1   **REVISION 1**

2   **Complex IR spectra of OH$^-$ groups in silicate glasses: implications for the use of the 4500**

3   **cm^{-1} IR peak as a marker of OH$^-$ groups concentration**

4   Charles Le Losq[1], George D. Cody[1], Bjorn O. Mysen[1]

6   *[1]: Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road*

7   *NW, Washington D.C. 20015, U.S.A.*

8   *[*]Corresponding author: clelosq@carnegiescience.edu*

12   **Abstract**

13   Previous studies of hydrous glasses and melts with infrared spectroscopy have led to the

14   conclusion that the IR combination peaks near 4500 and 5200 cm^{-1} reflect the existence of

15   OH$^-$ (hydroxyl) groups and H$_2$O$_{mol}$ water molecules in those materials. Here, we show that the

16   glass chemical composition can impact profoundly the intensities and frequencies of the

17   fundamental O-H stretching signal and, therefore, potentially those of the 4500 and 5200 cm^{-1}

18   combination peaks. In alkali silicate glasses, compositional effects can give rise to peaks

19   assigned to fundamental O-H stretching at frequencies as low as 2300 cm^{-1}. This expanded

20   range of Raman intensity assigned to O-H stretch is increasingly important as the ionic radius

21   of the alkali metal increases. As a result, the combination of the fundamental O-H stretch in

22   OH$^-$ groups with the Si-O-H stretch located near 910 cm^{-1} gives rise to a complex

23   combination signal that can extend to frequencies much lower than 4200 cm^{-1}. This

24   combination signal then becomes unresolvable from the high-frequency limb of the band

25   assigned to fundamental O-H stretch vibration in the infrared spectra. It follows that, when O-

26   H stretch signals from OH^- groups extend to below 3000 cm^{-1}, the 4500 cm^{-1} peak does not

27   represent the total OH^- signal. Under such circumstances, this infrared peak may not be a

28   good proxy for determining the concentration of OH^- hydroxyl groups for glassy silicate

29   materials.

30

Introduction

32   Water dramatically affects the physical properties of silicate melts and glasses (see the

33   review by Mysen & Richet, 2005), and, as a result, is of key importance in both industrial and

34   geologic processes. An important feature of water dissolved in glassy and molten silicate

35   materials is that it exists both as molecules (H_2O_{mol}) and as hydroxyl groups (OH^-) bonded to

36   the silicate network. It has often been stated that those two different species give rise to IR

37   combination peaks at ~5200 and ~4500 cm^{-1} respectively (Davis & Tomozawa, 1996; Efimov

38   & Pogareva, 2006; Malfait, 2009; Scholtze, 1960; Stolper, 1982). The OH^- groups are bonded

39   to the tetrahedral network of silicate glasses and melts, forming Si-OH and Al-OH bonds by

40   breakage of bridging oxygen bonds (Si-O-Si, Al-O-Al, and Si-O-Al) (see for instance

41   Moulson & Roberts, 1961; Scholtze, 1960; Stolen & Walrafen, 1976; Stolper, 1982). This

42   solution mechanism results in depolymerization of the silicate network (see for instance the

43   study of Mysen & Cody, 2005). In contrast, water dissolved in the form of H_2O_{mol} species

44   does not change melt polymerization. As a result, the dissolution of water as OH^- groups or as

45   H_2O_{mol} species has different effects on the polymerization and hence properties of hydrous

46   silicate amorphous materials. These differences are reflected in transport properties of

47   hydrous melts, glass transition temperature (see for instance Deubener et al., 2003), solidus

48 temperatures, melt/mineral phase equilibria, and element partitioning (see for a review Mysen

49 and Richet, 2005).

50   The water speciation, in terms of H_2O_{mol} species and OH^- groups, varies with total water

51 concentration and temperature (Behrens & Yamashita, 2008; Nowak & Behrens, 1995;

52 Stolper, 1982). It also depends on composition (Deubener et al., 2003; Moretti et al., 2014).

53 However, it is not known how temperature effects vary with bulk composition, and how bulk

54 compositional variables govern solution mechanisms and solubility.

