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Densities and Volumes of Hydrous Silicate Melts:

New Measurements and Predictions

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Abstract

The equilibrium molar volumes of four series of anhydrous and hydrous aluminosilicate glasses and liquids (0 to 11 mol% H₂O) were determined at one bar between 300 and 1050 K. The anhydrous compositions range from highly polymerized NaAlSi₃O₈ to depolymerized synthetic iron-free analogues of tephrite and foidite magma compositions (NBO/T = 0.8 and 1.5, respectively). For each sample the volume was derived from the room-temperature density of the glass and the thermal expansivity of the glass and supercooled liquid from 300 K to a temperature about 50 K higher than the standard glass transition. The partial molar coefficient of thermal expansion of water in hydrous silicate glasses is about $(6.2 \pm 3.5) \times 10^{-5}$ K⁻¹, and in the melts ranges from 11×10^{-5} to 36×10^{-5} K⁻¹. The present molar volumes of hydrous supercooled liquids are reproduced with the model of Ochs and Lange (1999) to within 1.1%, except for the hydrous foidite series. This agreement confirms that the partial molar volume of water ($\bar{V}_{\text{H}_2\text{O}}$) near the glass transition cannot depend strongly on the chemical composition of the silicate end-member, nor on water speciation. In order to reproduce the molar volumes of the foidite series, a combined model (using Lange (1997) and Courtial and Dingwell (1999) models and values derived from the new data) is used where an excess volume term between SiO₂ and CaO is introduced. Finally, our experimental data are better fit if $\bar{V}_{\text{H}_2\text{O}} = 23.8 \pm 0.5$ cm³ mol⁻¹ at 1273 K, and $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT} = 15.9 \pm 1.5$ cm³ mol⁻¹ K⁻¹. Contrasting trends are also observed for the configurational contributions to the expansivity

- 32 with a positive slope of $\frac{dV_i^{conf}}{dT}$ versus water for the most polymerized base compositions
33 (NBO/T \leq 0.21) and a negative slope for the two most depolymerized base compositions with
34 NBO/T of 0.86 and 1.51.

35 1. Introduction

36 As a major component of magmatic melts, water owes its importance to the influence
37 it exerts on their physical and chemical properties, and hence on magma ascent and phase
38 equilibria. The density of silicate liquids is for instance a critical parameter to determine
39 the depth at which crystal-melt density inversions occur (Agee, 2008). Water has recently
40 been suggested to play a critical role in buoyancy triggered supervolcano eruptions
41 (Malfait et al., 2014a). Its exceptional effects on viscosity are now rather well documented:
42 for example, addition of 1000 ppm H₂O lowers the viscosity of pure SiO₂ by 10 orders of
43 magnitude in the glass transition range (*e.g.* Mysen and Richet, 2005; and references
44 therein). Even though effects on density are usually less extreme, water nonetheless
45 remains an important component due to its low molecular weight, so that a 5 wt% water
46 content translates into about 15 mol % on an oxide basis. The effect of dissolved water on
47 volume properties is thus necessarily significant (Burnham and Davis, 1971).

48 Following Bottinga and Weill (1970), various authors have empirically set predictive
49 models of partial molar volumes (\bar{V}_i) and expansivities ($\partial\bar{V}_i/\partial T$) of oxide components
50 over wide temperature and composition ranges (*e.g.*, Bottinga et al., 1982; Knoche et al.,
51 1995; Lange and Carmichael, 1987; Lange, 1997). For hydrous silicate glasses, a review of
52 available density data indicated that the room-temperature partial molar volume of H₂O ($\bar{V}_{\text{H}_2\text{O}}$)
53 is independent of glass composition with a value of 12.0±0.5 cm³ mol⁻¹ (Richet et al.,
54 2000). This value is thus valid for polymerized, silica-rich to depolymerized, silica-poor
55 composition at 1 bar, but the partial molar compressibility of water markedly depends on
56 composition, indicating that $\bar{V}_{\text{H}_2\text{O}}$ may depend on melt composition at high pressure
57 (Malfait et al., 2011; Whittington et al., 2012). In fact, a compositionally dependent $\bar{V}_{\text{H}_2\text{O}}$
58 at high pressure has also been suggested based on the pressure dependence of water
59 solubility in silicate melts (Mysen and Acton, 1999; Mysen and Wheeler, 2000). For

60 instance the latter authors calculated a $\bar{V}_{\text{H}_2\text{O}}$ in haploandesitic melts from solubility data
61 which was negatively correlated with Al_2O_3 content. Despite these indications Malfait et
62 al. (2014b) have shown that, within the experimental uncertainties of about 1.3%, the \bar{V}
63 H_2O is independent of the silicate melt composition.

64 Few volume measurements exist for hydrous silicate melts at atmospheric pressure
65 (*e.g.* Burnham and Davis, 1971; Ochs and Lange, 1997; 1999; Bouhifd et al., 2001). From
66 their own expansivity measurements for three samples and the high-temperature, high-
67 pressure measurements of Burnham and Davis (1971) for a hydrous albitic liquid, Ochs
68 and Lange (1997, 1999) reported that dissolved water has a $\bar{V}_{\text{H}_2\text{O}} = 22.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ at
69 1273 K and 1 bar.

70 The main aim of the present study was to expand the available database for the 1-bar
71 density and volume of hydrous silicate glasses and liquids at high temperatures, knowing
72 that derivation of the pressure dependence of silicate liquid volumes depends upon
73 accurate 1 bar values as a function of temperature. Another aim of this work was to
74 determine whether the results for $\bar{V}_{\text{H}_2\text{O}}$ previously obtained are applicable to a
75 composition range wider than that of their input data.

76 We have thus measured the thermal expansion of hydrous glasses and liquids of four
77 synthetic iron-free series modeled after albite, tephrite, trachyte, and basanite/foidite
78 (hereafter “foidite” with individual samples labeled “NIQ”) whose compositions are
79 reported in Table 1. Also included in Table 1 is the sample selected in our preliminary
80 study to derive the partial molar volume of water in phonolitic glasses and liquids (Bouhifd
81 et al., 2001). The whole set of samples represent the range of polymerization states
82 relevant to natural magmas, and has been the subject of previous investigations of heat
83 capacity (Bouhifd et al., 2006; 2013), viscosity (Whittington et al., 2000; 2001; 2004;
84 2009), and compressibility (Richet et al., 2000; Whittington et al., 2012).

85

86 **2. Experimental methods**

87 The anhydrous glasses were synthesized from oxide and carbonate mixes through
88 repeated cycles of grinding and fusion at about 1600 °C. The chemical compositions are
89 reported in Table 1 as analyzed with the electron microprobe. The samples were then
90 hydrated at high temperatures at either 2 or 3 kbar in an internally heated vessel with the
91 procedure reported by Whittington et al. (2000). The hydration conditions and the water
92 contents measured by Karl-Fischer titration are given in Table 2. Samples of about 10 mg
93 were analyzed in this study, for which the uncertainty on the reported water content is
94 around 0.1 wt% H₂O (Behrens et al., 1996). The room-temperature densities of the glasses
95 included in Table 3 were measured by an Archimedean method with toluene as the
96 immersion liquid.

