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**REVISION 1**

**The nearly complete dissociation of water in glasses with strong aluminum avoidance**

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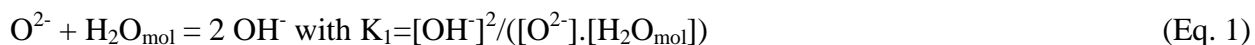
15       **Abstract** – Water is dissolved in silicate glasses and melts as hydroxyl groups  
16       and molecular water, with mostly hydroxyl groups at low water contents and  
17       mostly molecular water at high water contents. However, we recently predicted  
18       that water will be dissociated nearly completely in potassium aluminosilicate  
19       glasses with more alumina than silica because of the strong aluminum avoidance  
20       and the strong tendency for Al-O-Al linkages to hydrolyze in such glasses. In the  
21       present study, I test this prediction on hydrous  $K_2Al_2SiO_6$  glasses: the Raman and  
22       infrared absorption spectra show that water is indeed predominantly present as  
23       hydroxyl groups, even for glasses with more than 7 wt% water. This observation  
24       validates the previously proposed speciation reactions, demonstrates that  
25       variations in water speciation are related to the nature of the cations to which the  
26       hydroxyl groups are bonded, and indicates that the classical picture of water  
27       dissolution, with predominantly molecular water at high water contents, may not  
28       apply near compositional extremes.

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30       **Key words** – Potassium aluminosilicate glasses; Raman spectroscopy; Infrared  
31       absorption spectroscopy; Water speciation; Aluminum avoidance.

## INTRODUCTION

It has been known for nearly half a century that water is dissolved in silicate melts and glasses as hydroxyl groups (OH) and molecular water ( $\text{H}_2\text{O}_{\text{mol}}$ ) (Eq. 1) (Scholze, 1966; Stolper, 1982a, b).



Since these pioneering studies, a large experimental effort has been devoted to quantify the OH/ $\text{H}_2\text{O}_{\text{mol}}$  speciation as a function of composition and temperature with Fourier transform infrared (FTIR) spectroscopy (Behrens and Muller, 1995; Behrens and Nowak, 2003; Behrens et al., 1996; Behrens and Yamashita, 2008; Malfait, 2009; Nowak and Behrens, 1995, 2001; Shen and Keppler, 1995; Silver and Stolper, 1989; Silver et al., 1990; Stolper, 1982a, b) and nuclear magnetic resonance (NMR) spectroscopy (Schmidt et al., 2001). As a result, the OH/ $\text{H}_2\text{O}_{\text{mol}}$  speciation of magmatic glasses and melts is now relatively well known.

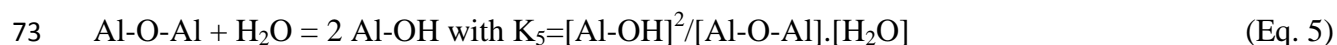
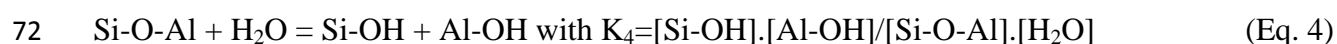
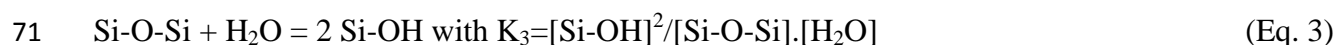
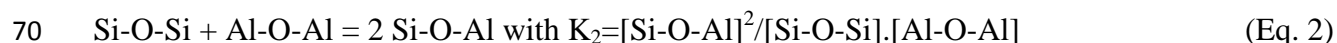
The nature of the hydroxyl groups has also been investigated. In Al-free silicate glasses, hydroxyl groups are mostly present as silanol groups (Si-OH), with additional free hydroxide (M-OH), i.e. hydroxyls that are ionically bonded to network modifiers (M, e.g. Mg, Ca), for highly depolymerized compositions (Farnan et al., 1987; Kummerlen et al., 1992; Xue and Kanzaki, 2004; Zotov and Keppler, 1998). **The amount of free hydroxide decreases with increasing degree of polymerization and decreasing cationic field strength of the network-modifying or charge-balancing cations (Xue and Kanzaki, 2004, 2008). Thus, no significant**

55 **amounts of free hydroxyls are expected for metaluminous alkali aluminosilicate glasses.** For  
56 Al-bearing glasses, initial NMR data were interpreted to indicate the absence of significant Si-  
57 OH and Al-OH groups (Kohn et al., 1989; Kohn et al., 1994). However, subsequent NMR and  
58 infrared spectroscopic studies demonstrated that water is dissolved in aluminosilicate glasses as  
59 Si-OH, Al-OH in addition to M-OH for more depolymerized compositions (Malfait and Xue,  
60 2010a, b; Sykes and Kubicki, 1993, 1994; Xue and Kanzaki, 2009; Xue, 2009; Xue and Kanzaki,  
61 2006, 2007, 2008; Zeng et al., 1999, 2000).

