 0.5 GPa, then the
476 shift rate with pressure decreases and at 2.5 GPa this band locates at $3424 \pm 5 \text{ cm}^{-1}$. The less intense
477 shoulder shifts to $3635 \pm 10 \text{ cm}^{-1}$ at 0.5 GPa and is not further affected by the additional pressure
478 increase. We note that the shape of the water envelope is strongly modified by further dissolution of
479 water into the structure. In our hydrous glasses (HGG3 – HGG 5), stretching vibrations of OH
480 (hydroxyl) and H_2O_m (molecular water) are represented by a single and broad asymmetrical band at
481 ca. 3570 cm^{-1} . In the HGG3 glass set (2.7 wt% H_2O), the frequency of the "total water" (OH+ H_2O_m)
482 Raman band is independent of pressure whereas in glasses with higher water contents, we observe a
483 slightly negative shift of the band by about 10 cm^{-1} and 17 cm^{-1} for the HGG4 (3.63 wt% H_2O) and
484 HGG5 (5.24 wt% H_2O) glass sets as pressure increases from 0.5 to 2.5 GPa (Table 5, Fig. 12). In the
485 water-rich glasses HGG4 and HGG5, the rate of shift with pressures increases above 1.5 GPa.

486

487

488

5. DISCUSSION

489 5.1. Dry Haplogranite glass structure

490

491 Melts and glasses along the (Na,K)AlO₂-SiO₂ join consist of a three-dimensional array of
492 interconnected silica and alumina tetrahedra where alkalis fully charge-balance the Al³⁺ cations
493 substituting for Si⁴⁺ in 4-fold coordination (Mysen, 1988). Although the presence of non-bridging
494 oxygens in our HGG compositions cannot be ruled out following previous studies on highly
495 polymerized anhydrous alkali- and alkaline-earth aluminosilicate glasses and liquids (e.g., Toplis et
496 al., 1997; Mysen and Toplis, 2007; Neuville et al., 2008), NMR studies performed on the HGG
497 samples show that high coordinated Al remains below detection limit (1-2%), suggesting that NBOs
498 are minor species on our samples (Malfait et al., 2012).

499 Two main groups of structural models have been proposed in the literature for (Na,K)AlO₂-SiO₂
500 glasses and are summarized here:

501 *Type 1 models (“two-unit models”)*: the Raman spectrum of SiO₂ glass displays two depolarized
502 bands at 1060 cm⁻¹ (band A) and 1190 cm⁻¹ (band B) that have been attributed to the stretch of Si-O°
503 bonds in two units with different intertetrahedral angles in the three-dimensional network (Mysen et
504 al., 1980a; Seifert et al., 1982). In this model, band A is associated with the small-angle unit and band
505 B with the large-angle unit. Following Mysen et al. (1980a), the A and B depolarized bands are
506 retained in the spectra of (Na,K)AlO₂-SiO₂ glasses and their position shifts toward lower frequencies
507 with increasing temperature and Al/(Al+Si) ratio due to the elongation and weakening of T-O bonds
508 upon substitution of Si by Al. The A and B bands correspond to vibrations of two distinct three-
509 dimensional units with the B band being associated to the unit with higher Al/(Al+Si) ratio whose
510 intensity is predicted to increase with pressure. Mysen et al. (1982) further extended this model by
511 defining four deconvolution bands in the HF intensity envelope of glasses along the NaAlO₂-SiO₂,
512 CaAl₂O₄-SiO₂, and MgAl₂O₄-SiO₂ joins. These four bands are centered at 1009 cm⁻¹, 1066 cm⁻¹,
513 1127 cm⁻¹ and 1190 cm⁻¹, respectively, in the spectrum of AS50 glass (Mysen et al., 1982; Seifert et
514 al., 1982) similar in composition to HGG0. In situ studies along the NaAlSiO₂-SiO₂ join (Neuville
515 and Mysen, 1996) have shown that the 1190/1127 intensity ratio increases with temperature but
516 decreases with pressure (Mysen et al., 1983). The 1190 cm⁻¹ band should correspond to “expanded”
517 Al-Si rings (“unit I”) with large inter-tetrahedral angle, while the 1127 cm⁻¹ band is interpreted as the
518 vibration of “dense” Al-Si rings (“unit II”) with small inter-tetrahedral angle.

519 Several observations indicate that this model cannot be fully applied to our haplogranite glasses: For
520 instance, the 1190 and 1127 cm⁻¹ bands are polarized in the almost dry HGG0 glasses but only
521 moderately polarized in our hydrous glasses (Fig. 5; Tab. 4). The 1190 cm⁻¹ band intensity decreases
522 with pressure as predicted by the above model. Nevertheless, this decrease occurs only above a

523 threshold pressure of 0.5-1.0 GPa. Most important, a linear increase of the 1127 cm⁻¹ band intensity
524 with pressure is not observed for deconvoluted spectra, except perhaps in the HGG3 set (Fig. 10).
525 *Type 2 models (“one-unit models”)*: In Al-bearing fully polymerized glasses, variably polarized
526 deconvolution bands in the HF envelope are attributed to vibrations in rings (*i.e.* 6-membered rings
527 in albite glass) whose frequency decrease with increasing Al/(Al+Si) ratio (McMillan et al., 1982;
528 Sharma et al., 1997). In HGG, the polarization of the bands at 1190 cm⁻¹ and 1140 cm⁻¹ indicate that
529 they correspond to symmetric stretching vibrations of Q⁴(Si) and Q⁴(1Al) units, respectively (Qⁿ:
530 TO₄ units with T = Al, Si; *n*: number of bridging oxygens; the number in parenthesis indicates the
531 number of oxygens Si tetrahedra share with Al tetrahedra). The depolarized nature of the bands at
532 1045 cm⁻¹ and 970 cm⁻¹ (Fig. 5; Table 4) indicates that they originate from anti-symmetric stretching
533 vibrations of Q⁴(2Al) and Q⁴(0Al)=Q⁴(Si) units, respectively (McMillan et al., 1992; Neuville and
534 Mysen, 1996; Mysen, 1999). Furthermore, stretching vibrations of Qⁿ species result in strongly
535 polarized bands at 950 (Q² units) and 1100 cm⁻¹ (Q³ units) (McMillan et al., 1992; Mysen and Frantz,
536 1993). The band at 1045 cm⁻¹ has also been correlated with increasing amounts of NBO (McMillan
537 and Wolf, 1995) and considered a doublet of Q² (Mysen, 1988; Malfait et al., 2008). These three
538 highly polarized bands are not observed in the HGG glasses, suggesting that alkalis already fully
539 balance the 4-fold coordinated Al and that increasing amounts of dissolved H do not create additional
540 NBOs (Fig. 10). Hence, on the basis of the high frequency bands measured in HGG glasses, *model 2*
541 is retained for the interpretation of the HGG glass structures presented below.

542

543 **5.2. Evolution of haplogranite glass structure with pressure**

544

545 On the basis of the above structural model, the spectroscopic observations and density data of the
546 HGG glasses are interpreted in terms of 1) ring statistics (the relative proportions of inter-connected
547 *n*-membered Al-Si rings) and average T-O-T intertetrahedral angle of each ring population, 2) Al/Si
548 ratios in different units and 3) water speciation and hydrogen-bond strength.

549

550 *5.2.1. Ring statistics and ring sizes*

551

552 Upon compression, the T-O-T angle decreases and hence could lead to a modification of the ring
553 statistics (Ruiz et al., 2002). Moreover, pressure can affect the intertetrahedral T-O-T angle by
554 modifying the Al/Si ratio of a given ring population. These effects are not easily discriminated by

555 Raman spectroscopy. However, an evolution of ring statistics with increasing pressure and water
556 content is suggested by the topological evolution of the LF envelope, as detailed below.

557 In the water-poor HGG0 glasses, increasing pressure progressively decreases the intensity of the D2
558 shoulder. This spectral evolution likely reflects a relative decrease in abundance of the smallest (3-
559 membered) rings (Pasquarello and Car, 1998; Ruiz et al., 2002, Thao To et al., 2008). As previously
560 stated, the observed frequency increase in the peak of the LF envelope may result either from i) a
561 positive shift of its low frequency (465 cm^{-1}) side, associated or not with a decrease in D1 intensity,
562 or ii) from a decrease in intensity of the 450 cm^{-1} region and a significant and concomitant increase
563 in the intensity of the D1 band. The D1 feature correlates with the presence of both 3- and 4-
564 membered rings (Thao To et al., 2008). The decrease in the proportion of 3-membered rings, as
565 suggested by the evolution of the D2 band, should correlate with a decrease in D1 intensity, unless a
566 significant proportion of 4-membered rings is created at the expense of larger rings ($n>4$).

567 The Raman data do not allow clarifying whether the change in the proportion of small ring
568 populations is preceded by deformation of their internal angles. The almost constant frequencies of
569 both D1 and D2 bands observed in our water-poor glasses suggest an absence of deformation upon
570 pressurization to 2.5 GPa (Figs. 7, 9a). Average internal angles of $\sim 136^\circ$ and 128° for the small rings
571 were calculated from our data considering the position of the LF envelope following the model of
572 Ruiz et al. (2002). The negligible pressure-induced shift of the D1 (up to 2.0 GPa) and D2 bands (up
573 to 2.5 GPa) contrasts with the average shift of $5.2\text{ cm}^{-1}/\text{GPa}$ and $1.5\text{ cm}^{-1}/\text{GPa}$ reported for these
574 bands in the *in situ* high pressure Raman study of SiO_2 glasses by Champagnon et al. (2008).
575 Possibly, the progressive overlap of the D1 band and a positive shift of the 465 cm^{-1} band with
576 pressure masks the expected positive shift of the D1 band in our HGG spectra. This observation may
577 lend support to the hypothesis that the 465 cm^{-1} band moves to higher frequency with pressure.
578 Alternatively, the constant frequency may arise either from i) the very low compressibility of the
579 smaller rings, ii) from Al-Si substitution in 3- and 4-membered rings counterbalancing the net
580 pressure effect or iii) from a partial relaxation of the internal angle of small 3-4 membered rings upon
581 glass decompression during quench. Available data do not permit to discriminate between these
582 processes, even if we suspect that the poor compressibility of the small rings may play a dominant
583 role. A possible partial relaxation upon decompression should produce a broadening of the LF
584 envelope as significant changes in Al coordination with increasing pressure have been ruled out by
585 NMR analysis of the same samples (Malfait et al., 2012).