97 Because the samples were initially densified as a result of their high-pressure
98 synthesis, the density of the sample was again measured after each thermal expansion
99 measurement to determine the extent of possible volume relaxation. Likewise, we checked
100 by weighing that no water loss occurred on heating at the highest temperatures. For the
101 hydrous glasses, the densities of the initial and relaxed glasses after expansivity
102 measurements are listed in Table 3.

103 The dilatometry apparatus was described in detail by Sipp and Richet (2002). Briefly,
104 the furnace was made of two Fibrothal half shells (from Kanthal) and regulated with a
105 P.I.D. controller. Temperatures were measured with a Pt-Pt/Rh 10% thermocouple placed
106 next to the sample. Upon heating we measured the length of the sample as a function of
107 temperature as the difference between the displacement of two SiO₂ rods, one resting on
108 the sample and the other on a reference cylinder of SiO₂ glass. These measurements were
109 made to within about 0.2 μm with linear variable differential transducers. Silica was

110 chosen as a reference material because its expansivity is approximately zero over the
 111 studied temperature intervals.

112 Because glasses and liquids are isotropic, the volume coefficient of thermal expansion
 113 α of all samples was obtained simply by multiplying the linear coefficient α_{linear} by 3:

$$114 \quad \alpha_{\text{glass or liquid}} = 3 \times \alpha_{\text{linear}} = 3/L \left(\partial L / \partial T \right) = 3 \times \partial \ln(L) / \partial T \quad (1)$$

115 where L is the length of the sample and T its temperature. To determine the coefficients of
 116 thermal expansion of glasses and liquids we have adopted the procedure described by
 117 Toplis and Richet (2000) for anhydrous silicate melts. Contrasting with the usual method
 118 with which samples are continuously heated through the glass transition, this procedure
 119 ensures that measurements are made for supercooled silicate liquids that are in internal
 120 thermodynamic equilibrium. The resulting improvement is that thermal expansion
 121 coefficients can then to be derived in a rigorous way from the sample length measured. At
 122 the beginning of the experiments the samples were heated continuously at a constant rate
 123 of 2 K min^{-1} from room temperature to a temperature corresponding to a viscosity of 10^{13}
 124 Pa s (T_{13}), known from our previous viscosity experiments. For liquids, this T_{13} was then
 125 taken as a reference temperature at which the sample was first held until a constant length
 126 was observed. The temperature of the sample was then increased or decreased by 10 K
 127 steps at 2 K min^{-1} and kept constant until a new equilibrium length was reached. Different
 128 temperatures over a range of ~ 50 to 70 degrees were studied in this manner. The time spent
 129 at each temperature was variable, more time being required at lower temperatures because
 130 of slower relaxation kinetics.

131 An important feature of this protocol is that two or more length changes can be
 132 measured for each temperature (i.e., upon heating and cooling), providing checks that the
 133 measured lengths do represent equilibrium values. This is the procedure described by
 134 Toplis and Richet (2000) for anhydrous samples, with the exception that we did not make a

135 final measurement at T_{13} , to limit the duration of the experiment and thus reduce the risk of
136 water exsolution. The slowness of water exsolution in the temperature interval investigated
137 makes accurate measurements possible in the supercooled liquid state near the glass
138 transition. Because length changes are measured with high precision, the expansivities are
139 generally determined to better than 3% (Toplis and Richet 2000). In this work we have set
140 a conservative upper limit of 5% for the experimental uncertainty.

141

142 **3. Results**

143 All experimental data for the thermal expansion of anhydrous and hydrous glasses and
144 liquids are reported in Tables 4-5.

145

146 *Thermal expansion of hydrous glasses*

147 In the initial measurements made on unrelaxed samples, expansion began to be
148 anomalously high at temperatures at which the viscosity was about 10^{16} Pa s as indicated
149 by extrapolation of the viscosity measurements by Whittington et al. (2000; 2001; 2004).
150 This anomaly signaled the onset of volume relaxation to the 1-bar density of the samples,
151 which were initially compacted as a result of their high pressure synthesis (Fig. 1). A
152 second measurement was then performed with the same heating rate on the relaxed sample
153 during which the sample length increased linearly with temperature up to T_{13} . No
154 variations of mass or room-temperature density were observed after this second
155 measurement.

156 For each glass we calculated the thermal expansion coefficient between room
157 temperature and the highest temperature up to which expansion was linear, *i.e.*, up to the
158 onset of volume relaxation for densified glasses and up to about T_{13} for relaxed glasses.
159 The calculated thermal expansion coefficients of densified glasses are systematically

160 higher than those of relaxed glasses by about 3 - 6 %, except for the sample “Teph 0.3” for
161 which a reverse effect is observed (*cf.* Table 5). These contrasts demonstrate that
162 differences in fictive pressures of only 2 or 3 kbar have minor but detectable effects on
163 glass expansivity.

164

165 *Thermal expansion of hydrous liquids*

166 The experiments were made on liquids over temperature intervals of up to 70 degrees
167 (*cf.* Fig. 2 a-d). Because the glass transition is lowered with increasing water contents, so
168 were the temperatures ranges investigated. Although minor penetration of the SiO₂ rod into
169 the sample took place at the highest temperatures, this effect was readily taken into account
170 with the procedure described by Toplis and Richet (2000) to determine the equilibrium
171 length. Within experimental uncertainties, the logarithm of the length varied linearly with
172 temperature for all supercooled liquids (see Fig. 2 for the hydrous Tephrite series). The
173 slopes of these lines thus represent the linear thermal expansion coefficient, which could
174 thus be determined from equation (1) and clearly increases with increasing water contents.

175 Possible water loss was a serious concern because the water contents of the samples
176 were much higher than the 1-bar solubility of water. However, no changes in sample
177 weight were observed after the experiments. As a more sensitive check, the viscosity of the
178 same supercooled liquids was measured in the same temperature ranges. No influence of
179 thermal history on the measured viscosities was apparent and the variations of the
180 viscosities with temperature were as smooth as for water-free samples. Owing to the
181 tremendous influence of water on viscosity, this excellent precision demonstrates
182 unequivocally, as discussed by Whittington et al. (2004), the lack of detectable water loss
183 during high-temperature measurements as long as the viscosity was higher than about 10⁹
184 Pa.s. Similar observations were made in viscosity measurements on andesite samples

185 which had the same room-temperature infrared spectra prior to and after high-temperature
 186 viscometry (Richet et al., 1996).