62

63 Recently, we have quantified the Si-OH and Al-OH abundances of nominally fully  
64 polymerized sodium and potassium aluminosilicate glasses with  $^1\text{H}$ ,  $^{27}\text{Al}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{29}\text{Si}$ - $^1\text{H}$   
65 NMR spectroscopy (Malfait and Xue, submitted; Malfait and Xue, 2010a, b). The derived  
66 concentrations enabled us to constrain the equilibrium constants ( $K_2$ - $K_5$ ) for the aluminum  
67 avoidance reaction (Eq. 2) (Loewenstein, 1954; Tossel, 1993) and the different hydrolysis  
68 reactions (Eqs. 3-5).

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75 **One of the striking results of the study on potassium aluminosilicate glasses was the**  
76 **strong aluminum avoidance ( $K_2=1340$ ) compared to sodium aluminosilicate glasses**  
77 **( $K_2=50$ ). Please note that this observation is not incompatible with the possible occurrence**

78 **of Al rich regions in orthoclase melts (Le Losq and Neuville, 2013; Rammensee and Fraser,**  
79 **1982), because the proposed Al/(Al+Si) ratio of these regions (~0.33) is low enough to easily**  
80 **accommodate a strong Al avoidance through the rearrangement of the next-nearest-**  
81 **neighbors. The strong** aluminum avoidance for potassium aluminosilicate glasses drives the  
82 hydrolysis of Al-O-Al linkages ( $K_5=27$ ) upon the addition of water. For dry glasses with  
83  $Al/(Al+Si)<0.5$ , Al-O-Al linkages can be avoided through rearrangement of the next-nearest-  
84 neighbors of Al, but for samples with higher Al contents, significant amounts of Al-O-Al must  
85 be present. As a result, most of the water added to such glasses will be consumed to hydrolyze  
86 the Al-O-Al bridges. Indeed, even at high water contents, little  $H_2O_{mol}$  is predicted to be present  
87 in these glasses (Fig. 1), resulting in very large  $OH/H_2O_{mol}$  ratios and values for  $K_1=[OH]^{-2}/([O^{2-}$   
88  $].[H_2O_{mol}]$ ).

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90 In this study, I test the predictions made by the speciation model derived from  $^1H$  and  
91  $^{27}Al$ - $^1H$  NMR data (Eqs. 2-5) by verifying one of its most striking predictions: **the nearly full**  
92 **dissociation of water in glasses for  $Al/(Al+Si)>0.5$ , even at high water content. For this, I**  
93 **synthesized  $K_2Al_2SiO_6$  glasses ( $Al/(Al+Si)=0.67$ ) with nominally 5 and 8 wt% water and**  
94 **determined the water speciation by Raman and FTIR spectroscopy. The spectra of the**  
95 hydrous  $K_2Al_2SiO_6$  glasses indicate that the concentration of  $H_2O_{mol}$  is indeed much lower  
96 compared to conventional compositions. This observation validates the results and methodology  
97 by Malfait and Xue (2010, subm.) and illustrates the strong effect of aluminum avoidance on  
98 water speciation.

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## EXPERIMENTAL METHODS

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102           The synthesis of a dry  $K_2Al_2SiO_6$  glass as starting material is extremely challenging due  
103 to the excessively high, still unknown, liquidus temperature ( $> 2000$  K) for this composition  
104 (Schaerer and Bowen, 1947). In order to synthesize the hydrous glasses, mixtures of  $K_2CO_3$ ,  
105  $Al_2O_3$  and  $SiO_2$  were decarbonated and sintered overnight at 1073 K and welded in Pt capsules  
106 with de-ionized water. Synthesis experiments were performed in an end-loaded piston cylinder  
107 apparatus (Boyd and England, 1960) with a talc-silica glass-MgO assembly at 0.7 GPa and 1923  
108 K for 30 and 60 minutes for nominal water contents of 5 and 8 wt%, respectively. The melts  
109 were quenched to glasses by switching of the power to the graphite furnace (quench rate  $\sim 150$   
110 K/s). The composition and homogeneity of the glasses was verified by electron microprobe  
111 analysis (JEOL, JXA-8200) with an acceleration voltage of 15 kV, using a large spot size (30  
112  $\mu m$ ) and low beam current (2 nA) to avoid the migration of potassium under the electron beam  
113 (Table 1). Natural orthoclase was used as a standard for all elements. Within analytical  
114 uncertainty, the compositions were found to be identical to the target composition. The  
115  $K_2Al_2SiO_6$ -5 sample contains euhedral crystals ( $\sim 20$ -50  $\mu m$ ) of  $K_2Al_2SiO_6$ , indicating that the  
116 liquidus temperature is above 1923 K for 5 wt% water, but the glass phase was otherwise  
117 homogenous. The  $K_2Al_2SiO_6$ -8 sample was completely glassy and homogenous. **The difficulty**  
118 **of preparing carbonate free glasses with very high  $K_2O$  content has been reported before**  
119 **(Bourgue and Richet, 2001; Malfait et al., 2007). Indeed, the Raman spectra contain a**  
120 **strong, relatively sharp band near  $1050\text{ cm}^{-1}$  and a very weak, broad band near  $1420\text{ cm}^{-1}$**   
121 **(Fig. 2). Similar bands at the same positions were observed for carbonate-bearing**  
122 **potassium silicate glasses (Bourgue and Richet, 2001). The carbonate content cannot be**  
123 **robustly quantified from the Raman spectra because our unusual glass composition lies far**