586 In the water-poor HGG0 glasses, the peak of the LF envelope shifts with pressure from 461 to 490
587 cm^{-1} (Figs. 7, 9a), i.e. $13 \pm 3\text{ cm}^{-1}/\text{GPa}$. This rate of shift is actually in good agreement with the 10.4
588 $\pm 0.8\text{ cm}^{-1}/\text{GPa}$ reported by Champagnon et al. (2008) for silica. We propose that this frequency
589 change records both the narrowing of the average T-O-T angle and a re-distribution of ring

590 populations, because of the decrease in relative proportion of the smallest rings ($n=3$). Both
591 processes concur with the linear increase of density with pressure (Lipinska-Kalita et al., 2005).

592 In hydrous glasses, a slight negative shift of the LF envelope would be expected when the proportion
593 of small-sized rings decreases with pressure ($n = 3, 4$). This shift cannot be resolved in our dataset.
594 Alternatively, both the populations of very large rings ($n > 6$) and small rings ($n= 3, 4$) are affected
595 resulting in the almost constant position of the peak of the LF envelope of the hydrous glasses. The
596 latter would be supported by the shrinkage of the main LF envelope with pressure in all glass sets,
597 suggesting that the width of the T-O-T angle distribution becomes narrower (Fig. 8). We propose that
598 the disappearance of the large values in the angle distribution indicates a decrease in relative
599 abundance of the largest rings ($n>4$) and is an important process of glass densification, independently
600 of water content. In fact, the shrinkage of the LF envelope parallels the evolution of the bulk glass
601 density with pressure. The specific evolution of 4-membered rings (increase at the expense of large
602 rings or decrease, like the 3-membered rings) cannot be definitively resolved with the available data
603 and requires further investigation.

604

605 *5.2.2. Units with variable Al/Si ratio*

606

607 In the water-poor HGG0 glasses, the HF envelope exhibits only minor changes with increasing
608 pressure (Fig.7) while larger spectral changes and significant negative shifts occur in the hydrous
609 glass sets (Figs.11, 12). These correspond to a relative decrease in intensity of the $\sim 1190\text{ cm}^{-1}$
610 deconvolution band and a concomitant increase in the relative intensity of the 970 cm^{-1}
611 deconvolution band for the intermediate water contents (e.g. HGG3, HGG4; Figs. 7, 10a, 13) at 0.5
612 GPa. As argued above, it can be excluded that these changes correspond to a decrease in the
613 abundance of polymerized Q^4 units and a concomitant increase in depolymerized Q^2 units. Water
614 addition may cause disorganization in the Si-Al rich domains without necessarily decreasing the
615 degree of polymerization (Zotov et al., 1992). The variations observed in our hydrous glasses upon
616 pressure increase could be interpreted as a reorganization or increase in order of the Si-Al domains in
617 a given unit (Kohn et al., 1992). Accordingly, the observed small negative shift of the HF envelope
618 (Fig. 9d) should mostly relate to an intensity decrease of its high frequency (1190 cm^{-1}) and an
619 intensity increase of its low frequency component (970 cm^{-1}). The negative shift could also stem
620 from a decrease of the average T-O-T angle and a consequent elongation and weakening of the T-O
621 bonds (Lee et al., 2006) but none of this was observed in the LF envelope.

622

623 *5.2.3. Water dissolution*

624

625 Different mechanisms have been proposed for the incorporation of water in the silicate network. In
626 depolymerized systems, water disrupts the T-O-T bonds and forms T-OH bonds (Xue and Kanzaki,
627 2008; Malfait et al. 2009). In polymerized systems, water dissolution mechanisms could occur *via* 1)
628 rupture of the T-O-T bonds followed by the formation of Si-OH and minor Al-OH units, leading to a
629 bulk network depolymerization (Xue and Kanzaki, 2008; Malfait et al. 2009); 2) bridging to alkalis
630 and formation of M-OH bonding with M = Na, K, Ca or Mg (Kohn et al., 1989; 1992; Xue and
631 Kanzaki, 2008); or 3) by formation of H_3O^+ that distorts the structure of the silicate (Sharma et al.,
632 1996; 1997). In the water-rich HGG glasses, the D1 band cannot be resolved and the D2 band is
633 much less intense with respect to the water-poor HGG0 glasses (Fig. 7). This observation may
634 suggest that water dissolution destabilizes the small-sized rings ($n=3$). In all hydrous glasses, the LF
635 feature envelope is located at higher but constant frequency (480 cm^{-1} , Fig.9a) with respect to the
636 almost dry HGG0 glasses at 1 atm - 0.5 GPa ($460\text{-}470\text{ cm}^{-1}$). This suggests a smaller average T-O-T
637 angle in hydrous glasses that correlates with the smaller $d\rho/dP$ at $P > 1.5\text{ GPa}$ compared to their
638 nearly anhydrous counterpart (Fig. 3a). Water dissolution clearly affects the distribution of T-O-T
639 angles. We propose that both compression of internal angles and the modification of ring statistics
640 concur in the frequency increase of the LF envelope. If our interpretation is correct, water dissolution
641 has a similar role as pressure increase by favoring the decrease in the population of very large (higher
642 than 6-membered) and very small (3-membered) ring types.

643

644 5.2.4 Hydrogen bonding strength

645

646 Spectroscopic data summarized above (*Type 2 model*) do not show conclusive evidence for an
647 increase in the proportion of NBOs in highly polymerized systems such as HGG haplogranites upon
648 water dissolution, as the addition of alkalis does (Kohn et al., 1989; Zotov et al., 1992). This
649 interpretation is consistent with the absence of a positive shift of the LF envelope in our hydrous
650 glasses (to be expected for the addition of alkalis as shown by Di Muro et al. (2006a)), and with the
651 absence of an increase in the intensity of deconvolution bands that could be related to Q^3 units in the
652 HF envelope with increasing water contents.

653 In our model proposed for the HGG glasses, water dissolves as i) molecular water, ii) alkali-OH
654 complexes and iii) “bridging” OH groups, *i.e.*, protons attached to a bridging oxygen in T-O-T
655 linkages. These observations do not rule out possible T-OH linkages as proposed by Malfait (2009).
656 Moreover, it has been shown that water, as well as excess alkalis (Na_2O) lead to an increase in the
657 Poisson’s ratio of haplogranite glasses, hence suggesting a decrease in the degree of polymerization
658 (Malfait and Sanchez-Valle, 2013). Further spectroscopic analyses are required to better understand

659 the mechanisms of water incorporation in haplogranite glasses. Kohn et al. (1992) suggest that the
660 non-linear dependence of viscosity on water content may be explained by assuming that bridging
661 hydroxyl groups have a larger effect on viscosity than molecular water. In Fig. 12, a decrease of the
662 asymmetry with water addition is observed at constant pressure. This reflects a possible decrease of
663 the OH/H₂O_m ratio with increasing total dissolved H₂O in agreement with previous studies (Dixon et
664 al., 1995; Zhang et al., 2003). Thus, the decrease in the OH/H₂O_m ratio with increasing bulk water
665 content (Stolper, 1982) is expected to reduce the effect of water on bulk viscosity. Our data suggest
666 that initial water dissolution operates on specific sites, and is efficient in decreasing the population of
667 both the very small and very large rings, probably due to the formation of water-rich domains as
668 reported by Zotov et al. (1992).

669 In the following discussion, we assume that even if the evolution of water speciation with pressure
670 may not be fully quenched, the main modifications on the network are still retained upon quench
671 (Table 4). The strength of the O-H linkage depends on the short-range environment around the OH⁻
672 species and may evolve during melt/glass densification. This interpretation is based on the
673 observation of the parallel evolution of the intensity of the Raman envelopes at 900 cm⁻¹ and 3600
674 cm⁻¹ with pressure.

675 The structural origin of the 900 cm⁻¹ Raman band in hydrous glasses is still debated. In aluminosilicate
676 glasses, a highly polarized band at this frequency has been attributed to vibration of T-O⁻
677 bonds in Q² species (Mysen and Virgo, 1986). However, our depolarized Raman data exclude this
678 interpretation for the HGG glasses as its intensity decreases or is not affected with increasing
679 pressure (Fig. 9c). On the other hand, Sharma et al. (1996; 1997) ascribed this band to a vibration of
680 the silicate framework associated to an anti-symmetric mode of a T-O-T group. Recent NMR
681 investigations (Xue and Kanzaki, 2004, 2006, 2008; Xue, 2009) as well as Raman and IR studies
682 (McMillan et al., 1993; Malfait, 2009) on the SiO₂-NaAlSiO₄ and SiO₂-NaAlSi₃O₈ joins have
683 assigned this band to T-OH vibrations. Malfait (2009) observed a negative shift of both the 900 and
684 the 3600 cm⁻¹ Raman bands accompanied by a negative shift with increasing pressure of the 4500
685 cm⁻¹ band observed by FTIR. In HGG glasses, however, only the 3600 cm⁻¹ band shifts whereas the
686 900 cm⁻¹ band remains at a constant frequency.