187

188 *Volume of dry and hydrous silicate glasses*

189 From 300 K to the glass transition, the volume of each glass sample was calculated
 190 from:

$$191 \quad V_{\text{glass}}(T) = V_{\text{glass}}(300 \text{ K}) \exp(\alpha_{\text{glass}}(T - 300)) \quad (2)$$

192 where $V_{\text{glass}}(300 \text{ K})$ is the volume at 300 K, and α_{glass} is the thermal expansion coefficient
 193 of the glass. The uncertainties on $V_{\text{glass}}(T)$ derived from equation (2) are given by:

$$194 \quad \Delta V_{\text{glass}}(T) = V_{\text{glass}}(T) (\Delta V_{\text{glass}}(300 \text{ K})/V_{\text{glass}}(300 \text{ K}) + (T - 300) \Delta \alpha_{\text{glass}} + \alpha_{\text{glass}} \Delta T) \quad (3)$$

195 From equation (3) the uncertainty in $\Delta V_{\text{g}}(T)$ is highest around the glass transition
 196 temperature T_{g} . The contribution of $\alpha_{\text{g}} \times \Delta T$ on $\Delta V_{\text{g}}(T)$ is so small that it can be neglected.
 197 For anhydrous glasses, the errors at T_{g} represent about 0.15 % of the molar volumes. For
 198 the hydrous glasses, the error is slightly higher, $\sim 0.20 \text{ cm}^3 \text{ mol}^{-1}$, which represents $\sim 0.7\%$
 199 of volume at the glass transition temperature.

200

201 *Volume of dry and hydrous silicate liquids*

202 All experimental volumes with their corresponding uncertainties for hydrous and
 203 anhydrous samples are reported in Table 6. For liquids, the volume is given by:

$$204 \quad V_{\text{liquid}}(T) = V_{\text{glass}}(T_{\text{g}}) \exp(\alpha_{\text{liquid}}(T - T_{\text{g}})) \quad (4)$$

205 where T_{g} is the glass transition temperature, $V_{\text{glass}}(T_{\text{g}})$, the volume at T_{g} is equal to V_{liquid}
 206 (T_{g}) and α_{liquid} is the thermal expansion coefficient of the silicate liquid.

207 The uncertainties on these values are given by:

$$208 \quad \Delta V_{\text{liquid}}(T) = V_{\text{liquid}}(T) (\Delta V_{\text{glass}}(T_{\text{g}})/V_{\text{g}}(T_{\text{g}}) + (T - T_{\text{g}}) \Delta \alpha_{\text{liquid}}) \quad (5)$$

209 In the investigated temperature ranges the uncertainties on the supercooled liquid volumes
 210 are less than $0.2 \text{ cm}^3 \text{ mol}^{-1}$ which corresponds to about 0.7%. In equation (5) we assume
 211 $\Delta\alpha_g = \Delta\alpha_l = 5\%$ and we again consider that the contribution of $\alpha_{\text{liquid}} \Delta T$ to the error is too
 212 small to be taken into account. The uncertainties become unacceptably large if the data are
 213 extrapolated too far beyond the range of the measurements because of the $(T - T_g)$ term.
 214 For all compositions studied, the volume increases markedly on heating above the glass
 215 transition, and this increase is the highest for the highest water contents (*cf.* Fig. 3 a-c).

216 Table 5 lists the linear fits made to our experimental data for glasses and supercooled
 217 liquids with the following equations:

218 For glasses:
$$V_{\text{glass}} (\text{cm}^3 \text{ mol}^{-1}) = a_{\text{glass}} + \left(\frac{dV}{dT}\right)_{\text{glass}} T (\text{K}) \quad (6)$$

219

220 and for liquids:
$$V_{\text{liquid}} (\text{cm}^3 \text{ mol}^{-1}) = a_{\text{liquid}} + \left(\frac{dV}{dT}\right)_{\text{liquid}} T (\text{K}) \quad (7)$$

221 Liquid volumes were calculated by using the viscosimetric or calorimetric glass transition
 222 temperature as the starting point and the experimentally determined expansivity over
 223 temperature intervals of 50 K.

224

225

226 **4. Discussion**

227 Following Bottinga and Weill (1970), one generally assumes that the 1-bar partial
 228 molar volumes of oxides in silicate liquids do not depend on composition over a range of
 229 40-80 mol% SiO₂. Therefore, the density of a silicate liquid can be expressed by the
 230 following equation (8):

$$\rho_{liquid}(T) = \frac{\sum X_i \times M_i}{V_{liquid}(T)}$$

231 where X_i is the mole fraction of oxide i , M_i its gram formula weight, and $V_{liquid}(T)$ is the
 232 volume of the silicate liquid at temperature T . Likewise, the molar volume of a melt is

$$233 \quad V_{liquid}(T) = \sum X_i \times \left[\bar{V}_i(T_{ref}) + \frac{d\bar{V}_i}{dT} \times (T - T_{ref}) \right] \quad (9)$$

234 where $\bar{V}_i(T_{ref})$ is the partial molar volume of oxide i at reference temperature T_{ref} , and
 235 $\frac{d\bar{V}_i}{dT}$ is the partial molar thermal expansivity of oxide i .

236 At high pressure, an additional term needs to be included to deal with the compressibility
 237 of silicate liquid components (*e.g.* Lange 1994) so that equation (7) becomes:

$$238 \quad V_{liquid}(T) = \sum X_i \times \left[\bar{V}_i(T_{ref}) + \frac{d\bar{V}_i}{dT} \times (T - T_{ref}) + \frac{d\bar{V}_i}{dP} \times (P - P_{ref}) \right] \quad (10)$$

239 where $\frac{d\bar{V}_i}{dP}$ is the partial molar compression of oxide i , P is the pressure and P_{ref} is the
 240 reference pressure (usually 1 bar). However, equation (10) cannot be extrapolated to GPa
 241 pressures because it does not account for the marked decrease of the compressibility with
 242 increasing pressures (Lange, 1994; Jing and Karato, 2009). Third-order Birch-Murnaghan
 243 equations of state have thus been used instead to describe the compression of volatile-
 244 bearing silicate melts (*e.g.* Jing and Karato, 2009; Malfait et al., 2014a,b).

245

246 The most widely used density/volume calculation model for hydrous silicate melts is
 247 the one proposed by Ochs and Lange (1999), which is an extension to hydrous liquids of

248 the model derived by Lange (1997) for anhydrous silicate melts from the glass transition to
249 super-liquidus temperatures. Below, the experimentally determined volumes are compared
250 with the predictions of the models of Lange (1997) and Ochs and Lange (1999) for
251 anhydrous and hydrous supercooled melts, respectively.

252

253 *Anhydrous supercooled silicate melts*

254 As reported in Table 7, the model of Lange (1997) (with the partial molar volume for
255 TiO_2 taken from Lange and Carmichael, 1987) reproduces the present volume data for
256 most of the anhydrous melts to better than 1%, and trachyte volumes to about 1.3%. Hence
257 these deviations are consistent with the stated uncertainties of the experimental data and of
258 the model values.