124 **outside the calibration ranges for existing quantification models (Morizet et al., 2013).**  
125 **Nevertheless, a comparison of the intensity of the 1050 cm<sup>-1</sup> band in the Raman spectra our**  
126 **glasses to the spectra of Bourgue and Richet (2001) indicates a carbonate content on the**  
127 **order of 2.1 and 0.8 wt% (CO<sub>2</sub> equivalents) in the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6-5</sub> and the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6-8</sub> glass,**  
128 **respectively. Note that these estimates may be off by as much as a factor of two due to**  
129 **differences in glass composition between our potassium aluminosilicate glasses and the**  
130 **aluminum-free glasses studied by Bourgue and Richet.**

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132 The Raman spectra were collected with a LabRam Raman spectrometer, equipped with  
133 an external Argon laser (514 nm, 6 mW measured at the sample surface). The infrared absorption  
134 spectra were collected on double polished sections (540 μm thick) with a Bruker Hyperion 3000  
135 microscope connected to a Vertex 70 interferometer. Spectra were collected on three spots per  
136 section with a spectral resolution of 4 cm<sup>-1</sup>. In order to compare the Raman and infrared  
137 absorption spectra of the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses to those of a sample with a more typical OH/H<sub>2</sub>O<sub>mol</sub>  
138 speciation, the infrared and Raman spectra of a hydrous haplogranitic sample with similar water  
139 content (Malfait et al., 2014) were also measured.

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## 141 **RESULTS AND DISCUSSION**

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143 The Raman spectrum of the haplogranitic glass (Fig. 2) displays two major bands related  
144 to vibrations of hydrous species: a strong, broad band for the fundamental O-H stretching  
145 vibration near 3600 cm<sup>-1</sup> and a weaker, narrower band for the fundamental H-O-H bending  
146 vibration near 1600 cm<sup>-1</sup>. The former band contains signal from both OH and H<sub>2</sub>O<sub>mol</sub>, the latter

147 from  $\text{H}_2\text{O}_{\text{mol}}$  only. The band near  $1600\text{ cm}^{-1}$  is within the noise for the spectra of the  $\text{K}_2\text{Al}_2\text{SiO}_6$   
148 glasses. This suggests, at least qualitatively, that the concentration of  $\text{H}_2\text{O}_{\text{mol}}$  is low in these  
149 glasses. The contrasting behavior between the haplogranitic and  $\text{K}_2\text{Al}_2\text{SiO}_6$  glasses is confirmed  
150 by the FTIR spectra (Fig. 3): the overtone related to  $\text{H}_2\text{O}_{\text{mol}}$  near  $5200\text{ cm}^{-1}$  is much stronger than  
151 the overtone related to OH near  $4500\text{ cm}^{-1}$  in the haplogranitic glass, but this is reversed for the  
152  $\text{K}_2\text{Al}_2\text{SiO}_6$  glasses. Unfortunately, the range in water content for which  $\text{K}_2\text{Al}_2\text{SiO}_6$  glasses can be  
153 synthesized is relatively narrow: at water contents up to at least 5 wt%, the liquidus temperature  
154 exceeds the melting temperature of the Pt capsules and at water contents above 8 wt%, the melts  
155 cannot be quenched to a glass. As a result, it was not possible to synthesize a set of samples with  
156 a range of OH/ $\text{H}_2\text{O}_{\text{mol}}$  ratios and to determine the molar absorption coefficients for the 4500 and  
157  $5200\text{ cm}^{-1}$  bands from an internally consistent calibration.

158

159 **The band near  $3600\text{ cm}^{-1}$  has a more pronounced tail to lower wavenumbers for the**  
160  **$\text{K}_2\text{Al}_2\text{SiO}_6$  glasses compared to the haplogranitic glass (Fig. 2). In a seminal paper,**  
161 **Libowitzky (1999) demonstrated that the frequency of the O-H stretching vibrations**  
162 **correlates with the hydrogen bond strength. Thus, Raman and infrared absorption bands**  
163 **at lower wavenumbers indicate strong hydrogen bonding and short OH...O lengths.**  
164 **Because water-rich glasses typically display both high degrees of hydrogen bonding and**  
165 **high  $\text{H}_2\text{O}_{\text{mol}}$  contents, the correlation between hydrogen bonding and O-H stretching**  
166 **frequency (Libowitzky, 1999) produces a secondary correlation between the O-H stretching**  
167 **frequency and water speciation. Several studies tried to use this secondary correlation to**  
168 **derive OH/ $\text{H}_2\text{O}_{\text{mol}}$  speciation data from the Raman spectra of hydrous glasses, with**  
169 **variable success (Behrens et al., 2006; Chabiron et al., 2004; Le Losq et al., 2013; Zajacz et**



170 **al., 2005). It is important to note that, despite the secondary correlation between the O-H**  
171 **stretching frequency and water speciation, the presence of Raman signal at relatively low**  
172 **wavenumbers does not *a priori* imply the presence of molecular water. In fact, there are**  
173 **numerous minerals that contain hydroxyl groups with O-H stretching vibrations far below**  
174 **3600 cm<sup>-1</sup> (Behrens and Muller, 1995; Libowitzky, 1999).**

175

176 In summary, both the Raman (Fig. 2) and infrared absorption (Fig. 3) spectroscopic data  
177 provide strong evidence for the predominance of OH over H<sub>2</sub>O<sub>mol</sub> in the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses.  
178 Thus, the vibrational spectroscopic data confirm the prediction of the OH/H<sub>2</sub>O<sub>mol</sub> speciation  
179 based on NMR spectroscopic data on samples with lower Al contents (Fig. 1) and validate the  
180 analytical procedure and speciation model (Malfait and Xue, submitted; Malfait and Xue, 2010a,  
181 b) with independent methods.