55   FTIR spectroscopy may be used to examine such effects by using the combination peaks

56 often located near 4500 and 5200 cm^{-1} in the spectra. However, as a first step, it is necessary

57 to ascertain exactly what governs the frequency and integrated intensity of the 4500 and 5200

58 cm^{-1} combination peaks in the IR spectra of hydrous silicate glasses (and melts). An example

59 of this is the recent work of Malfait (2009) who concluded that the 4500 cm^{-1} IR peak is

60 formed by the combination of the fundamental O-H stretching mode at ~3600 cm^{-1} with the

61 Si-O-H, and presumed Al-O-H, stretching vibrational mode. The Al-O-H vibrational mode

62 can occur near 800 cm^{-1}, whereas the Si-O-H is near 920 cm^{-1}. Combined with the

63 fundamental O-H stretching mode at 3600 cm^{-1} in simple aluminosilicate glasses, the exact

64 frequency of the 4500 cm^{-1} would be somewhat correlated, therefore, with the Al/Si of the

65 glass. Concerning the 5200 cm^{-1} peak, it is attributed to arise from the combination of the

66 3600 cm^{-1} stretching and 1630 cm^{-1} bending modes of H_2O_{mol} species (Scholtze, 1960;

67 Stolper, 1982),

68   The infrared signal assigned to O-H stretch in OH^- and H_2O_{mol} species, usually

69 characterized by an asymmetric band centered near 3600 cm^{-1}, can have a complex shape in

70 some silicate glasses, where broad bands extend into the 2000-3000 cm^{-1} frequency range (see

71 for instance data on sodium silicate glasses of Uchino et al., 1991; Zotov & Keppler, 1998). If

72   those bands are from OH⁻ groups, then their combination with the Si-O-H stretch mode

73   located near 910 cm^{-1} (Zotov & Keppler, 1998) will give OH⁻ combination signals at

74   frequencies significantly lower than 4500 cm^{-1}. However, if the low-frequency signals are

75   from O-H stretch in H_2O_{mol} species, their combination with the H_2O_{mol} bending mode near

76   1630 cm^{-1} will result in signals in the range of the OH⁻ combination peak. In both cases, using

77   the intensities of the 4500 and 5200 cm^{-1} peaks would be not appropriate to determine the

78   [OH⁻] and [H_2O_{mol}] concentration in the glass. To evaluate impacts of such effect and their

79   consequence for the determination of [OH⁻] and [H_2O_{mol}], we studied alkali (Li, Na, K)

80   silicate glasses containing different amount of dissolved water by using FTIR and Raman

81   spectroscopies.

82

Experimental methods

84   Anhydrous KS4 ($K_2Si_4O_9$), NS4 ($Na_2Si_4O_9$) and LS4 ($Li_2Si_4O_9$) glasses were synthetized

85   by mixing pure anhydrous SiO_2, K_2CO_3, Na_2CO_3 and Li_2CO_3 powders and grinding them

86   under ethanol for about 1 hour. The powders were placed in a Pt crucible and heated at about

87   1.5°/min until reaching 1000°C before bringing the samples to complete melting. Melting was

88   accomplished near 1200°C for the KS4 composition, 1400 °C for the NS4 composition, and

89   1600°C for the LS4 composition, in agreement with their respective liquidus temperature

90   (Eppler, 1963; Schairer & Bowen, 1955; Schairer & Bowen, 1956). Melts were quenched to

91   glass by placing the bottom of the crucible in liquid H_2O. The resulting starting materials

92   were stored at 110°C to avoid reaction with atmospheric water, an effect particularly critical

93   for the KS4 glass (Schairer & Bowen, 1955). Chemical analysis of the starting glasses, shown

94   in Table 1, were obtained by using a JEOL FE-SEM equipped with an energy dispersive

95   spectrometer. Measurements were performed on 25 x 25 micron areas with a 15 kV and 1.04

96   nA current. Lithium was quantified by difference.

97   Hydrous glasses were synthesized by melting the starting glasses together with known

98   amounts of H_2O in a piston-cylinder apparatus (Boyd & England, 1960). To this end, glasses

99   were first crushed to powder in ethanol, and then heat-treated at 400°C for 1 hour to ensure

100   complete removal of the ethanol. Then, glass powder and liquid H_2O were added in ~10 mm

101   long, 5 mm diameter platinum capsules, which were welded shut and placed in ¾-inch

102   diameter furnace assemblies, based on the design of Kushiro (1976). The products were then

103   subjected to the desired pressure (1.5 GPa) and temperature (1450 ˚C for NS4, 1550 °C for

104   KS4 and 1650 ˚C for LS4) for 90 minutes. Temperatures were measured with type S

105   thermocouples with no correction for pressure on their *emf*. Such pressure effects may be as

106   much as 10°C (Mao et al., 1971). Pressure was calibrated against the melting point of NaCl

107   and the calcite-aragonite transformation (Bohlen, 1984). Estimated uncertainties are ~10°C

108   and ~0.1 GPa, respectively.