259 The exception is the experimental dataset for the anhydrous foidite composition
260 which is the least silicic and most calcic composition, containing about 43 mol% SiO_2 and
261 27.6 mol% CaO (Table 7). Equation (9), which is widely used to predict the volume of
262 silicate melts at 1 bar, carries the assumption that molar volume follows a linear variation
263 with composition. To explain the foidite anomaly, we first note that the volume data
264 reported by Tomlinson et al. (1958) show a non-ideal mixing between CaO and SiO_2 in the
265 binary system CaO-SiO_2 . Lange and Carmichael (1987) suggested an excess volume term
266 between CaO and SiO_2 for silicate melts in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system having a
267 molar fraction of $\text{CaO} > 0.5$. Courtial and Dingwell (1995) found a non-linear composition
268 dependence of molar volume in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. Combining the model of
269 Courtial and Dingwell (1999) valid for compositions in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$,
270 which includes an excess volume term between CaO and Al_2O_3 , with the partial molar
271 volumes for TiO_2 , Na_2O and K_2O given by Lange (1997), reproduces the molar volume of

272 foidite composition within experimental uncertainties. The partial molar volumes for
 273 oxides used in all the calculations are given in Table 7.

274

275 *Hydrous supercooled silicate melts*

276 For hydrous silicate melts, the model of Ochs and Lange (1999) reproduces the
 277 present hydrous supercooled liquid volumes to within 1.15%. This agreement confirms that
 278 the partial molar of water ($\bar{V}_{\text{H}_2\text{O}}$) cannot depend strongly on the chemical composition of
 279 the silicate end-member. However, the agreement between our experimental data and the
 280 model of Ochs and Lange (1999) deteriorates with increasing water content (Table 7). To
 281 improve the prediction for our own experiments we derived new values for $\bar{V}_{\text{H}_2\text{O}}$ and
 282 $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT}$.

283 The starting point of this determination is the observation that, for all series of
 284 hydrous glasses, the trends in $\left(\frac{\partial V}{\partial T}\right)$ as a function of water content vary somewhat
 285 systematically with the NBO/T of the anhydrous end-member (Fig. 4a). The highly
 286 polymerized albite has a lower value of $0.70 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ compared to foidite, the
 287 most depolymerized composition, with a value of $1.51 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$.

288 Considering all data, we observe that $\left(\frac{\partial V}{\partial T}\right)$ increases linearly with increasing water
 289 content, with partial molar values of $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT}$ between 14.3×10^{-3} and $17.5 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$
 290 for our set of compositions. As an approximation, a constant $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT}$ of $(15.9 \pm 1.6) \times 10^{-3} \text{ cm}^3$
 291 $\text{mol}^{-1} \text{ K}^{-1}$ could thus be assumed, a value 40% higher than the $(9.5 \pm 0.8) \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$
 292 derived by Ochs and Lange (1999), as shown in Fig. 4b. We then used this new value for
 293 $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT}$ to determine a partial molar volume of $23.8 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ for water dissolved in
 294 silicate melt at a reference temperature of 1273 K.

295 This volume at 1273 K is 4% higher than that derived by Ochs and Lange (1999),
 296 and combined with our higher $\frac{d\bar{v}_{H_2O}}{dT}$, suggests that at 1473K the hydrous component in
 297 melts has a volume of 27.0 cm³ mol⁻¹ rather than 24.8 cm³ mol⁻¹. In arc basalts, which
 298 commonly contain ≥ 3 wt.% H₂O (~10 mol%), this difference between the two values
 299 translates to a difference of ~20-25 kg m⁻³ in the density of the liquid. Although a relatively
 300 small uncertainty in the overall magma density, of the order of 1%, this difference is
 301 equivalent to a pressure uncertainty of 1-2 kbars. Tholeiitic basalts are typically much
 302 drier, so the difference is smaller, of the order of 10 kg m⁻³ for 1 wt.% H₂O. However, even
 303 this small difference can be critical when calculating whether plagioclase crystals should
 304 be positively or negatively buoyant, as discussed by Ochs and Lange (1999).

305 Along with the partial molar volume and expansivity of other oxides reported by
 306 Lange (1997), the new values for water described above allow our data to be reproduced
 307 with a smaller error (see Table 7 for a comparison between both models). The present
 308 calibration covers water contents from 0 to about 3 wt% H₂O, and care should be exercised
 309 in extrapolating beyond this range. However it is notable that no previous study has
 310 detected any dependence of the partial molar volume properties of water (including
 311 compressibility and expansivity) on water content.

312

313 *Effect of water on α_{glass} and α_{liquid}*

314 The present thermal expansion coefficients of the silicate glasses and liquids are
 315 plotted against water content in Fig. 5a-b. Within its 5% estimated uncertainty α varies
 316 linearly with water content up to about 11 mol% H₂O for both kinds of phases. Note that
 317 from the definition of α as $\frac{1}{V} \frac{dV}{dT}$, it is impossible for α to be a linear function of water
 318 content if partial molar volumes and thermal expansivities are also additive, as assumed in
 319 equation 10 and supported by the available data. Over the measured range of three or four

320 water contents per base composition, the variations in α are most reasonably described as
 321 linear (Fig. 5). For hydrous glasses, all data show an expansivity increase as a function of
 322 water content, except for the trachyte series where an apparently slightly negative slope is
 323 found ($10^5 \alpha = 2.4738 - 0.01790 x_{\text{H}_2\text{O}}$). For the trachyte series, a linear extrapolation of the
 324 best fit of the data yields a value of $0.7 \times 10^{-5} \text{ K}^{-1}$ for the partial molar thermal expansion
 325 coefficient of water in glass. For the other compositions, the partial molar thermal
 326 expansion coefficient of H_2O in glass varies between $4.8 \times 10^{-5} \text{ K}^{-1}$ to $9.4 \times 10^{-5} \text{ K}^{-1}$. The
 327 results also point to a small pressure dependence of the expansivity as determined from the
 328 differences between the data for compacted and relaxed glasses, where compacted glasses
 329 show a higher expansivity (Table 5).

330 In summary, the average of the partial molar thermal expansion coefficient of water in
 331 silicate glasses is about $(6.2 \pm 3.5) \times 10^{-5} \text{ K}^{-1}$. This is consistent with several previous studies.
 332 Shelby and McVay (1976), Jewell et al. (1990) and Jewell and Shelby (1992) demonstrated
 333 the slight influence of water on thermal expansion for a variety of glasses containing 600
 334 or 1850 ppm H_2O . The observations of Tomozawa et al. (1983) for hydrated $\text{Na}_2\text{Si}_3\text{O}_7$
 335 glasses indicate that α_g is twice as great for a sample with 22 mol% H_2O than for the
 336 water-free glass, which corresponds to a mean coefficient of about $4 \times 10^{-5} \text{ K}^{-1}$ for the water
 337 component. This value is very similar to the figure of $6 \times 10^{-5} \text{ K}^{-1}$ derived from the data of
 338 Ochs and Lange (1997) for hydrous albite glasses. Although there is some scatter in the
 339 extrapolated values, there is no obvious systematic trend as a function of silicate
 340 composition.