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## IMPLICATIONS

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185 The strong dissociation of water in the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses is directly related to the  
186 instability of the Al-O-Al linkages associated with the strong aluminum avoidance in potassium  
187 aluminosilicate glasses, evidenced by high equilibrium constants for reactions 2 and 5. **The**  
188 **strong tendency for Al-O-Al linkages to hydrolyze compared to other oxygen bridges has**  
189 **also been observed for zeolite materials (Stebbins et al., 1999).** The potassium aluminosilicate  
190 glasses provide a model system where the strong variation of the OH/H<sub>2</sub>O<sub>mol</sub> speciation can be  
191 rationalized in terms of the nature of the cations to which the hydroxyl groups are bonded. Future  
192 work on the nature of the cations to which the hydroxyl groups are covalently (e.g. Si<sup>4+</sup>, Al<sup>3+</sup>) or

193 ionically (e.g.  $Mg^{2+}$ ,  $Ca^{2+}$ ) bonded may help to rationalize, and ultimately predict, the  
194 compositional variations of the  $OH/H_2O_{mol}$  speciation in geologically relevant melts and glasses.  
195 The strong dissociation of water in  $K_2Al_2SiO_6$  glasses with high water content strongly contrasts  
196 to what was observed for all other investigated compositions, for which  $H_2O_{mol}$  is the dominant  
197 species at high water contents (Behrens and Yamashita, 2008; Stolper, 1982a, b). This strikingly  
198 different behavior exemplifies the role of aluminum avoidance on the water speciation and  
199 indicates that the classical picture of water dissolution, with predominantly molecular water at  
200 high water contents, may not apply near extremes in compositions.

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## REFERENCES

204

205

206 Behrens, H. and Muller, G. (1995) An infrared spectroscopic study of hydrogen feldspar ( $HAISi_3O_8$ ).  
207 Mineralogical Magazine 59, 15-24.

208 Behrens, H. and Nowak, M. (2003) Quantification of  $H_2O$  speciation in silicate glasses and melts by IR  
209 spectroscopy - In situ versus quench techniques. Phase Transitions 76, 45-61.

210 Behrens, H., Romano, C., Nowak, M., Holtz, F. and Dingwell, D.B. (1996) Near-infrared spectroscopic  
211 determination of water species in glasses of system  $MAISi(3)O(8)$  ( $M=Li, Na, K$ ): An interlaboratory  
212 study. Chemical Geology 128, 41-63.

213 Behrens, H., Roux, J., Neuville, D.R. and Siemann, M. (2006) Quantification of dissolved  $H_2O$  in silicate  
214 glasses using confocal microRaman spectroscopy. Chemical Geology 229, 96-112.

215 Behrens, H. and Yamashita, S. (2008) Water speciation in hydrous sodium tetrasilicate and hexasilicate  
216 melts: constraint from high temperature NIR spectroscopy. Chemical Geology 256, 306-315.

217 Bourgue, E. and Richet, P. (2001) The effects of dissolved  $CO_2$  on the density and viscosity of silicate  
218 melts: a preliminary study. Earth and Planetary Science Letters 193, 57-68.

219 Boyd, F.R. and England, J.R. (1960) Apparatus for phase equilibrium measurements of pressures up to 50  
220 kbars and temperatures up to  $1750^\circ C$ . . Journal of Geophysical Research 65.

221 Chabiron, A., Pironon, J. and Massare, D. (2004) Characterization of water in synthetic rhyolitic glasses  
222 and natural melt inclusions by Raman spectroscopy. Contributions to Mineralogy and Petrology  
223 146, 485-492.

224 Farnan, I., Kohn, S.C. and Dupree, R. (1987) A study of the structural role of water in hydrous silica glass  
225 using cross-polarization magic angle spinning NMR. Geochimica Et Cosmochimica Acta 51, 2869-  
226 2873.

227 Kohn, S.C., Dupree, R. and Smith, M.E. (1989) A multi-nuclear magnetic-resonance study of the structure  
228 of hydrous albite glasses. Geochimica Et Cosmochimica Acta 53, 2925-2935.

229 Kohn, S.C., Smith, M.E. and Dupree, R. (1994) Comment on "A model for  $H_2O$  solubility mechanisms in  
230 albite melts from infrared spectroscopy and molecular orbital calculations" by D. Sykes and J.D.  
231 Kubicki. Geochimica Et Cosmochimica Acta 58, 1377-1380.