687 The negative shift of the water combination band and the decrease in intensity of the 900 cm⁻¹ band
688 may thus record a weakening of the O-H bond upon increasing pressure (Fig. 9c). The negative shift
689 of the water combination band occurs in both the nearly anhydrous HGG0 glass, in which only OH
690 units are expected, as well as in the hydrous HGG4 and HGG5 sets, where water is dissolved as
691 molecular and hydroxyl species (Stolper, 1982). The almost constant frequency of the 900 cm⁻¹ band
692 could suggest that pressure does not induce significant changes on the possible Si-OH and/or Al-OH
693 linkages in the HGG glasses. According to this interpretation, the weakening of the O-H bond during

694 densification of the HGG haplogranite glasses would increase above a pressure threshold of ~ 1.5
695 GPa. We propose that the O-H weakening is related to increasing interaction of H with neighboring
696 oxygen and to progressive partitioning of the H-bond on several anions (Sharma et al., 1996; 1997).
697 If this interpretation is correct, our data suggest that the relaxation of the O-H bond is independent
698 from and precedes the relaxation of the bulk glass structures. In other terms, relaxed O-H structures
699 can coexist with quenched unrelaxed bulk silicate glass structures. The observation that the negative
700 frequency shift of the O-H stretching envelope is quenched in most glasses suggests that the O-H
701 bond weakens during compression, but that this process does not represent the elastic part of the
702 densification process. Although Hui et al. (2009) proposed an increase of the OH/H₂O_m ratio with
703 pressure, this is not consistent with the negative shift of the 3600 cm⁻¹ band (Di Muro et al., 2006;
704 Fig. 12) and with the small increase in V*_{H2O} at the highest pressures of this study (Table 3).

705

706 **5.3. Effect of structural changes on melt physical properties**

707

708 The evolution with pressure of the density and viscosity of silicate melts relates to structural changes
709 occurring upon densification of the silicate network (Kushiro, 1978). Allwardt et al. (2005, 2007)
710 reported a nonlinear relationship of pressure and the increase in Al-coordination in depolymerized
711 glasses and concluded that increasing Al-coordination is an important component for densification,
712 especially at high densifications (>5%). However, an Al NMR study of our anhydrous and hydrous
713 haplogranites do not show significant changes in Al-coordination with pressure to 3.5 GPa
714 suggesting that changes in Al coordination do not play a major role in the densification of these
715 glasses in this pressure range (Malfait et al., 2012). Hence, in our haplogranitic glasses the
716 compaction of the structure upon pressure increase is achieved by topological arrangements. These
717 include the reduction of the average inter-tetrahedral bond angle (Figs. 9a, 13) and possibly a
718 redistribution of ring sizes (Figs. 8, 13), as identified in our study and by previous authors (Mysen et
719 al., 1983; Poe et al., 2001; Seifert et al., 1982; Sharma et al., 1979). Water addition favors a
720 reorganization of the ring sizes and average T-O-T angles at low pressure, these show small
721 variations with pressure increase. Compaction is in this case accommodated by a small distortion of
722 the rings and possible reorganization of the Al/Si rich domains.

723 The viscosity of melts displays a more complex relation with pressure at high temperature: the
724 viscosity of more polymerized melts decreases with increasing pressure but increases with pressure
725 for depolymerized compositions (e.g., Kushiro, 1976; 1978a; 1978b; Kushiro et al., 1976; Scarfe et
726 al., 1979; McMillan and Wilding, 2009). The negative pressure dependence of viscosity has been
727 explained by progressive increase of 5-fold coordinated Si and Al in densified melts (Kushiro, 1976,
728 McMillan and Wilding, 2009). In high temperature anhydrous systems, Bottinga and Richet (1995)

729 observed a positive correlation of viscosity with both pressure and network modifier content. Ardia
730 et al. (2008) have shown that the viscosity of dry rhyolite melts decreases linearly with pressure at
731 high temperature ($T > 1000^\circ\text{C}$) whereas the viscosity of hydrous rhyolites decreases with pressure at
732 high temperature but increases at low temperatures close to T_g (Ardia et al., 2008; Hui et al. 2009).
733 Following Al NMR results on hydrous rhyolites that show a negligible increase in 5-fold coordinated
734 Al up to 3.5 GPa (Malfait et al., 2012), we note that the anomalies in the pressure dependence of the
735 viscosity of hydrous rhyolites cannot be fully explained by Al coordination changes. These
736 anomalies could be interpreted as variations of the activation volume of viscosity (V_a), representing
737 the volume requirement for local motion and structural rearrangement (Ardia et al., 2008). In
738 anhydrous glasses, the decrease in viscosity with pressure is larger in the low-pressure range with
739 respect to higher pressures (i.e. $d\eta/dP$ decreases mostly at 1.0-1.5 GPa) (Ardia et al., 2008). In
740 hydrous glasses, the viscosity increases with pressure and results in a positive $d\eta/dP$ (Hui et al.,
741 2009). On the basis of our Raman results, we ascribe the changes of the pressure effect on viscosity
742 to an evolution of the densification mechanisms operating at different pressures.

743 On the basis of our spectral data, we propose that in hydrous compositions increasing pressure
744 triggers a reorganization of the Al- and Si-rich domains above 1.0-1.5 GPa. Malfait et al. (2012) only
745 reported a slight increase in Al coordination in hydrous glasses above 1.5 GPa that would not be
746 detectable in our Raman spectra. It is therefore plausible that this reorganization could result from an
747 increase in Al coordination, which in turn affects the observed decrease in the densification rate with
748 pressure. At higher pressures than explored here, possible modification of the network ring sizes and
749 angles becomes less favorable in hydrous glasses, the increase in Al coordination being a more likely
750 process for further compaction of the structure.

751 We have inferred that the compaction of the hydrous rhyolite network is mainly achieved by a
752 redistribution and homogenization of ring sizes and a decrease of the average intertetrahedral angle at
753 pressures below 1.5 GPa, whereas above this pressure, the dominant densification mechanism is the
754 redistribution of Al/Si rich domains. The observed structural modifications are thus consistent with
755 the increase of the activation energy of viscous flow for hydrous liquids with pressure through
756 variation of the activation volume of viscosity.

757

758

6. CONCLUSION

759

760 The densification mechanisms of haplogranite glasses have been investigated as a function of water
761 content and pressure using density measurements and Raman spectroscopy. The main conclusions
762 are summarized in Fig. 13. Densities and derived molar volumes display a linear dependence on
763 pressure for the nearly anhydrous glasses. The densities of hydrous glasses rapidly increase linearly

764 up to 1.5 GPa but the densification rate decreases above this pressure. Densification upon pressure
765 increase is associated first with a slight decrease of the partial molar volume of water up to 1.0 GPa,
766 followed by an increase above this pressure that correlates with the reported higher H_2O_m/OH^- ratio
767 at high pressure. Almost anhydrous liquids accommodate the increase in compression by distortion
768 of the silicate network, including namely changes in T-O-T angles and average ring sizes. Pressure
769 increase leads to an increase of the ordering of the Si/Al domains in the network of the water-poor
770 liquids. The effect of pressure on the viscosity of nearly anhydrous compositions is reduced at higher
771 pressures by a reorganization of the network. Water dissolved into the glass structure reduces
772 significantly the range of possible ring sizes. In the hydrous glasses, the increase in density is thus
773 essentially accommodated by a reorganization of ring sizes to an average ring (i.e., 6-membered ring)
774 without major variations on the average T-O-T angles.

775

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782

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- 1078

1079 **Figure caption:**

1080

1081 Fig. 1: Strategy for the treatment of Raman spectra in the spectral domain related to vibrations of the
1082 aluminosilicate framework: a) subtraction of the baseline (dotted) from the raw spectra; b) Long
1083 correction using Eq. 3, and c) normalization with respect to the highest peak of the LF envelope,
1084 smoothing of the data by using the Loess equation (3%) (line in c). See details in the text.

1085

1086 Fig. 2: Example of cubic baseline subtraction to the Raman spectral domain related to OH-stretching
1087 vibration (here the spectrum of the HGG5 glass at 0.5 GPa) and subsequent smoothing (grey line;
1088 Loess equation 3%).

1089

1090 Fig. 3: a) Measured densities vs. quench pressure for the synthesized HGG glasses and comparison
1091 with measured densities for dry albite glasses (Kushiro, 1976) and calculated densities for dry
1092 rhyolites quenched at 0.5 GPa using the pressure release technique (Withers and Behrens, 1999).
1093 Lines are guidelines and the arrow indicates the data point with the anomalously low density for
1094 HGG4 at 2.5 GPa discussed in the text. This glass is not considered for further discussion. b)
1095 Measured densities vs. water content for HGG and rhyolitic glasses at various pressures. The rhyolite
1096 glasses of Withers and Behrens (1999) were obtained by rapid quench (>100 °/s) with pressure
1097 release from 0.3 GPa (black stars) and by slow cooling (ca. 100-150 °/min) from 0.5 GPa (white
1098 stars). Errors of density measurement are smaller than symbol size.

1099

1100 Fig. 4: Molar volume of the haplogranitic matrix vs. total dissolved water in molar fraction
1101 (calculated as molecular water) at various pressures. Symbols are the calculated values for HGG at
1102 the corresponding pressure. Lines are fits at each pressure (0.5, 1.0, 1.5, and 2.5 GPa) assuming ideal
1103 mixing volumes. The fit lines yield the partial molar volume of the dry silicate (V_{sil}) and of water
1104 ($V^*_{\text{H}_2\text{O}}$) as they intercept with the y-axis at 0 and 1, respectively (Table 3). Errors are calculated by
1105 propagating experimental errors in the density measurements.