109   Transmission infrared spectra were recorded using a Jasco[®] IMV-4000 multi-channel

110   infrared spectrometer with a 10X objective, an MCT detector and the standard light source, a

111   100μm aperture, and 1000 acquisitions. The hydrous glasses were double-polished to a

112   thickness in the 20-110 μm range by using oil in order to avoid any reaction of their surface

113   with water. For KS4 composition glasses, two sets of samples were used. One was ~20 μm

114   thick and was used for recording the 3600 cm^{-1} O-H stretching band. However, those ~20 μm

115   samples were to thin for acquisition of combination signals. Consequently, another thicker set

116   of samples (~100 μm) were prepared for this purpose. The glass samples were placed on BaF_2

117   windows during measurements. After each spectrum, the sample was moved aside and a

118   background spectrum was recorded at the same spot. Division of sample spectra by

119   background spectra gave the final absorbance spectra, which were normalized to samples

120   thicknesses.

121   Raman spectra were recorded using a Jasco[®] NRS3100 spectrometer, equipped with a

122   holographic notch filter, a single monochromator, and a 1024x128 Andor[®] DV401-F1 CCD

123   Peltier-cooled at -71°C. A Coherent[®] solid laser line of 490 nm was used to excite samples,

124   with a power of ~44 mW on the sample. The laser beam was focused through a 50X

125   Olympus[®] lens. Measurements were done with a 1200 grooves/mm grating. Frequency

126   accuracy of the Raman spectrometer was checked by using the 520.7 cm^{-1} Raman peak of

127   pure silicon. All spectra are unpolarized. After acquisition, a baseline constrained in the

128   spectral portions devoid of signal near 2000 and 3900 cm^{-1} was subtracted from the spectra.

129   The intensities of baseline-subtracted spectra were normalized to their total spectral area

130   (calculated between 250 and 3900 cm^{-1}). Further details about spectra processing are available

131   in Le Losq et al. (2014a).

132   Total water concentration of glasses was estimated by using the FTIR and Raman spectra.

133   Absorption coefficients for the 4500 and 5200 cm^{-1} IR peaks in NS4 glasses are available in

134   the literature. We used the protocol of Yamashita et al. (2008) together with their absorption

135   coefficients, which were derived by using total water concentrations determined

136   independently with Karl-Fisher titration. Because of that and despite the fact that the present

137   study will discuss the use of the 4500 cm^{-1} IR peak for inferring $[OH^-]$ abundance, the FTIR-

138   based $[OH^-]$ + $[H_2O_{mol}]$ sum is not affected by possible error in the assignments and

139   attributions of the IR absorption peaks. As IR absorption coefficients are not available for

140   KS4 and LS4 glasses, Raman spectroscopy was used to estimate the water concentration of

141   these glasses. A protocol similar to that described in Le Losq et al. (2012) was used. The

142   variations of the areas of the Raman signals assigned to O-H stretching, located between 2000

143   and 4000 cm^{-1}, was calibrated with the FTIR-based total water concentrations of the same

144   NS4 glasses. This calibration was then used with the other LS4 and KS4 glass series to

145   determine their water concentration. More details are available in Le Losq et al. (2014a).

146   Table 2 reports the measured water concentrations of the glasses.

147

148   **Results**

149   In the FTIR spectra of hydrous alkali silicate glasses, strong peaks at ~1630 (ν_B H-O-

150   H), ~2350 (A in Fig. 1), ~2800 (B in Fig. 1) and ~3570 cm^{-1} (C in Fig. 1) are observed. The

151   IR spectra of hydrous NS4 glasses are similar to those previously published for NS4 hydrous

152   compositions (e. g., Uchino et al., 1991; Zotov & Keppler, 1998). Spectra of hydrous KS4 and