- 232 Kummerlen, J., Merwin, L.H., Sebal, A. and Keppler, H. (1992) Structural role of H<sub>2</sub>O in sodium silicate  
233 glasses: results from <sup>29</sup>Si and <sup>1</sup>H NMR spectroscopy. *Journal of Physical Chemistry* 96, 6405-6410.
- 234 Le Losq, C., Moretti, R. and Neuville, D.R. (2013) Speciation and amphoteric behaviour of water in  
235 aluminosilicate melts and glasses: high-temperature Raman spectroscopy and reaction equilibria.  
236 *European Journal of Mineralogy* 25, 777-790.
- 237 Le Losq, C. and Neuville, D.R. (2013) Effect of the Na/K mixing on the structure and the rheology of  
238 tectosilicate silica-rich melts. *Chemical Geology* 346, 57-71.
- 239 Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in  
240 minerals. *Monatshefte für Chemie* 130, 1047-1059.
- 241 Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates.  
242 *American Mineralogist* 39, 92-96.
- 243 Malfait, W.J. (2009) The 4500 cm<sup>-1</sup> infrared absorption band as a combination of the fundamental (Si,Al)-  
244 OH and O-H vibrations. *American Mineralogist* 94, 849-852.
- 245 Malfait, W.J., Halter, W.E., Morizet, Y., Meier, B.H. and Verel, R. (2007) Structural control on bulk melt  
246 properties: single and double quantum <sup>29</sup>Si NMR spectroscopy on alkali-silicate glasses.  
247 *Geochimica Et Cosmochimica Acta* 71, 6002-6018.
- 248 Malfait, W.J., Seifert, R., Petitgirard, S., Perrillat, J.-P., Mezouar, M., Ota, T., Nakamura, E., Lerch, P. and  
249 Sanchez-Valle, C. (2014) Supervolcano eruptions driven by melt buoyancy in large silicic magma  
250 chambers. *Nature Geoscience* 7, 122-125.
- 251 Malfait, W.J. and Xue, X. (submitted) Hydroxyl speciation in felsic magmas. *Geochimica Et Cosmochimica*  
252 *Acta*.
- 253 Malfait, W.J. and Xue, X.Y. (2010a) The nature of hydroxyl groups in aluminosilicate glasses: quantifying  
254 Si-OH and Al-OH abundances along the SiO<sub>2</sub>-NaAlSiO<sub>4</sub> join by <sup>1</sup>H, <sup>27</sup>Al-<sup>1</sup>H and <sup>29</sup>Si-<sup>1</sup>H NMR  
255 spectroscopy. *Geochimica Et Cosmochimica Acta* 74, 719-737.
- 256 Malfait, W.J. and Xue, X.Y. (2010b) The partial <sup>1</sup>H NMR spectra of Al-OH and molecular H<sub>2</sub>O in hydrous  
257 aluminosilicate glasses: component-resolved analysis of <sup>27</sup>Al-<sup>1</sup>H cross polarization and <sup>1</sup>H spin-echo  
258 MAS NMR spectra. *Solid State Nuclear Magnetic Resonance* 37, 60-68.
- 259 Morizet, Y., Brooker, R.A., Iacono-Marziano, G. and Kjarsgaard, B.A. (2013) Quantification of dissolved  
260 CO<sub>2</sub> in silicate glasses using micro-Raman spectroscopy. *American Mineralogist* 98, 1788-1802.
- 261 Nowak, M. and Behrens, H. (1995) The speciation of water in haplogranitic glasses and melts  
262 determined by in situ near-infrared spectroscopy. *Geochimica Et Cosmochimica Acta* 59, 3445-  
263 3450.
- 264 Nowak, M. and Behrens, H. (2001) Water in magmas: a slippery problem gets more grip. *Earth and*  
265 *Planetary Science Letters* 184, 515.
- 266 Rammensee, W. and Fraser, D.G. (1982) Determination of activities in silicate melts by Knudsen cell  
267 mass spectrometry - I. The system NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub>. *Geochimica Et Cosmochimica Acta* 46,  
268 2269-2278.
- 269 Schairer, J.F. and Bowen, N.L. (1947) Melting relations in the systems Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-  
270 SiO<sub>2</sub>. *American Journal of Science* 245, 193-204.
- 271 Schmidt, B.C., Behrens, H., Riemer, T., Kappes, R. and Dupree, R. (2001) Quantitative determination of  
272 water speciation in aluminosilicate glasses: a comparative NMR and IR spectroscopic study.  
273 *Chemical Geology* 174, 195-208.
- 274 Scholze, H. (1966) Gases and water in glass. *Glass Industry* 47, 546-551,622-628.
- 275 Shen, A.H. and Keppler, H. (1995) Infrared spectroscopy of hydrous silicate melts to 1000C and 10 kbar:  
276 direct observation of H<sub>2</sub>O speciation in a diamond anvil cell. *American Mineralogist* 80, 1335-  
277 1338.
- 278 Silver, L. and Stolper, E. (1989) Water in albitic glasses. *Journal of Petrology* 30, 667-709.