1106

1107 Fig. 5: Unpolarized (black), parallel (VV, grey above), and perpendicular (VH, grey lower plot)
1108 polarized spectra of the nearly anhydrous composition at 1 atm (a), and (b) of the HGG3 glass with
1109 2.7 wt% H₂O, synthesized at 0.5 GPa. Spectra are VV-polarized when the electric vectors of the
1110 incoming and scattered light are parallel and VH-polarized when they are perpendicular. Spectra
1111 were treated as illustrated in Fig. 1, without normalization and smoothing. Numbers in black indicate
1112 the frequency of the vibrational bands whereas the grey numbers in italic indicate experimental
1113 frequencies values of bands in the polarized spectra (Table 3). The difference in recorded intensity

1114 between (a) and (b) is due to shorter acquisition time for the hydrous sample to avoid exsolution of
1115 H₂O.

1116

1117 Fig. 6: Deconvolution strategy for the HF envelope, normalized to the peak high of the LF envelope
1118 (Fig. 1), here applied to all the synthesized glasses at 0.5 GPa. Six deconvolution bands with fixed
1119 position and shape (width/intensity ratio, highlighted by the grey zones), imposed by the
1120 deconvolution of the polarized spectra (Fig. 5), are used to treat the HF envelope. The "PeakFit"
1121 software is used to optimize the r^2 value (min. 0.997) predefining the 6 deconvolution bands marked
1122 by the representative frequencies (see text). Generated line is created by the deconvolution strategy.

1123

1124 Fig. 7: Treated and smoothed spectra of the nearly anhydrous HGG0 glasses synthesized at different
1125 pressures. The dotted lines represent the frequencies of interest discussed in the text which values are
1126 given in italic. The most intense envelope (LF) shifts from 461 at room conditions (*469 cm⁻¹* at 0.5
1127 GPa) to $493 \pm 5 \text{ cm}^{-1}$, the HF envelope displays a slight negative shift from 1141 to 1133 cm^{-1} (± 10
1128 cm^{-1}), and the main water band is negatively shifted from $3447 \pm 10 \text{ cm}^{-1}$ to $3424 \pm 10 \text{ cm}^{-1}$. The four
1129 different spectral region discussed in the text are shown with different background colors.

1130

1131 Fig. 8: Full Width at Half Maximum (FWHM*) of the LF envelope (non smoothed) vs. pressure of
1132 glass synthesis. The width is measured at the half-height of the LF envelope, without any specific
1133 deconvolution of the envelope.

1134

1135 Fig. 9: Experimental frequencies and intensities of the normalized spectra (with Long correction,
1136 without smoothing) previous deconvolution vs. pressure. (a) position of the LF main envelope and of
1137 the D1 defect band only for HGG0 (crosses); (b) normalized intensity of the D2 band; (c) normalized
1138 intensity of the 900 cm^{-1} band for the hydrous glasses; (d) Frequency of the HF envelope; and (e)
1139 intensity of the HF envelope. Error on the frequency is $\pm 5 \text{ cm}^{-1}$ for the LF spectral region and ± 10
1140 cm^{-1} for HF region. The error for the intensities is calculated considering the variation of the
1141 intensities in the frequency errors.

1142

1143 Fig. 10: Spectral evolution of the HF envelope in terms of area variation of the deconvoluted bands
1144 (Fig. 6) vs. pressure in % deviation from the reference value of the glasses of the same composition
1145 synthesized at 0.5 GPa, here (a) for the nearly anhydrous glasses. (b) Deconvoluted band at 1045 cm^{-1} ,
1146 NBO structure, for all the different glass compositions vs. pressure.

1147

1148 Fig. 11: Treated and smoothed spectra of all the investigated glasses synthesized at 0.5 GPa, with
1149 from the bottom to the top the increasing bulk water content. The vertical dotted lines represent the
1150 frequencies of interest discussed in the text, roman numbers in quotation marks depicting band
1151 labels, italic numbers accurate frequencies, both used in the text.

1152

1153 Fig. 12: Treated and smoothed spectra of the hydrous HGG glasses at different pressures. Vertical
1154 dotted lines identify the frequency values of the Raman bands of interest described in the text: LF
1155 main envelope ($480 \pm 5 \text{ cm}^{-1}$) and the shoulder formed by the D2 defect band ($590 \pm 5 \text{ cm}^{-1}$), the
1156 broad MF envelope at 800 cm^{-1} , the HF envelope with the band at 900 cm^{-1} , and the OH-stretching
1157 region at high frequencies. The numbers in italic are the effective experimental frequencies picked
1158 from the spectra (Table 5, error ± 5 for LF, $\pm 10 \text{ cm}^{-1}$ for HF). Note the different x-axis scale of the
1159 low and high frequency sides.

1160

1161 Fig. 13: Schematic representation of the effect of pressure on the physical properties of water-poor
1162 (left) and water-rich (right) glasses. A) Viscosity η and T_g , B) density, C) evolution of the T-O-T
1163 mean angle, D) Al-coordination (Malfait et al., 2012); E) ring population. At the bottom (F), the
1164 pressure effect on the Raman water band, where the intensities of the water-poor Raman spectra
1165 (bottom left) were increased to highlight the band shifts. Viscosity is expressed as the value at T_{ae}
1166 close to the T_g .

Table 1: Calculated quench temperature at viscosities of $10^{9.3}$ and 10^{12} Pa s.

<i>model:</i>			Ardia et al., 2008	Hui et al., 2009	Ardia et al., 2008	Hui et al., 2009
sample	H ₂ O (wt%)	P (GPa)	T_{ae} (°C) $\eta=10^{9.3}$ Pas		T_{ae} (°C) $\eta=10^{12}$ Pas	
HGG0	0.15	1 atm	895	879	749	710
		0.5	873	874	731	714
		1.0	852	859	713	700
		1.5	830	838	695	675
		2.0	808	817	677	655
		2.5	786	798	659	640
HGG3	2.69	0.5	500	540	365	438
		1.0	478	545	347	444
		1.5	456	551	329	452
		2.0	435	560	311	463
		2.5	413	571	293	470
HGG4	3.63	0.5	440	502	309	405
		1.0	419	504	290	409
		1.5	397	509	272	416
		2.0	375	517	254	425
		2.5	353	526	236	436
HGG5	5.24	0.5	362	454	234	364
		1.0	340	453	216	365
		1.5	318	456	198	370
		2.0	297	462	180	377
		2.5	275	469	162	387

Table 2

Table 2: density and molar volume of HGG glasses at increasing water contents and quench pressures and calculated density at various

	P (GPa)	pyrex pycnometer - method 2					V^a (cm ³ /mol)		calculated			
		#1	#2	#3	#4	average			WB 1999 ^b	T=25°C;P run ^c	T, P run ^d	
HGG0	0.0001	2.290	2.309	2.309	2.306	2.305	<i>9.0</i>	27.8	2.3		2.367	2.291
	0.5	2.340	2.338			2.340	<i>1.4</i>	27.4	2.0	2.387	2.457	2.376
	1.0	2.371	2.375			2.374	<i>2.8</i>	27.0	2.1		2.558	2.47
	1.5	2.409	2.411			2.411	<i>1.4</i>	26.6	2.1		2.668	2.572
	2.0	2.442	2.438	2.439		2.441	<i>2.1</i>	26.2	2.1		2.788	2.683
	2.5	2.491	2.479	2.488		2.487	<i>6.2</i>	25.7	2.2		2.919	2.804
HGG3	0.5	2.300	2.298	2.300	2.301	2.301	<i>1.3</i>	26.1	2.0	2.344	2.298	2.226
	1.0	2.346	2.347	2.347	2.346	2.348	<i>0.5</i>	25.6	2.0		2.382	2.305
	1.5	2.400	2.407	2.401	2.406	2.405	<i>3.5</i>	25.0	2.1		2.473	2.39
	2.0	n.a.									2.571	2.481
	2.5	2.434	2.435	2.436	2.435	2.436	<i>0.7</i>	24.7	2.0		2.677	2.58
HGG4	0.5	2.294	2.294	2.294	2.294	2.295	<i>0.3</i>	25.6	2.0	2.328	2.242	2.174
	1.0	2.336	2.339	2.336	2.338	2.338	<i>1.2</i>	25.1	2.0		2.321	2.248
	1.5	2.385	2.385	2.385	2.384	2.386	<i>0.5</i>	24.6	2.0		2.405	2.327
	2.0	n.a.									2.496	2.412
	2.5	2.366	2.369	2.366	2.368	2.368	<i>1.5</i>	24.8	2.0		2.594	2.503
HGG5	0.5	2.261	2.258	2.260	2.258	2.260	<i>1.5</i>	25.1	2.0	2.301	2.154	2.091
	1.0	2.317	2.314	2.316	2.314	2.316	<i>1.5</i>	24.5	2.0		2.224	2.157
	1.5	2.325	2.327	2.324	2.327	2.327	<i>1.5</i>	24.3	2.0		2.299	2.227
	2.0	n.a.									2.379	2.303
	2.5	2.376	2.377	2.375	2.379	2.378	<i>1.8</i>	23.8	2.0		2.466	2.383

errors are given in italic on the last digit number.

a) molar volume calculated as described by Richet et al. (2000) (assuming water as H₂O).

b) calculated as indicated by Withers and Behrens (1999) for rhyolitic glasses quenched at 0.5 GPa with a T ramp of 200°/min.

c, and d) calculated following Lange and coworkers (Lange and Carmichael, 1987; Lange, 1996; 1997; Ochs and Lange, 1999).

Table 4: Deconvolution and depolarization ratios of HF bands.