341 For the liquids, all compositions show an increase of the thermal expansion
 342 coefficient as a function of water content. The derived partial molar thermal expansion
 343 coefficient of water for silicate melts range from 11×10^{-5} to $36 \times 10^{-5} \text{ K}^{-1}$, and the average of
 344 $\bar{\alpha}_{\text{H}_2\text{O}}^{\text{liq}}$ for the hydrous melts studied is about $(24.5 \pm 10) \times 10^{-5} \text{ K}^{-1}$. No systematic variation

345 of $\bar{\alpha}_{H_2O}^{liq}$ is observed with the NBO/T of the anhydrous end-members or any other
 346 characteristic of the silicate melt composition.

347

348 *Configurational thermal expansion*

349 The differences observed between the expansion of hydrated glasses and liquids
 350 reflect the existence of configurational contributions to the expansivities of the liquids,
 351 which are nonexistent in the glasses. Linear fits of molar volume ($\text{cm}^3 \text{mol}^{-1}$) and thermal
 352 expansivity of glasses and supercooled liquids in the albite, tephrite, trachyte and foidite
 353 hydrous compositions are reported in Table 8. Because no compositional effects were
 354 observed for thermal expansion of glasses, as discussed above, the complexities affecting
 355 melts must find their roots in the structural changes that begin to take place at the glass
 356 transition. As discussed for the heat capacity or viscosity (*e.g.* Bouhifd et al., 1998; Richet,
 357 1984; and references therein), the thermal expansivity of silicate liquids is made up of
 358 vibrational and configurational parts. Hence one can write that:

$$359 \quad \frac{dV_i}{dT} = \frac{dV_i^{vib}}{dT} + \frac{dV_i^{conf}}{dT} \quad (11)$$

360 where $\frac{dV_i^{vib}}{dT}$ and $\frac{dV_i^{conf}}{dT}$ are the vibrational and configurational contributions, respectively,

361 to $\frac{dV_i}{dT}$. The abrupt jump in thermal expansivity at the glass transition reflects the

362 contribution of $\frac{dV_i^{conf}}{dT}$.

363 Combining the results for the present glass compositions except the hydrous trachyte

364 series we find that $\frac{dV_i^{vib}}{dT}$ is $(1.5 \pm 0.5) \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ for the water component. With

365 respect to this vibrational contribution to expansivity, water behaves similarly to alkali

366 oxides, with a partial molar value between that of Li_2O and Na_2O (Shelby and McVay,

367 1976; Richet et al., 2000).

368 For the configurational contribution to expansivity, we find two distinct trends versus
 369 the water contents of the liquids: one for polymerized and the other for depolymerized
 370 compositions (Fig. 6). For instance, for the three compositions with $NBO/T \leq 0.21$, a
 371 positive slope of $\frac{dV_i^{conf}}{dT}$ versus water content is observed. In contrast, a negative slope is
 372 observed for the most depolymerized compositions with NBO/T of 0.86 and 1.51 (for the
 373 anhydrous end-member). This contrast is consistent with other effects of dissolved water
 374 that behave differently depending for polymerized or depolymerized compositions, at least
 375 at atmospheric pressure. For instance, the partial molar heat capacity of OH^- for
 376 depolymerized melts is close to double the value for polymerized melts (Bouhifd et al.,
 377 2013). Likewise the addition of water increases the Poisson's ratio for polymerized melts,
 378 but decreases it for depolymerized melts (Malfait and Sanchez-Valle, 2013). All these
 379 features thus support the idea that the solubility mechanisms of water strongly depend on
 380 silicate composition and polymerization (*e.g.* Kohn, 2000; Mysen and Richet, 2005; Xue
 381 and Kanzaki, 2006; Malfait and Sanchez-Valle, 2013; Robert et al., 2014; and references
 382 therein). The fascinating enigma remains that despite this conclusion, the partial molar
 383 properties of the dissolved hydrous component clearly do not depend on water speciation.

384

385 5. Conclusion

386 The \bar{V}_{H_2O} at atmospheric pressure can be considered as independent of silicate
 387 composition in glasses, and in supercooled liquids near the glass transition temperature, as
 388 reported previously by Richet et al. (2000), and Ochs and Lange (1999) and Bouhifd et al.
 389 (2001), respectively. This behaviour seems to be valid too at high pressure (up to about 20
 390 GPa) (*e.g.* Malfait et al., 2014*b*; and references therein). This uniform volume of dissolved
 391 water in silicate melts will simplify the construction of general density model for H_2O
 392 bearing magmas at high pressure and high temperature. However, contrasting trends are

393 observed in this study for the configurational contributions to the expansivity with a
394 positive slope of $\frac{dV_i^{conf}}{dT}$ versus water for the most polymerized compositions and a
395 negative slope for the two most depolymerized compositions. Measurements at high water
396 contents and high temperatures are needed to explore these effects further, and to
397 determine their importance for magmas inside the Earth.

398

399

400

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596 **Figure Captions**
597

598 **Figure 1.** Difference between the expansion of compacted and relaxed glasses at a heating
599 rate of 2 K min⁻¹ for the sample “Trach 3.5” sample containing about 10 mol. % H₂O,
600 which was synthesized at 3 kbar and 1300 °C. Note that a constant slope is observed up to
601 T_{13} (temperature at which the viscosity is 10¹³ Pa.s) once a sample hydrated at a high
602 pressure has relaxed to the 1-bar configuration.
603

604 **Figure 2.** Variations of sample lengths in natural logarithm with temperature for anhydrous
605 and hydrated tephrite liquids. (a) Anhydrous tephrite liquid between 880 and 920 K; (b)
606 Teph 0.3 liquid (1.74 mol% H₂O) between 820 and 860 K; (c) Teph 1.5 liquid (5.22 mol%
607 H₂O) between 750 and 800 K; (d) Teph 3 liquid (8.31 mol% H₂O) between 670 and 740
608 K. Vertical scales change between panels because the thermal expansion of hydrous liquids
609 increases at higher water contents.
610

611 **Figure 3.** Molar volumes in the glass transition range for hydrous trachyte glasses and
612 supercooled liquids. (a) Anhydrous trachyte glass and liquid; (b) Trach 1.5 (5.42 mol%
613 H₂O) glass and liquid; (c) Trach 3.5 (10.12 mol% H₂O) glass and liquid. The studied
614 temperature ranges are lower for higher water contents since the glass transition
615 temperature decreases with increasing water content.
616