- 279 Silver, L.A., Ihinger, P.D. and Stolper, E. (1990) The influence of bulk composition on the speciation of  
280 water in silicate glasses. *Contributions to Mineralogy and Petrology* 104, 142-162.
- 281 Stebbins, J.F., Zhao, P., Lee, S.K. and Cheng, X. (1999) Reactive Al-O-Al sites in a natural zeolite: triple-  
282 quantum oxygen-17 nuclear magnetic resonance. *American Mineralogist* 84, 1680-1684.
- 283 Stolper, E. (1982a) The speciation of water in silicate melts. *Geochimica Et Cosmochimica Acta* 46, 2609-  
284 2620.
- 285 Stolper, E. (1982b) Water in silicate glasses - an infrared spectroscopic study. *Contributions to*  
286 *Mineralogy and Petrology* 81, 1-17.
- 287 Sykes, D. and Kubicki, J.D. (1993) A model for H<sub>2</sub>O solubility mechanisms in albite melts from infrared  
288 spectroscopy and molecular orbital calculations. *Geochimica Et Cosmochimica Acta* 57, 1039-  
289 1052.
- 290 Sykes, D. and Kubicki, J.D. (1994) A model for H<sub>2</sub>O solubility mechanisms in albite melts from infrared  
291 spectroscopy and molecular orbital calculations - reply. *Geochimica Et Cosmochimica Acta* 58,  
292 1381-1384.
- 293 Tossel, J.A. (1993) A theoretical study of the molecular basis of the Al avoidance rule and of the spectral  
294 characteristics of Al-O-Al linkages. *American Mineralogist* 78, 911-920.
- 295 Xue, X. and Kanzaki, M. (2009) Proton distributions and hydrogen bonding in crystalline and glassy  
296 hydrous silicates and related inorganic materials: insights from high-resolution solid-state nuclear  
297 magnetic resonance spectroscopy. *Journal of the American Ceramic Society* 92, 2803-2830.
- 298 Xue, X.Y. (2009) Water speciation in hydrous silicate and aluminosilicate glasses: direct evidence from  
299 <sup>29</sup>Si-<sup>1</sup>H and <sup>27</sup>Al-<sup>1</sup>H double resonance NMR. *American Mineralogist* 94, 395-398.
- 300 Xue, X.Y. and Kanzaki, M. (2004) Dissolution mechanisms of water in depolymerized silicate melts:  
301 Constraints from <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy and ab initio calculations. *Geochimica Et*  
302 *Cosmochimica Acta* 68, 5027-5057.
- 303 Xue, X.Y. and Kanzaki, M. (2006) Depolymerization effect of water in aluminosilicate glasses: Direct  
304 evidence from <sup>1</sup>H-<sup>27</sup>Al heteronuclear correlation NMR. *American Mineralogist* 91, 1922-1926.
- 305 Xue, X.Y. and Kanzaki, M. (2007) Al coordination and water speciation in hydrous aluminosilicate glasses:  
306 Direct evidence from high-resolution heteronuclear <sup>1</sup>H-<sup>27</sup>Al correlation NMR. *Solid State Nuclear*  
307 *Magnetic Resonance* 31, 10-27.
- 308 Xue, X.Y. and Kanzaki, M. (2008) Structure of hydrous aluminosilicate glasses along the diopside-  
309 anorthite join: A comprehensive one- and two-dimensional <sup>1</sup>H and <sup>27</sup>Al NMR study. *Geochimica Et*  
310 *Cosmochimica Acta* 72, 2331-2348.
- 311 Zajacz, Z., Halter, W., Malfait, W.J., Bachmann, O., Bodnar, R.J., Hirschmann, M.M., Mandeville, C.W.,  
312 Morizet, Y., Müntener, O., Ulmer, P. and Webster, J.D. (2005) A composition-independent  
313 quantitative determination of the water content in silicate glasses and silicate melt inclusions by  
314 confocal Raman spectroscopy. *Contributions to Mineralogy and Petrology* 150, 631-642.
- 315 Zeng, Q., Nekvasil, H. and Grey, C.P. (1999) Proton environments in hydrous aluminosilicate glasses: a <sup>1</sup>H  
316 MAS, <sup>1</sup>H/<sup>27</sup>Al and <sup>1</sup>H/<sup>23</sup>Na TRAPDOR NMR study. *Journal of Physical Chemistry B* 103, 7406-7415.
- 317 Zeng, Q., Nekvasil, H. and Grey, C.P. (2000) In support of a depolymerization model for water in sodium  
318 aluminosilicate glasses: Information from NMR spectroscopy. *Geochimica Et Cosmochimica Acta*  
319 64, 883-896.
- 320 Zotov, N. and Keppler, H. (1998) The influence of water on the structure of hydrous sodium tetrasilicate  
321 glasses. *American Mineralogist* 83.

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**TABLES**

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Table 1. Electron microprobe results, IR absorbances and predicted OH/H<sub>2</sub>O<sub>mol</sub> ratio.