HGG0; 0.15 wt% H₂O						HGG3; 2.69 wt% H₂O				
VV						VV				
Peak	Center ^a	FWHM	% Area	dep ratio		Center ^a	FWHM	% Area	dep ratio	
1	801	94	24.4	0.179	faint pol.	799	94	23.9	0.296	dep.
2	904	61	4.8	0.151	faint pol.	907	87	18	0.19	faint pol.
3	980	95	10.2	0.147	faint pol.	982	92	10.6	0.552	dep.
4	1059	97	21.5	0.227	faint pol.	1044	90	12.4	0.476	dep.
5	1133	82	24.5	0.082	pol.	1126	106	25	0.204	faint pol.
6	1191	77	14.6	0.082	pol.	1187	98	10.1	0.174	faint pol.
VH						VH				
1	796	84	24.8			794	84	19.9		
2	917	97	7.3			902	83	10.3		
3	977	85	8.5			977	92	18.5		
4	1040	101	32.3			1047	80	16.6		
5	1140	113	17.7			1140	126	19.2		
6	1186	95	9.4			1197	274	15.5		

a) position of the band in cm^{-1} ($\pm 10 \text{ cm}^{-1}$).

Table 5: Raman band position of the HGG glasses at increasing water contents and quench pressures.

	P (GPa)	LF region ($\pm 5 \text{ cm}^{-1}$)			HF region ($\pm 10 \text{ cm}^{-1}$)		water band ($\pm 10 \text{ cm}^{-1}$)	
		LF band	D2	D2 - smooth ^b	1050 shoulder	HF band	peak pos.	H ₂ O tot ^a
HGG0	0.0001	461	595	591	1052	1130	3506 ^c	0.15
	0.5	469	596	590	1049	1141	3447 ^c	0.15
	1.0	468	594	590	1055	1132	3459 ^c	0.13
	1.5	474	596	590	1047	1129	3434 ^c	
	2.0	482	596	590	1051	1135	3421 ^c	
	2.5	493	594	590	1053	1133	3424 ^c	
HGG3	0.5	485	583	590	1056	1138	3577	
	1.0	483	581	590	1047	1143	3581	
	1.5	486	578	590	1044	1133	3568	
	2.0	482	581	590	1038	1126	3573	
	2.5	482	581	590	1053	1134	3575	
HGG4	0.5	488	574	590	1053	1138	3580	
	1.0	483	576	593	1049	1134	3578	
	1.5	488		590	1048	1133	3577	
	2.0	486		590	1053	1132	3570	
	2.5 ^d	486		590	1048	1124	3563	
HGG5	0.5	483		584	1057	1138	3574	
	1.0	485		587	1057	1130	3570	
	1.5	483		590	1053	1132	3567	
	2.0	488		590	1049	1129	3564	
	2.5	486		590	1036	1121	3557	

a) water content calculated by internal calibration, see di Muro et al. (2006a)

b) D2 frequency after smoothing

c) highest peak after smoothing, related error is $\pm 8 \text{ cm}^{-1}$.

d) not considered for the discussion.

Table 3: Molar volume of dry silicate and partial molar volume of molecular water

	P (GPa)	V_{sil}		$V_{\text{H}_2\text{O}}^*$	
HGG at P:					
	0.50	27.42	22	12.82	<i>100</i>
	1.00	27.04	20	11.23	<i>100</i>
	1.50	26.49	33	12.17	<i>100</i>
	2.50	25.79	30	13.74	<i>100</i>
literature data:					
Ab/O	0.01-0.4	27.49	<i>1</i>	11.22	<i>28</i>
Ab/S-BP	0.1-0.7	26.29	<i>10</i>	14.54	<i>36</i>
Or	2	27.95	<i>14</i>	15.15	<i>90</i>
Hapl/D	0.04-0.33	26.71	9	13.33	58
RhyoK/S	0.11-0.45	27.55	<i>10</i>	11.37	<i>109</i>
RhyoP/S	0.07-0.51	27.55	4	11.24	37
Rhyo/Oc	0.02-0.59	26.28	<i>15</i>	12.55	<i>137</i>

error in italic is based on the last digit.

literature data are summarized by Richet et al. (2000). In detail:

Ab/O: Orlova (1963), Ab/S-BP: Silver and Stolper (1989),

Or, RhyoK/S, RhyoP/S: Silver et al. (1990), Hapl/D:

Dingwell et al. (1996), and Rhyo/Oc: Ochs and Lange

(1999).