617 **Figure 4.** Thermal expansivity of hydrous melts versus water content (mol%). (a)
618 Experimental results up to about 11 mol%. (b) Extrapolation of the thermal expansivity to
619 water end-member. These extrapolations lead to $\frac{d\bar{v}_{H_2O}}{dT} = 15.9 \pm 1.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$.
620

621 **Figure 5.** Coefficients of thermal expansion of hydrous (a) glasses; (b) liquids. All
622 compositions (apart from the hydrous trachyte glasses) show an increase of the coefficient
623 of thermal expansion with increasing water content.
624

625 **Figure 6.** Configurational contribution to expansivity for anhydrous and hydrous liquids
626 studied in this work. The results for phonolite previously reported by Bouhifd et al. (2001)
627 are also shown. Two different trends are observed: one for the polymerized hydrous melts
628 (with NBO/T ≤ 0.21), and the second one for depolymerized melts (with an NBO/T ≥

629 0.86). For polymerized hydrous melts, an increase of $\frac{dV_i^{conf}}{dT}$ versus water content is
630 observed, whereas the opposite trend is observed for depolymerized melts.
631

Figure 1.

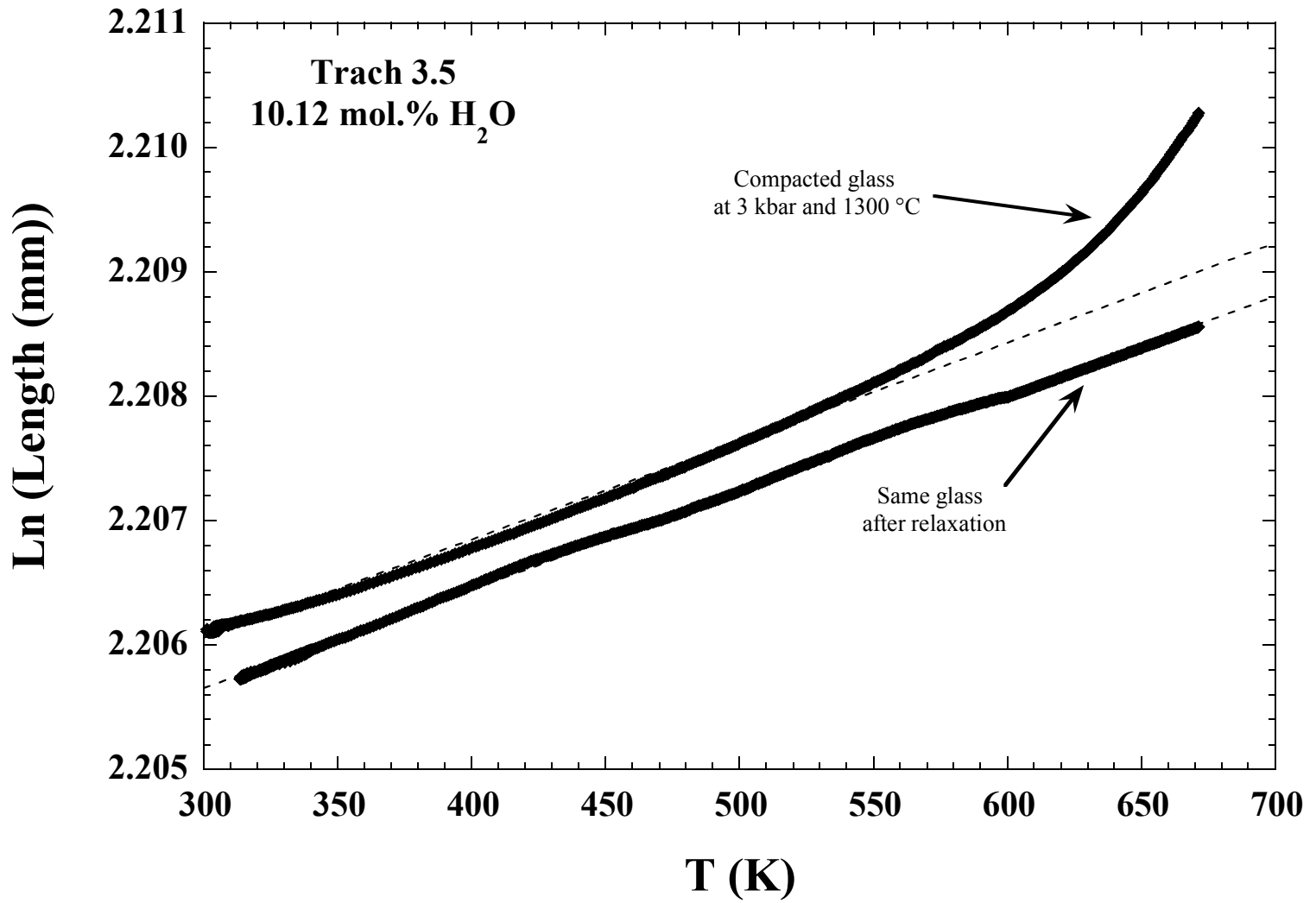


Figure 2.