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		<u>K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub>-5</u>	<u>K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub>-8</u>
SiO <sub>2</sub>	(wt%)	22.2 ± 0.2	21.4 ± 0.2
Al <sub>2</sub> O <sub>3</sub>	(wt%)	36.5 ± 0.3	35.2 ± 0.1
K <sub>2</sub> O	(wt%)	34.2 ± 0.4	32.5 ± 0.2
Total <sup>a</sup>	(wt%)	92.9 ± 0.5	89.0 ± 0.2
H <sub>2</sub> O <sup>b</sup>	(wt%)	5.3	8.5
H <sub>2</sub> O <sup>c</sup>	(wt%)	n.d. <sup>e</sup>	7.2
Formula		K <sub>2.00</sub> Al <sub>1.97</sub> Si <sub>1.02</sub> O <sub>6</sub>	K <sub>1.98</sub> Al <sub>1.98</sub> Si <sub>1.02</sub> O <sub>6</sub>
A <sub>4500</sub>	(cm <sup>-1</sup> )	3.0 ± 0.5	4.9 ± 0.5
A <sub>5200</sub>	(cm <sup>-1</sup> )	0.19 ± 0.04	1.7 ± 0.2
A <sub>4500</sub> /A <sub>5200</sub>		15.8 ± 4.2	2.9 ± 0.4
		<b>18.9<sup>+7.0</sup><sub>-16.5</sub></b>	<b>9.1<sup>+10.8</sup><sub>-7.5</sub></b>
OH/H <sub>2</sub> O <sub>mol</sub> <sup>d</sup>			

<sup>a</sup> Low totals are related to dissolved H<sub>2</sub>O and CO<sub>2</sub>.

<sup>b</sup> Nominal water content.

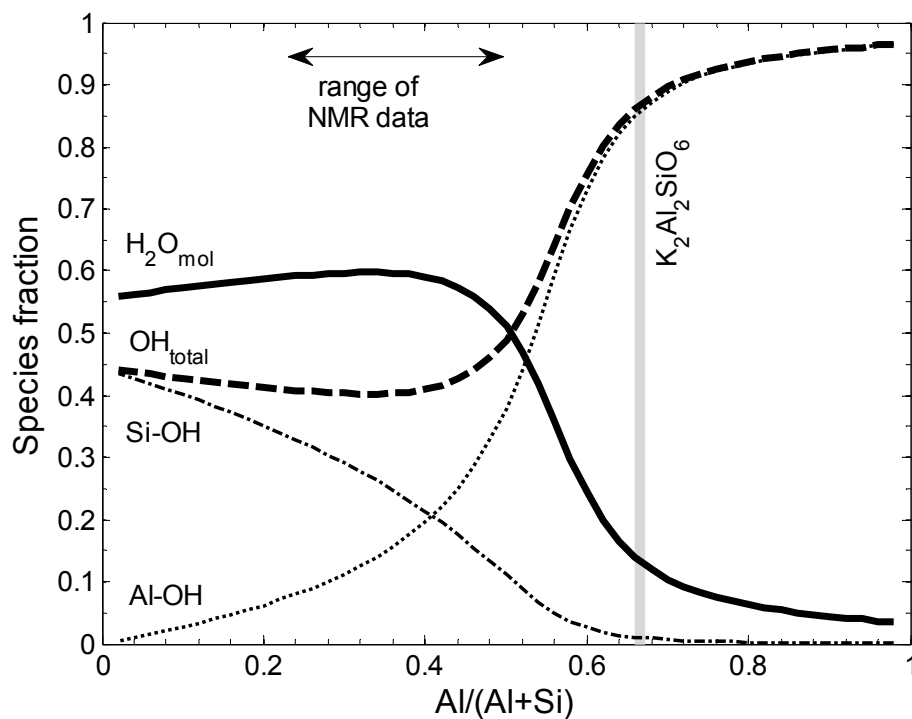
<sup>c</sup> Determined by Karl Fischer Titration (KFT).

<sup>d</sup> Predicted by Malfait and Xue, *subm.*

<sup>e</sup> No homogenous fraction of the heterogeneous sample (glass and crystals) could be measured by KFT.