Figure 1

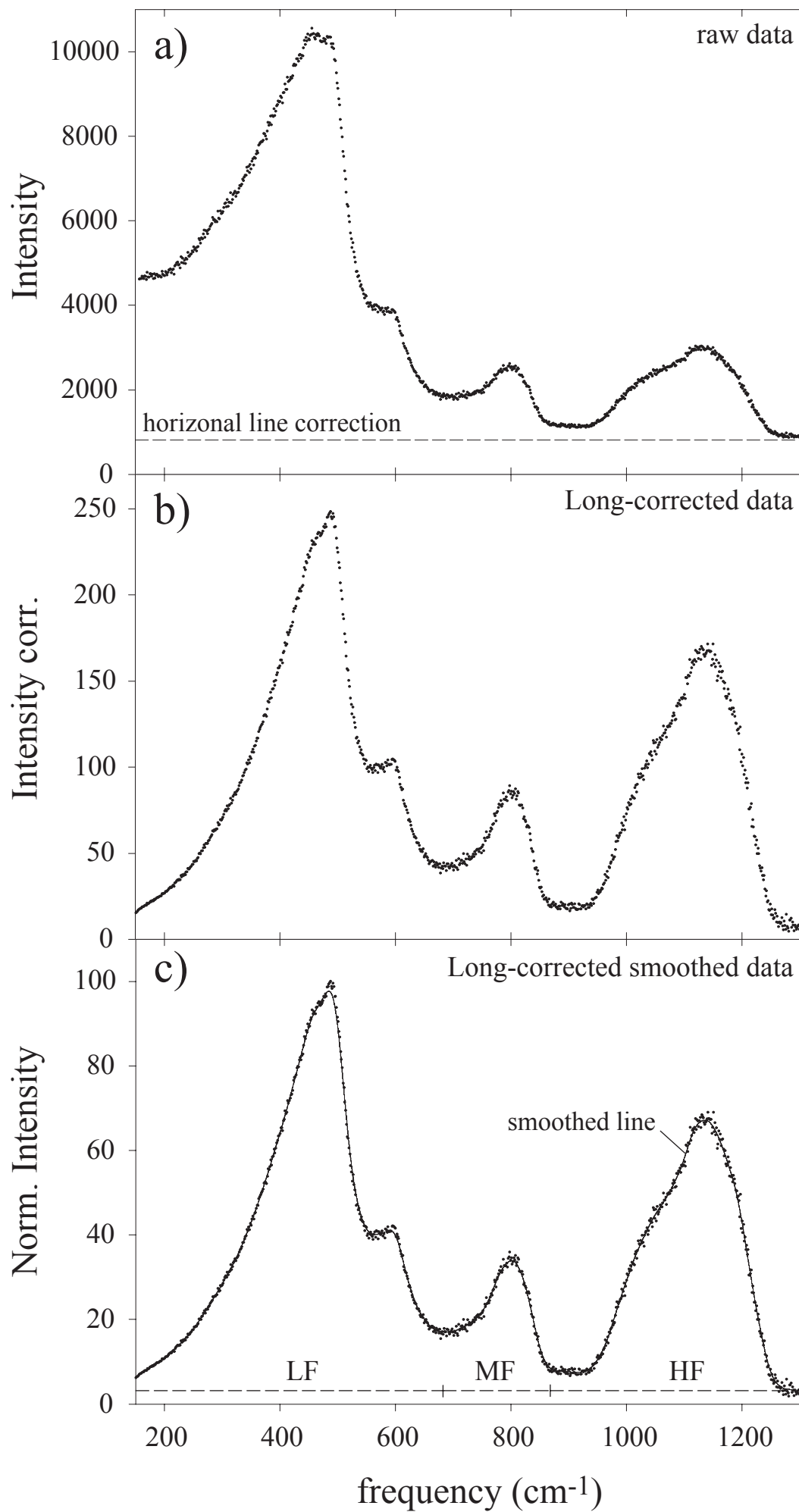


Figure 2

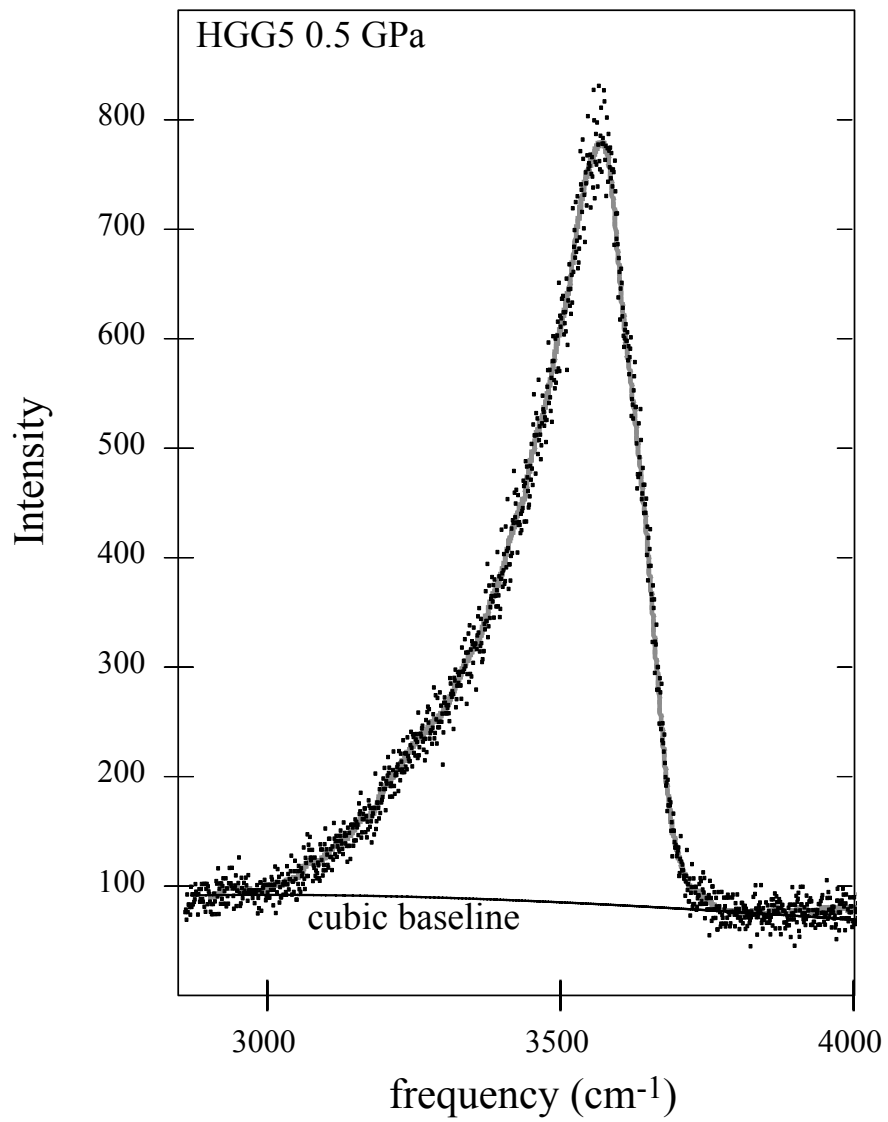


Fig. 3

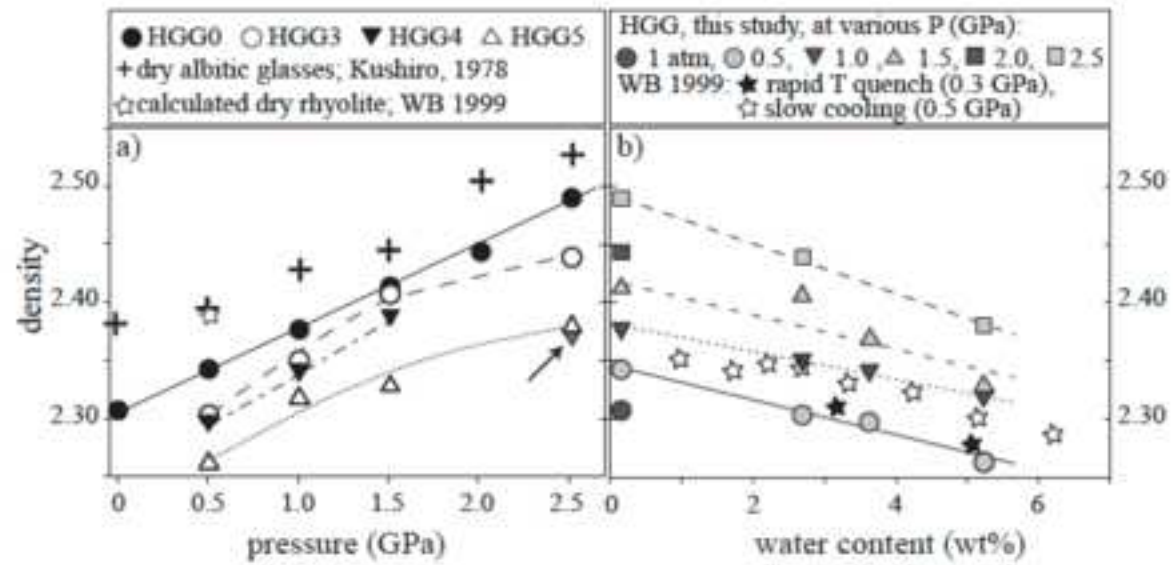


Figure 4

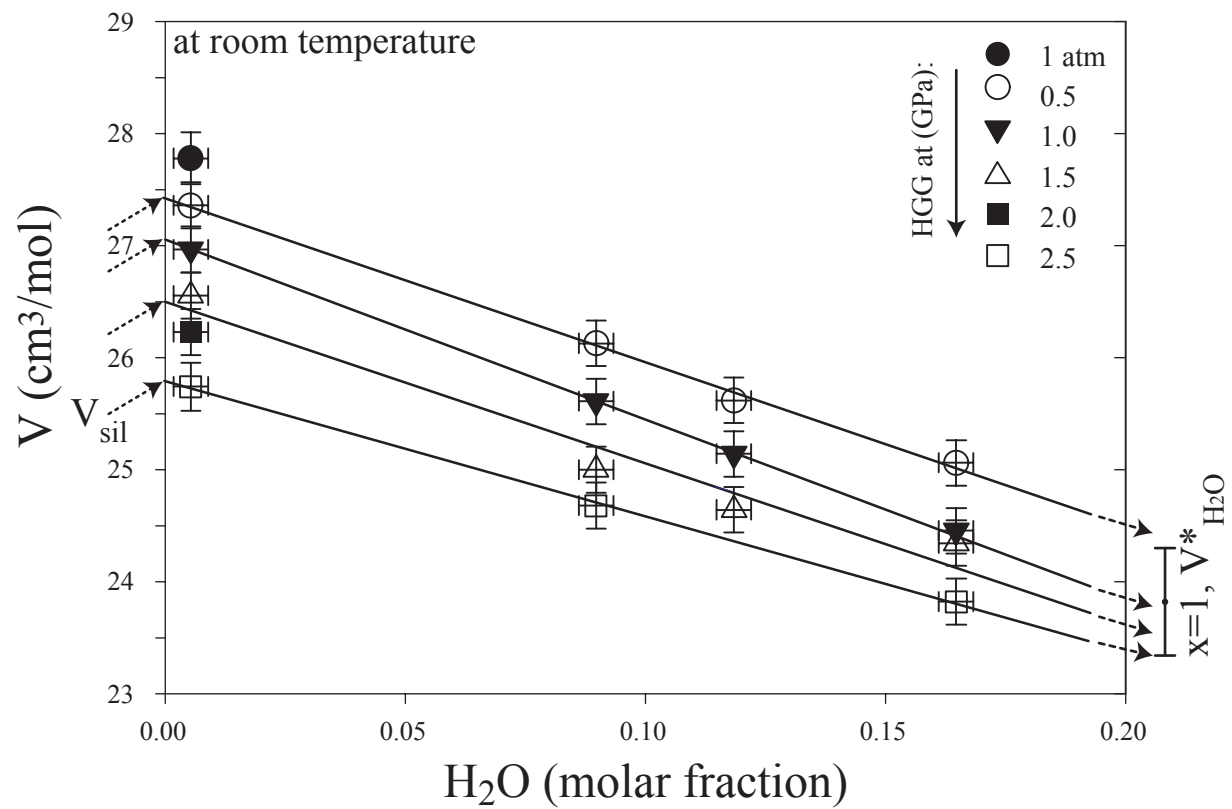


Figure 5