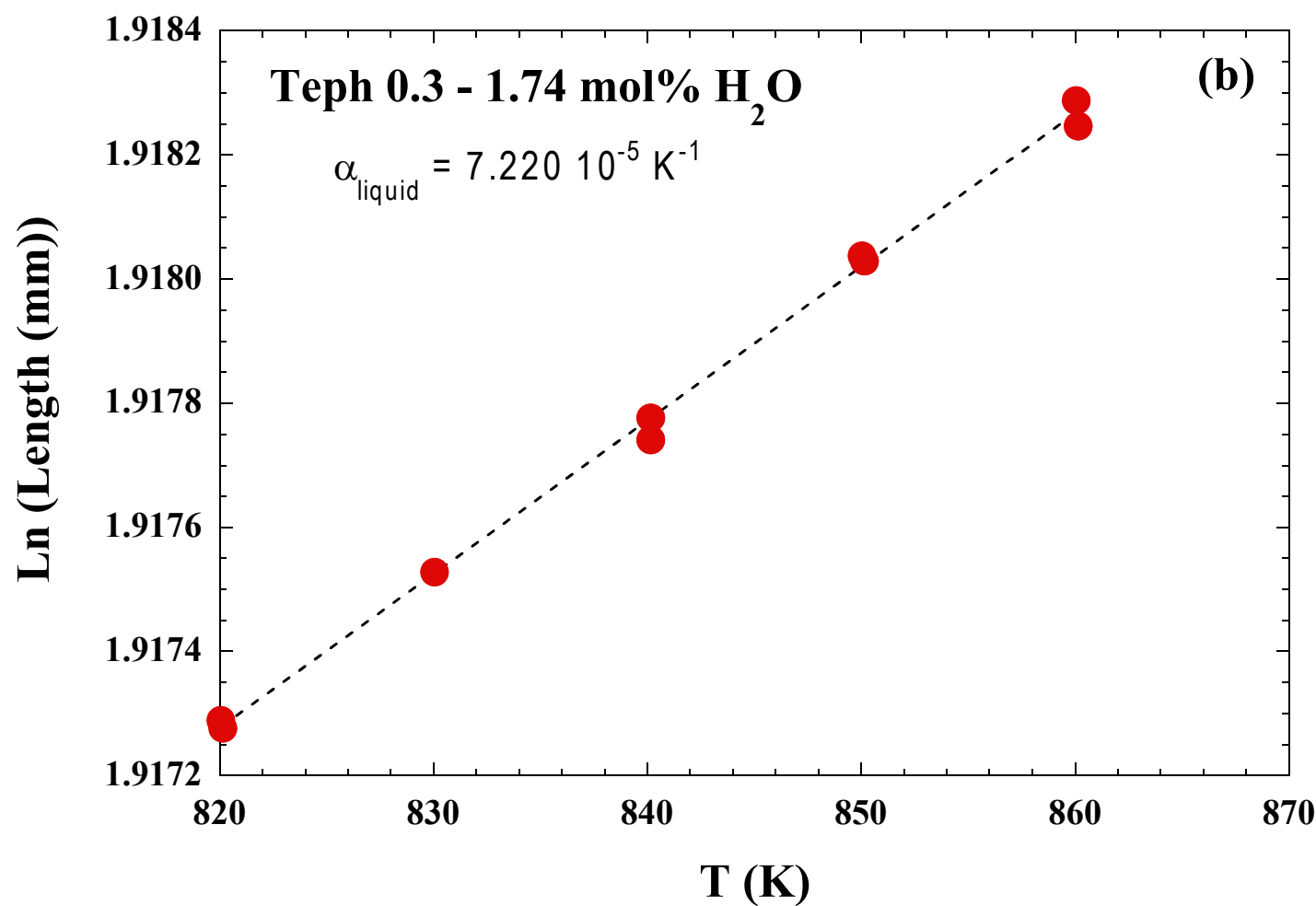
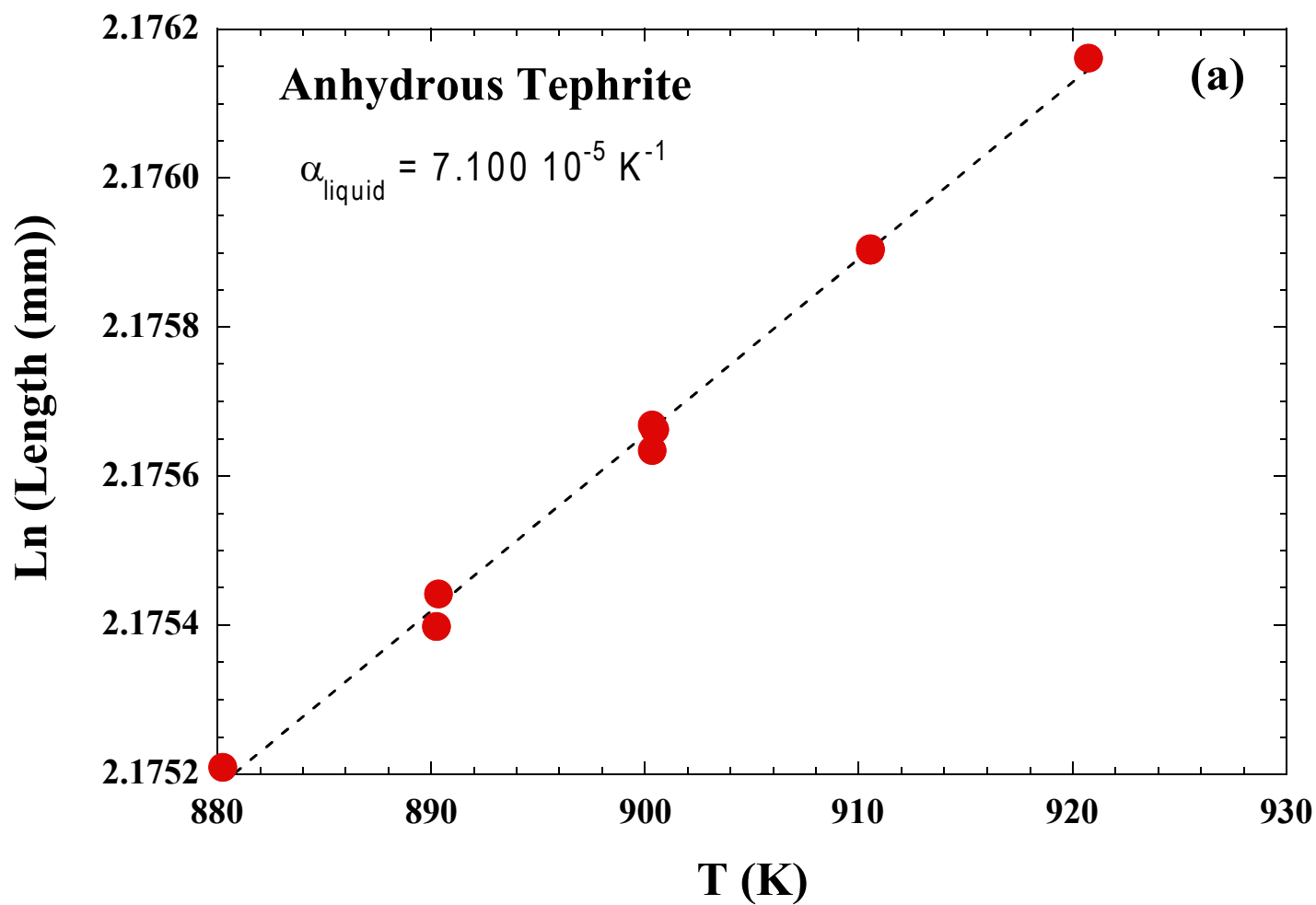


Figure 2.