153   LS4 glasses have not been reported in the literature to our knowledge.

154   The three peaks (A, B, and C) in the 2000-4000 cm^{-1} portion of FTIR spectra are

155   attributed to stretching of O-H bonds in H_2O_{mol} and OH$^-$ groups. The 1630 cm^{-1} peak is

156   assigned to the bending vibrational mode of H_2O_{mol} species (Bartholomew et al., 1980;

157   Scholtze, 1960; Uchino et al., 1991; Wu, 1980; Zotov & Keppler, 1998). The other small

158   peaks located at frequencies below 2000 cm^{-1} probably arise from overtones of the vibrational

159   modes of the glass silicate network (see the study of Efimov & Pogareva, 2006 for instance)

160   and are neglected because of their minor importance regarding the topic of this study. Above

161   3800 cm^{-1}, peaks from the combination modes are present but not visible at the scale of

162   Figure 1. They will be discussed in detail latter.

163   In the IR spectra of all glasses, the peaks A and B are broad, whereas the peak C is

164   considerably sharper. Absorbance values of those peaks are reported in Table 2. At given

165   water concentration, the absorbance intensities vary strongly as a function of the ionic radius

166   of the alkali metal (Fig. 1). The absorbance intensities of peaks A and B increase strongly

167   with increasing ionic radius of alkali, whereas that of peak C decreases. In a given

168   composition, increasing water content results in a general absorbance increase of all

169   contributions, but the absorbance of the ~3600 cm^{-1} contribution increases slightly more

170   rapidly than the others (Table 2 and Fig. 1).

171   The three peaks in the infrared spectra, A, B and C, are also visible in Raman spectra

172   of the same glasses (Fig. 2). As already emphasized by FTIR data (Fig. 1), the comparison of

173   the spectra of the silicate glasses containing 17.6 mol% H_2O highlights that with increasing

174   the ionic radius of the alkali, peaks A and B grow at the expense of the peak C. For

175   comparison purposes, the Raman spectrum of a pure SiO_2 glass with 20 mol% H_2O is also

176   reported in Figure 2. In this latter spectrum, the signal intensity below 3000 cm^{-1} is negligible

177   compared with the intensity between 3000 and 4000 cm^{-1}. The two peaks located near 3595

178   and 3650 cm^{-1} can be attributed to O-H stretching from OH$^-$ groups in different environments

179   (*the 3595 cm^{-1} peak is only observed in H_2O-rich silica glasses*), but their attribution remains

180   unclear and is subjected to speculation (see for instance the studies of Davis & Tomozawa,

181   1996; Efimov & Pogareva, 2006; Holtz et al., 1996; Mysen & Virgo, 1986a).

182   The shape of the peaks near 4500 and 5200 cm^{-1} in the IR spectra also varies

183   significantly with the glass composition at given total water content (Fig. 3). In IR spectra of

184   the LS4 glasses, two asymmetric peaks are observed at ~4520 and ~5240 cm^{-1}. Their

185   intensities increase with increasing water concentration, but in different ways. The ~4520 cm$^-$

186   ^{1} peak is more intense than the ~5240 cm^{-1} peak in the IR spectrum of the LS4 + 3.3 mol%

187   H_2O glass (Figs. 3, 4). In contrast, at 17.6 mol% H_2O, the ~5240 cm^{-1} peak is more intense

188   than the ~4520 cm^{-1}. Therefore, the intensity of the ~4520 cm^{-1} peak increases less and less

189   with water addition, whereas that of the ~5240 cm^{-1} peak shows an opposite trend (Fig. 4). If

190   these two IR peaks are attributed to OH$^-$ (4520 cm^{-1}) and H_2O_{mol} (5240 cm^{-1}) species, as has

191 commonly been the case (see Introduction), their intensity variations are consistent with a

192 decrease of the OH^-/H_2O_{mol} ratio with increasing water concentration in LS4 glass. In addition

193 to those two peaks, a small and broad peak near 4000 cm^{-1} is visible. This peak is well

194 separated from the ~4520 cm^{-1} peak (Fig. 3, LS4 spectra). Its intensity increases with water

195 concentration, but is also affected by the high-frequency tail of the 3600 cm^{-1} peak. Indeed,

196 this tail shifts toward high frequency and probably varies in intensity with increasing water

197 concentration (Fig. 3). This topological evolution probably affects the shape of the peak

198 located near 4000 cm^{-1}. The origin of the latter is unresolved but may involve unidentified

199 combination modes of both H_2O_{mol} and OH^- species (see the discussion of Stolper, 1982 and

200 also Davis & Tomozawa, 1996; Efimov & Pogareva, 2006).