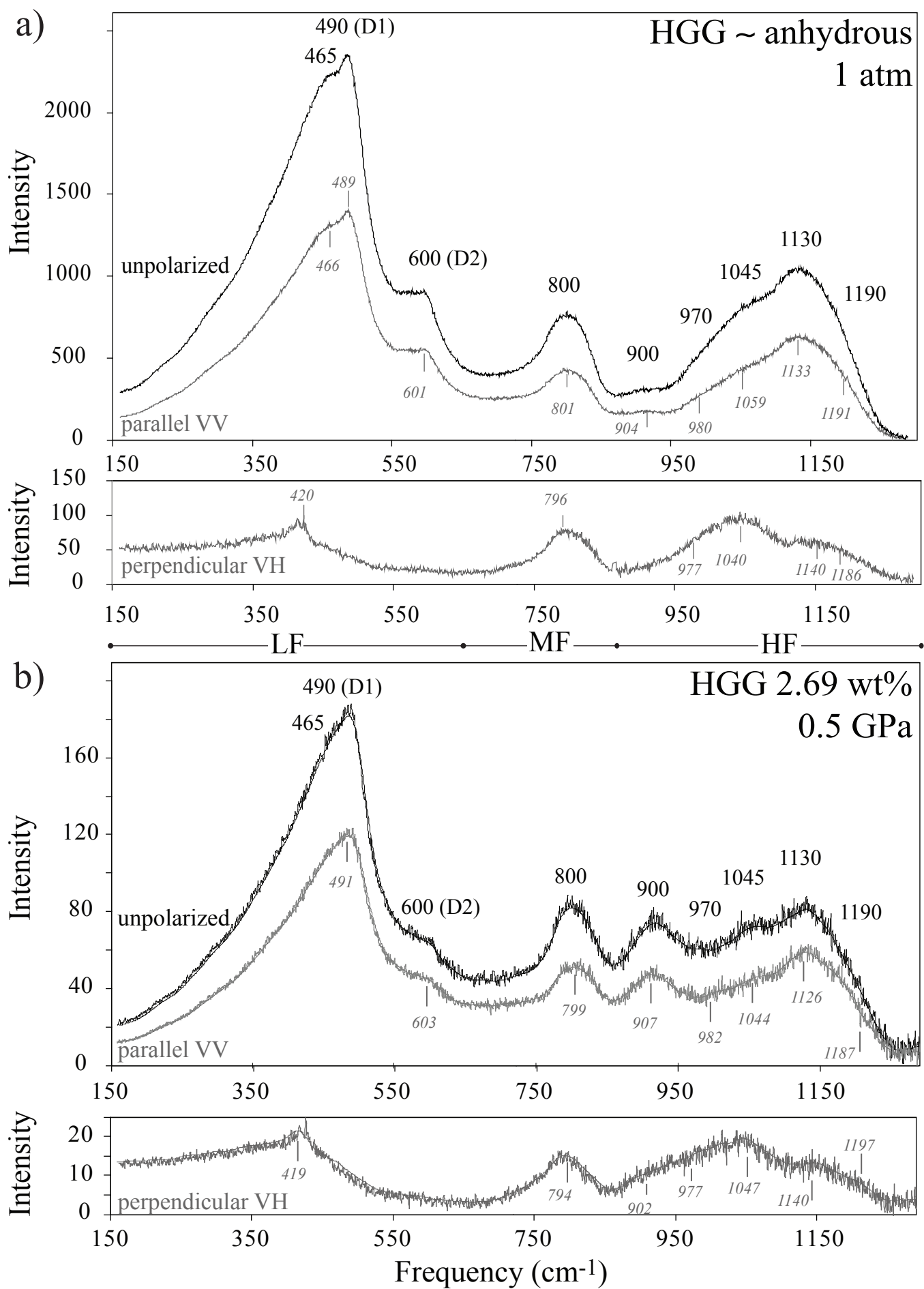


Figure 6

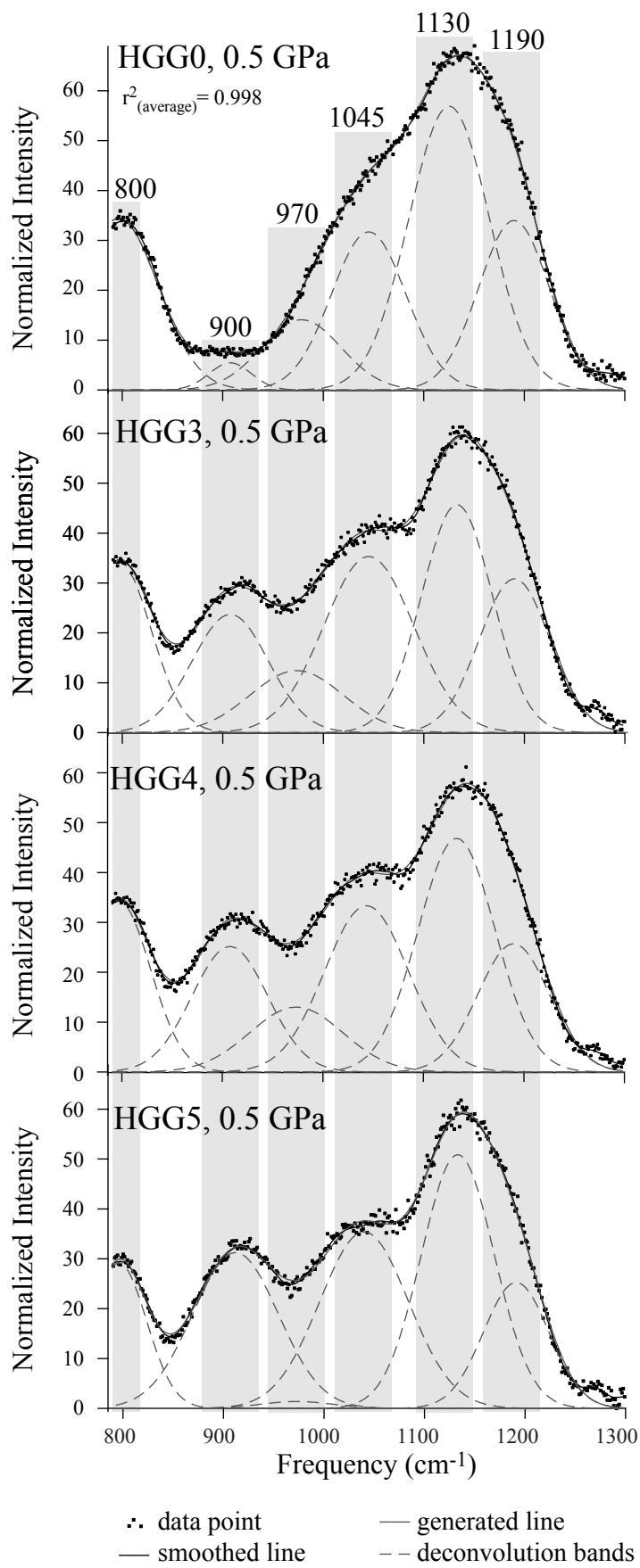


Figure 7

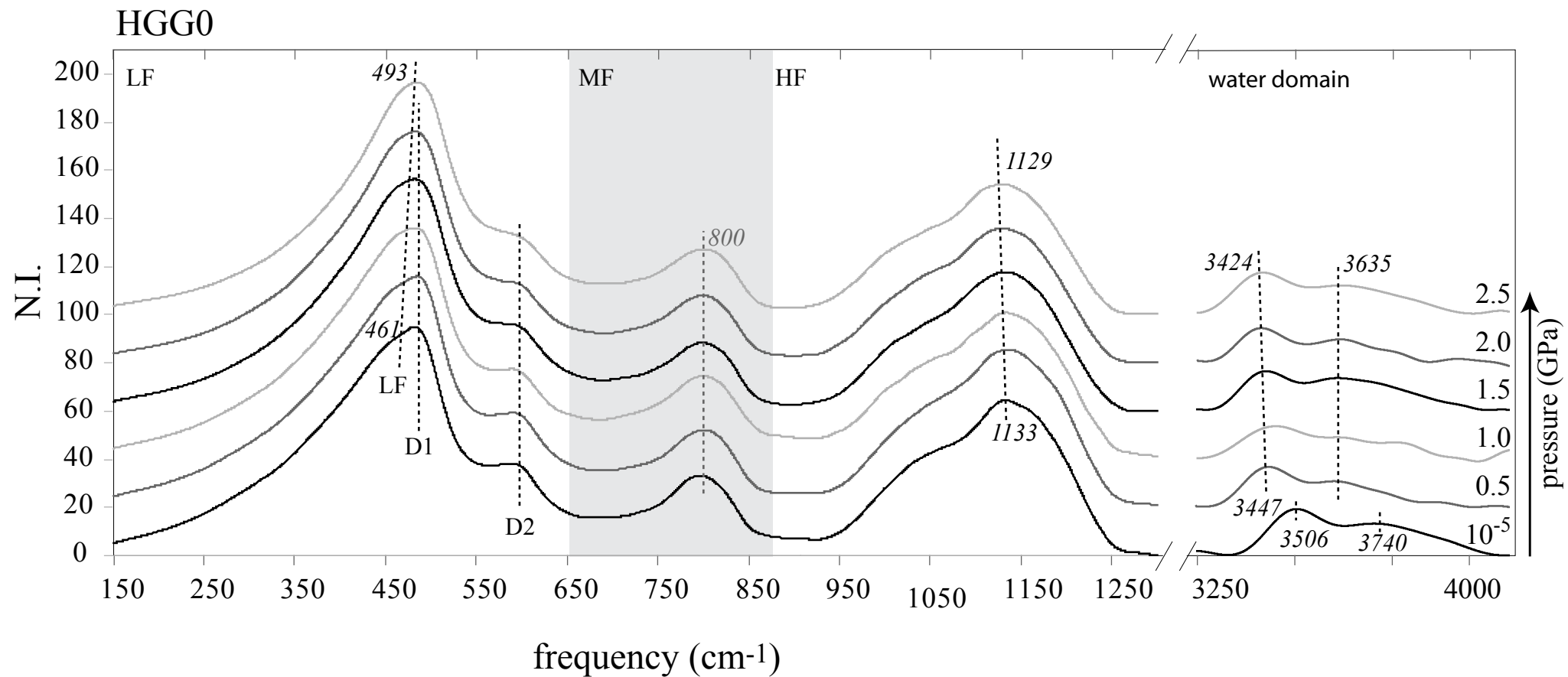


Figure 8

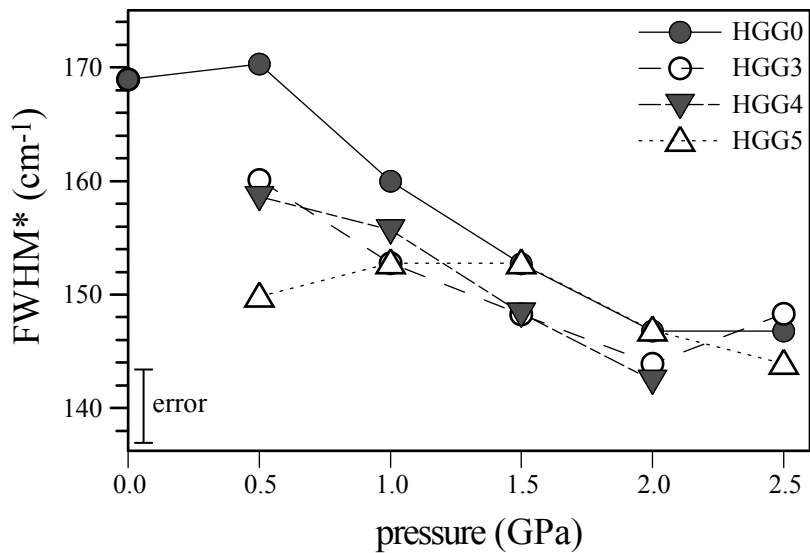


Figure 9