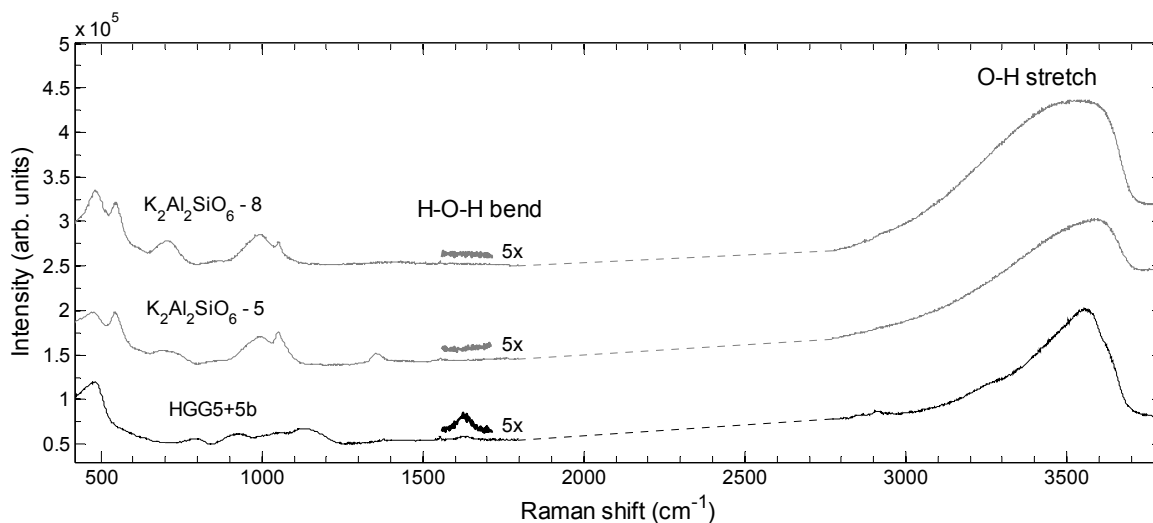
329

## FIGURES



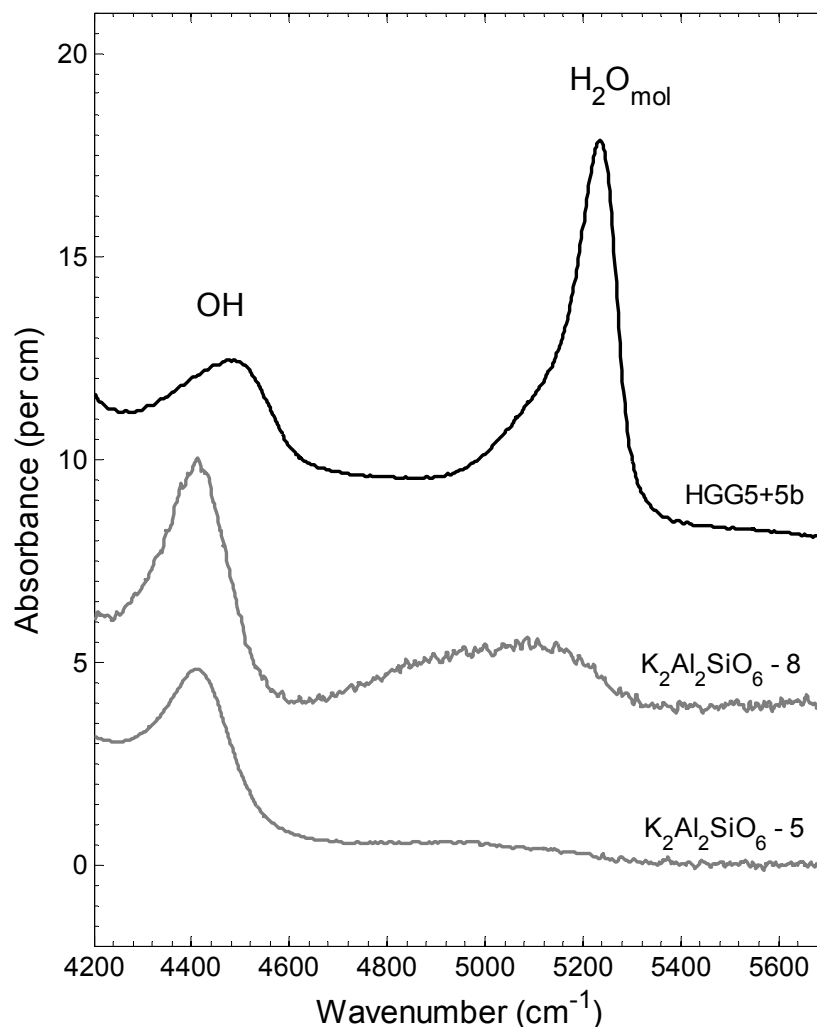
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331 Figure 1. Predicted abundances of  $\text{H}_2\text{O}_{\text{mol}}$ ,  $\text{OH}_{\text{total}}$ , Si-OH and Al-OH for metaluminous  
332 potassium aluminosilicate glasses with ca. 8 wt% water (Eq 2-5) (Malfait and Xue, submitted).  
333 Molecular water is the most abundant species for  $\text{Al}/(\text{Al}+\text{Si}) < 0.5$ , but hydroxyl groups are  
334 predicted to be more abundant at higher Al contents. The model is calibrated for Al/(Al+Si)  
335 ratios between 0.25 and 0.50, but its extrapolation predicts that water will be predominantly  
336 present as Al-OH for the  $\text{K}_2\text{Al}_2\text{SiO}_6$  composition investigated in this study (grey line).



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339 Figure 2. Raman spectra of a hydrous haplogranitic (HGG5+5b, 7.7 wt% water) and two hydrous  
340 K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses (nominally 5 and 8 wt% water). A band for the H-O-H bending mode near  
341 1600 cm<sup>-1</sup> is present for the haplogranitic glasses, but absent for the K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses. The  
342 sharp band near 1050 cm<sup>-1</sup> is related dissolved carbonate groups.



343

344 Figure 3. FTIR spectra of a hydrous haplogranitic (HGG5+5b, 7.7 wt% water) and two hydrous  
345 K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses (nominally 5 and 8 wt% water); intensities are normalized to a section  
346 thickness of 1 cm. For the haplogranitic glass, the band near 5200 cm<sup>-1</sup>, related to H<sub>2</sub>O<sub>mol</sub>, is  
347 larger than the band near 4500 cm<sup>-1</sup>, related to hydroxyl groups; this is reversed for the  
348 K<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub> glasses.

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