201 The three peaks near 4000, 4520 and 5236 cm^{-1} also are observed in the IR spectra of

202 NS4 hydrous glasses. Their intensities vary with water concentration in a way similar to that

203 observed in the LS4 spectra (Figs. 3, 4). However, the separation of the ~4000 and ~4520 cm$^-$

204 ^{1} peaks is less pronounced in NS4 spectra than in LS4 spectra (Fig. 3). It becomes even less

205 pronounced in the KS4 spectra, in which the peaks in the 3900-4700 cm^{-1} range are poorly

206 defined (Fig. 3). In the KS4 + 3.3 mol% H_2O spectrum, a small peak at ~4510 cm^{-1} is

207 observed, and there is no peak near 5200 cm^{-1}. No peak is observed near 4000 cm^{-1}, but the

208 high-frequency end of the 3600 cm^{-1} O-H stretch band affects the intensity of the spectrum in

209 the 3800-4200 portion of spectra (Fig. 3). In the KS4 + 9.4 mol% H_2O glass spectrum, the

210 ~4510 cm^{-1} peak is barely visible. The IR absorbance between 3800 and 4800 cm^{-1} shows a

211 global, nearly linear, decay. There is no intensity near 5200 cm^{-1} in this spectrum. At 17.6

212 mol% H_2O, the ~4510 cm^{-1} contribution is very broad and preceded by another broad small

213 peak centered near 4050 cm^{-1}. Finally, a small symmetric peak is present at ~5230 cm^{-1} in the

214 spectrum of this water-rich composition.

215   The absence of the ~5200 cm^{-1} peak in the IR spectra of the KS4 with 3.3 and 9.4

216   mol% H_2O and its low intensity in the spectrum of KS4 with 17.6 mol% H_2O (Figs. 3, 4)

217   indicate that essentially all the water is present as OH^- groups in KS4 compositions, in

218   agreement with results from ^{1}H NMR spectroscopy (Le Losq et al., 2014a). In addition, the IR

219   results and previous ^{1}H NMR data (Le Losq et al., 2014a) both indicate that, at fixed water

220   concentration, the OH^-/H_2O_{mol} ratio increases strongly with increasing ionic radius of alkali in

221   the order Li < Na < K (Fig. 3; Le Losq et al., 2014a). However, despite their very high OH^-

222    $/H_2O_{mol}$ ratios, the KS4 hydrous glasses show the less resolved OH^- combination peaks in

223   their IR spectra in comparison to the NS4 and LS4 compositions (Fig. 3). Interestingly, they

224   also show the highest intensities in the 4000-4700 cm^{-1} portion of spectra (see comparison in

225   Fig. 5).

226

Discussion

228   Increasing the ionic radius of the alkali cation in hydrous silicate glasses, formed by

229   quenching melts equilibrated at high temperature and pressure, produces in both the FTIR and

230   Raman spectra a strong intensity increase of two peaks at frequencies below 3000 cm^{-1} and

231   attributed to O-H stretch in H_2O_{mol} and OH^- groups (Figs. 1, 2 and 5). The exact frequency of

232   the contribution B also decreases by ~100 cm^{-1} with increasing the alkali ionic radius (Figs. 2,

233   5). Such effect probably arises from the modification of the inter-oxygen O-O distance around

234   protons (e.g. the distance of O-H··O bonds, with ·· hydrogen bond) as a function of the ionic

235   radius of the alkali. Indeed, from ^{1}H NMR spectroscopy of the same alkali silicate glasses, a

236   decrease of the mean O-O distance around protons does occur with increasing the ionic radius

237   of the alkali (Le Losq et al., 2014a). This mean O-O distance is ~287 pm in LS4 glasses and

238   ~255 pm in KS4 glasses (Le Losq et al., 2014a). The frequency of the IR and Raman bands

239   assigned to O-H stretching is related to the inter-oxygen O-O distance around protons

240   (Nakamoto et al., 1955; Novak, 1974; Wall & Hornig, 1965). From the data compilation of

241   Novak (1974), the mean O-O distances of ~287 and ~255 pm correspond to mean O-H stretch

242   frequency of ~3500 and ~2300 cm^{-1}, respectively. These frequencies correspond to the main

243   peaks C and A in the FTIR and Raman spectra of LS4 and KS4 glasses (Figs. 2, 3). Therefore,

244   FTIR and Raman data confirm that increasing the alkali ionic radius in hydrous binary silicate

245   glasses promotes a decrease of O-O distances around protons.