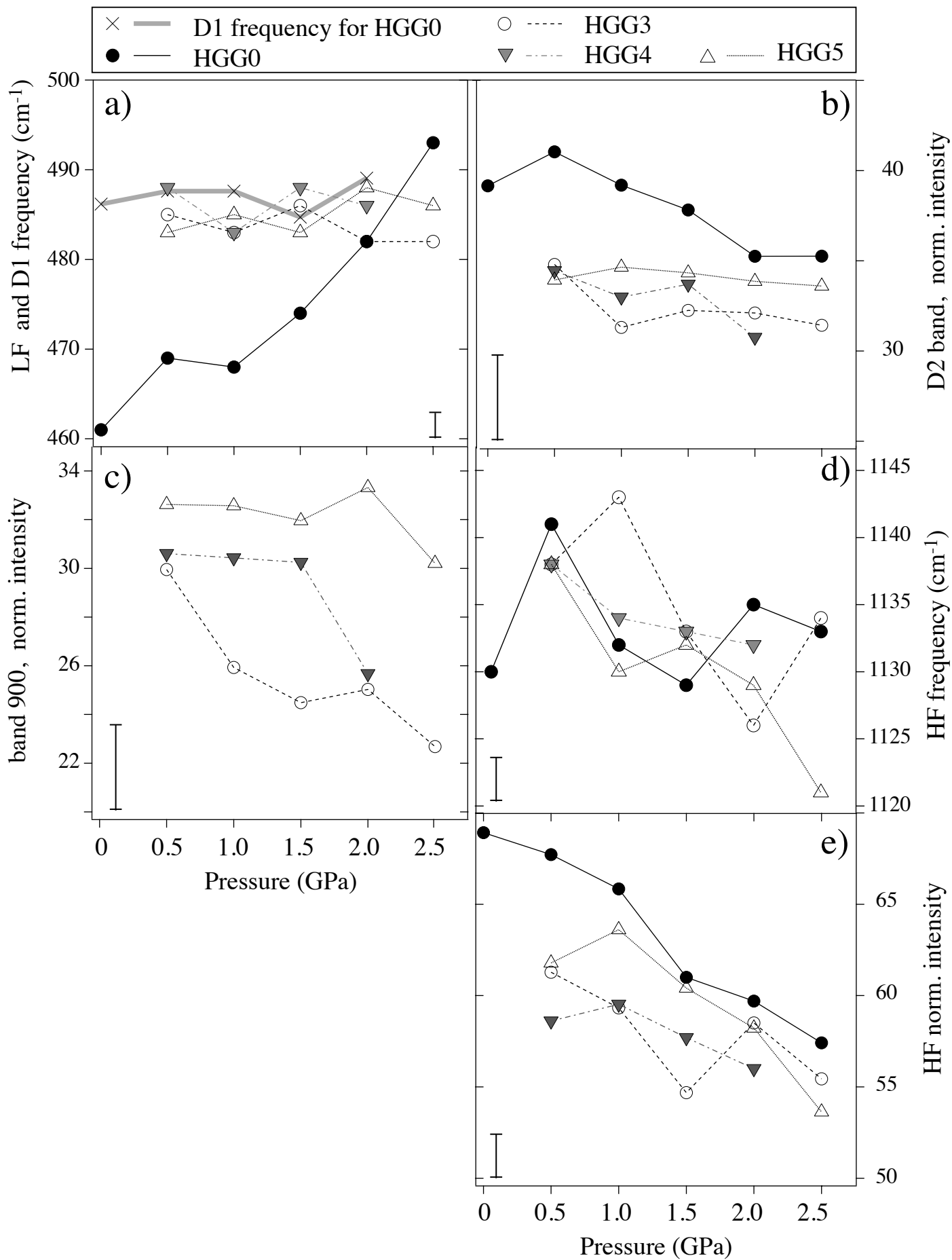


Figure 10

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Fig. 10

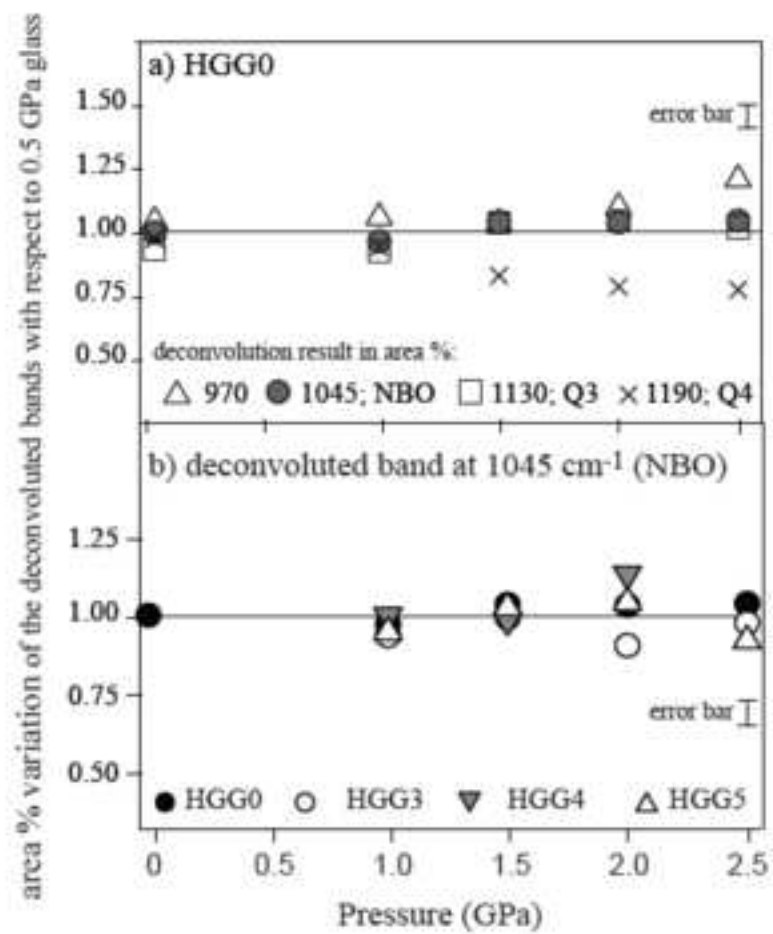


Figure 11

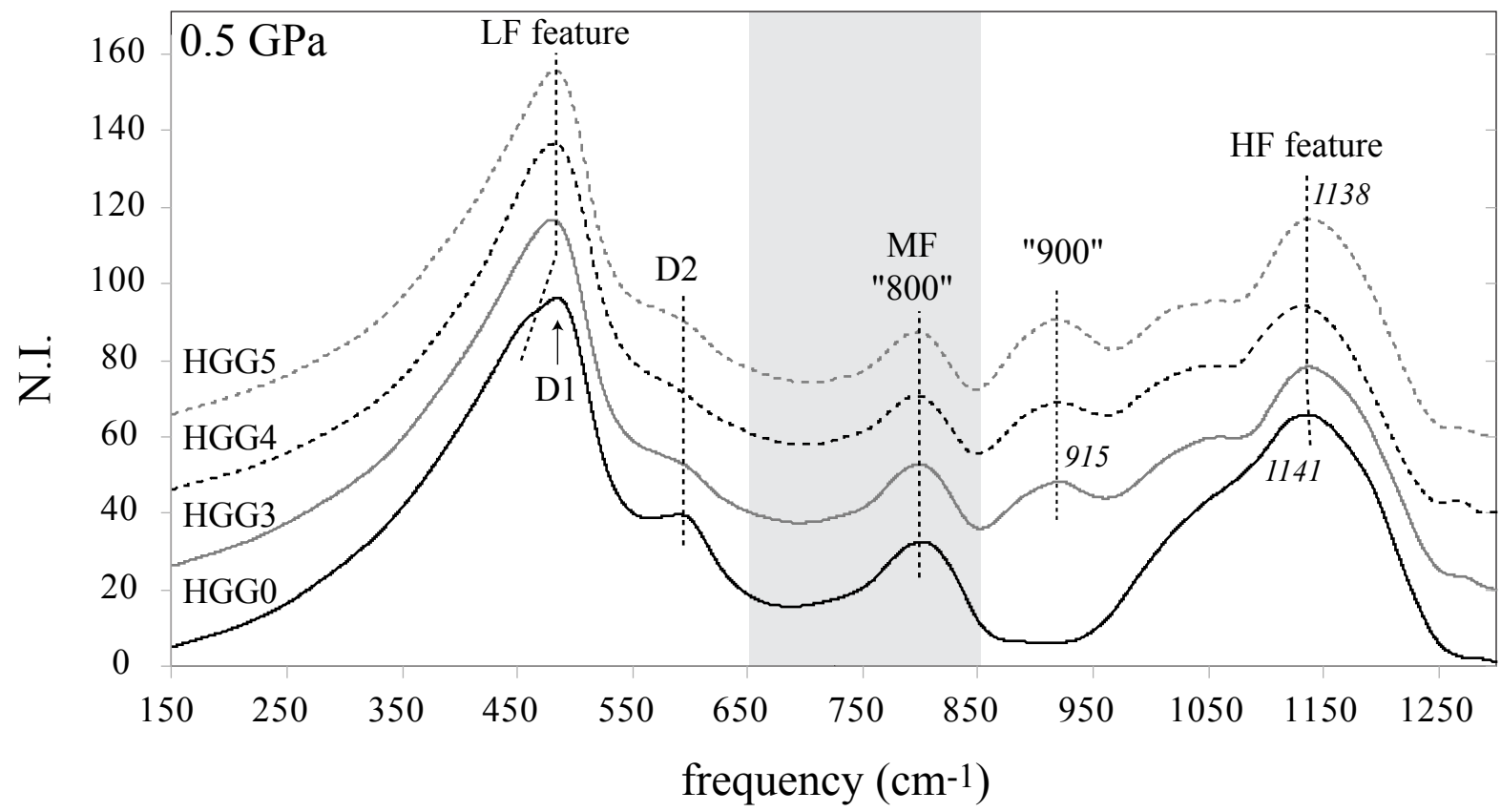


Figure 12