246   An increase of the alkali ionic radius also results in a significant increase of the OH$^-$

247   /H_2O_{mol} ratio, so that the hydrous KS4 glasses, for example, contain mostly OH$^-$ groups at

248   least up to the maximum total water content of this study (17.6 mol % H_2O). Given that peaks

249   A and B are well expressed in the KS4 glasses (Figs. 1, 2, 3 and 5), it appears that those two

250   peaks arise from O-H stretch in OH$^-$ groups. Therefore, their combination with the Si-O-H

251   stretch vibrational mode located near 910 cm^{-1} (Fig. 2) must give a complex OH$^-$ combination

252   signal. This is indeed observed when superimposing the spectra of the 17.6 mol% glasses

253   (Fig. 5, bottom). As the alkali ionic radius increases, the intensity of peaks A and B increase.

254   As a result, the intensity between 4100 and 4400 cm^{-1} also increases (arrow in Fig. 5, bottom),

255   and the signal between 4000 and 4700 cm^{-1} becomes less and less resolved. Consequently, the

256   combination of the O-H fundamental stretch signals from OH$^-$ groups with the signal assigned

257   to Si-O-H stretching can result in a broad combination signal that extends from 4700 cm^{-1}

258   down to at least 3800 cm^{-1}, and thus becomes mixed with the unattributed ~4000 cm^{-1} peak

259   and with the high-frequency end of the O-H stretching band in the IR spectra (Fig. 5).

260

261   **Implication**

262   The IR combination signal of OH$^-$ groups is often reported to be near 4500 cm^{-1}

263 because most of the signals assigned to O-H stretch are located above 3000 cm^{-1} in many

264 aluminosilicate glasses (Stolper, 1982). However, the data reported here show that IR

265 combination signals used to study the speciation of water in glasses and melts can be complex

266 because of the strong dependence of the O-H stretch frequency on the O-O distances around

267 protons, and hence, on the glass structure. In any study of hydrous silicate glasses, the strong

268 dependence of the proton environment as a function of the type of metallic cation within the

269 silicate network of glasses must be kept in mind, because this dependence affects the IR

270 combination signals and therefore the accuracy of the determination of water speciation with

271 IR spectroscopy. The combination peaks in IR spectra of alkali-rich or alkaline-earth rich

272 natural compositions, such as alkali phonolite and phono-trachyte for instance, may,

273 therefore, be broadened as illustrated in the simple compositions used in this study. However,

274 this is purely speculative at this time and has to be investigated. In all cases, we advise users

275 to check the occurrence and importance of low-frequency (<3000 cm^{-1}) O-H stretching

276 signals in glasses before using the 4500 and 5200 cm^{-1} combination peaks as proxies for [OH$^-$

277] or [H$_2$O$_{mol}$]. If those low-frequency O-H stretching signals are significant, any use of the

278 combination peaks to determine [OH$^-$] or [H$_2$O$_{mol}$] is problematic.

279

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379

380   Table 1: Chemical composition of LS4, NS4 and KS4 anhydrous glasses. nom. mol%, nom.

381   wt% and meas. wt% refer respectively to the nominal compositions in mol and wt%, and to

382   the measured composition in wt%. *Lithium has been determined by difference. Errors are

383   given at the 1σ confidence interval.

		SiO_2	Li_2O*	Na_2O	K_2O
LS4	nom. mol%	80.00	20.00	0.00	0.00
	nom. wt%	88.94	11.08	0.00	0.00
	meas. wt%	88.77(94)	11.23(75)	*n.a.*	*n.a.*
NS4	nom. mol%	80.0	20.0	0.00	0.00
	nom. wt%	79.50	0.00	20.50	0.00
	meas. wt%	80.38(36)	*n.a.*	19.62(31)	*n.a.*
KS4	nom. mol%	80.0	20.0	0.0	0.0
	nom. wt%	71.84	0.00	0.00	28.16
	meas. wt%	71.16(49)	*n.a.*	*n.a.*	28.84(28)

384
385

386   Table 2: Water concentration in mol and wt% of glasses. Nom.: nominal water concentration.

387   I_A, I_B and I_C FTIR absorbance intensities correspond to those observed on Fig. 1 for peaks A,

388   B and C (as this is for indicative purpose, no error are indicated). Errors are given at the 2σ

389   confidence interval.

390

Glass	nom. mol% H_2O	nom. wt% H_2O	Wt% H_2O FTIR	Wt% H_2O RAMAN	FTIR absorption, cm^{-1} I_A	I_B	I_C
	3.28	1.12	-	0.97(30)	38.6	49.5	76.1
LS4	9.40	3.35	-	3.61(30)	98.3	152.8	277.2
	17.64	6.67	-	6.75(30)	190.0	316.3	603.7
	3.28	1.00	1.21(12)	0.98(30)	96.4	100.0	37.1
NS4	9.40	3.00	2.89(18)	3.25(30)	238.6	264.3	124.8
	17.64	6.00	6.00(29)	5.96(30)	500.5	604.2	383.7
	3.28	0.90		1.04(30)	172.4	166.0	31.8
KS4	9.40	2.71	-	2.76(30)	344.6	345.4	65.1
	17.64	5.44	-	4.84(30)	702.1	729.9	138.2

391

392

393

394   Figure 1: FTIR spectra of LS4 (top), NS4 (middle) and KS4 (bottom) glasses with 0.0, 3.3,

395   9.4 and 17.6 nom. mol% water (from bottom to top in the figures respectively). A, B and C

396   are visual markers for the three observed peaks attributed to the O-H stretch (ν_s O-H) in

397   H_2O_{mol} and OH^- groups. The peak at 1630 cm^{-1} arises from the bending of H_2O_{mol} (ν_B H-O-

398   H). Signal below 1300 cm^{-1} is at saturation and therefore not shown here. Spectra are offset of

399   5 absorbance units for clarity.

400

401   Figure 2: Raman O-H stretching signal in the KS4, NS4 and LS4 glasses with 17.6 nom.

402   mol% H_2O. For comparison, the peak assigned to O-H stretch in a SiO_2 glass with 20 mol%

403   H_2O is also shown (made at 1.5 GPa - 1650°C). A, B and C are visual markers for the three

404   observed peaks (see also Figure 1). Small sharp peaks near 2330 cm^{-1} arise from the N_2

405   atmospheric signal. Insert: signals from the Si-O-Si bending (the 500 cm^{-1} band) and the Si-O

406   stretching modes (the 1100 cm^{-1} band) of the KS4 + 17.6 mol% H_2O are shown (see Le Losq

407   et al., 2014b; Mysen, 1990; Mysen & Cody, 2005; Mysen et al., 1982 for more details and

408   attributions for silicate species); the signal from the Si-O-H stretch may give rise to the peak

409   near 910 cm^{-1} that is perfectly visible on this spectrum (Malfait, 2009; Spiekermann et al.,

410   2012; Zotov & Keppler, 1998).

411

412   Figure 3: Details of the 3800 - 5600 cm^{-1} region of the FTIR spectra of KS4, NS4 and LS4

413   glasses. From bottom to top in the figures: 0.0, 3.3, 9.4, 17.6 nom. mol% H_2O. Spectra are

414   offset of 1 absorbance unit for clarity. The dotted lines indicate the presence of peaks in the

415   spectra (see text).

416

417   Figure 4: Absorbance of the peaks located at ~4500 and ~5200 cm^{-1}, observed on the spectra

418   of hydrous glasses presented in Figure 3, reported as a function of the nominal water content

419   of glasses. Absorbance was measured at the maximum intensity of peaks. Please note that

420   those values were measured on spectra for which no background subtraction was applied, so

421   that those values cannot be used to retrieve the water concentration of the glasses. Lines are

422   guides for the eyes.

423

424   Figure 5: Top: 2000-4000 cm^{-1} portion of spectra of 17.6 mol% H_2O KS4, NS4 and LS4

425   glasses, the A, B and C marker correspond to those on figure 1; Bottom: 3800 - 5600 cm^{-1}

426   region of same spectra. The arrows are used as visual marker for highlighting the effects

427   produced by an increase of the ionic radius of the alkali in the glasses (see text).

428

429