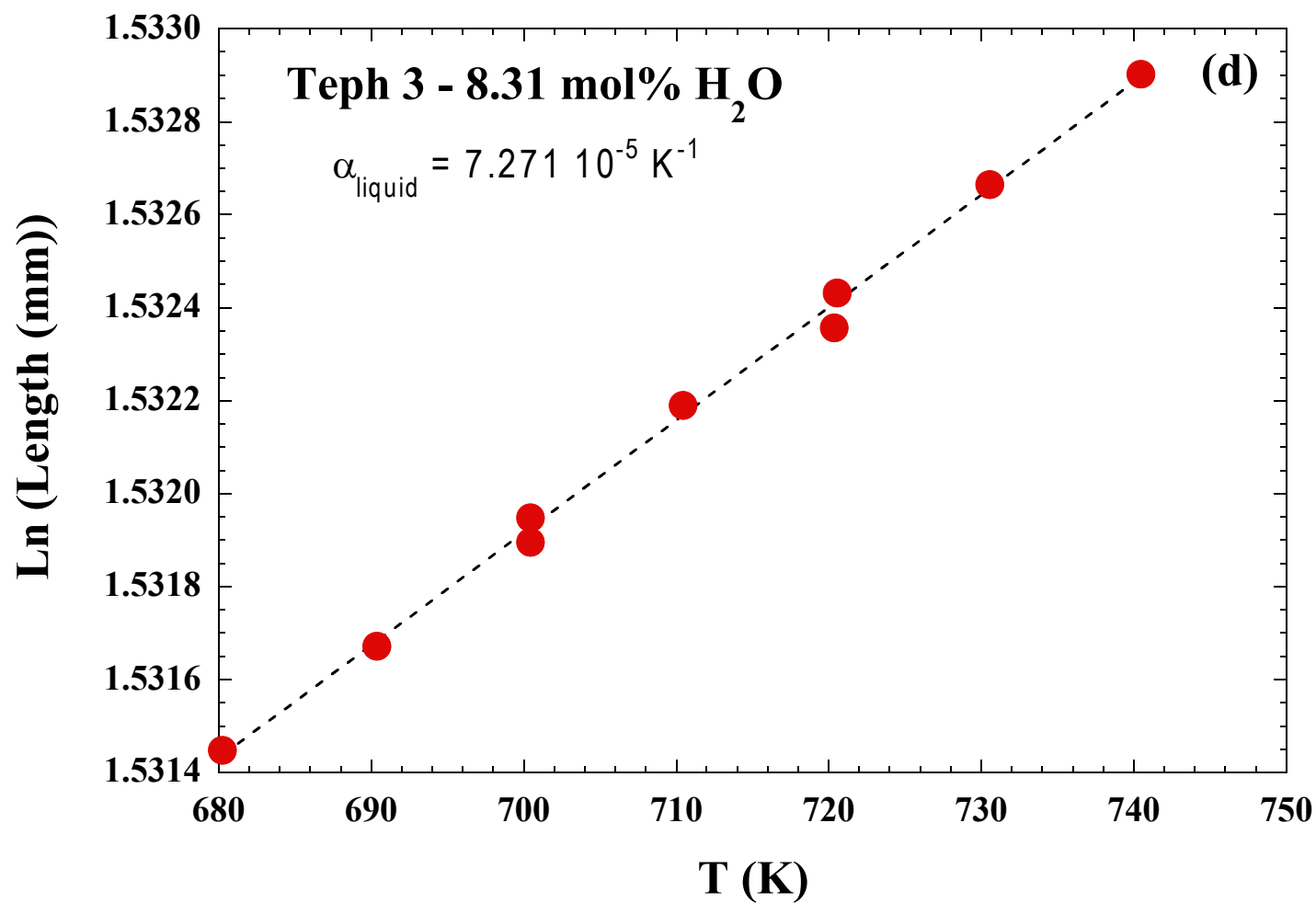
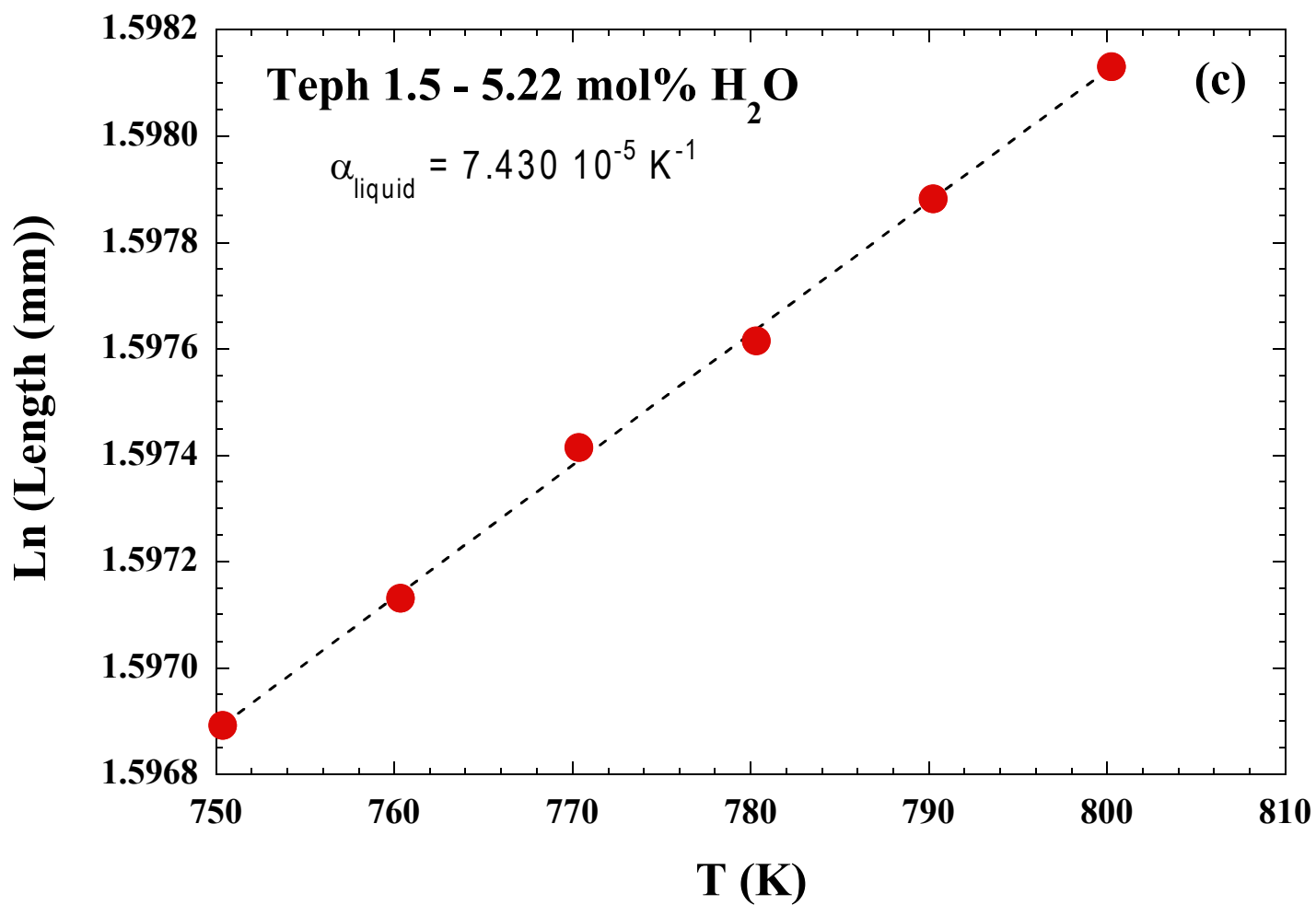


Figure 3.

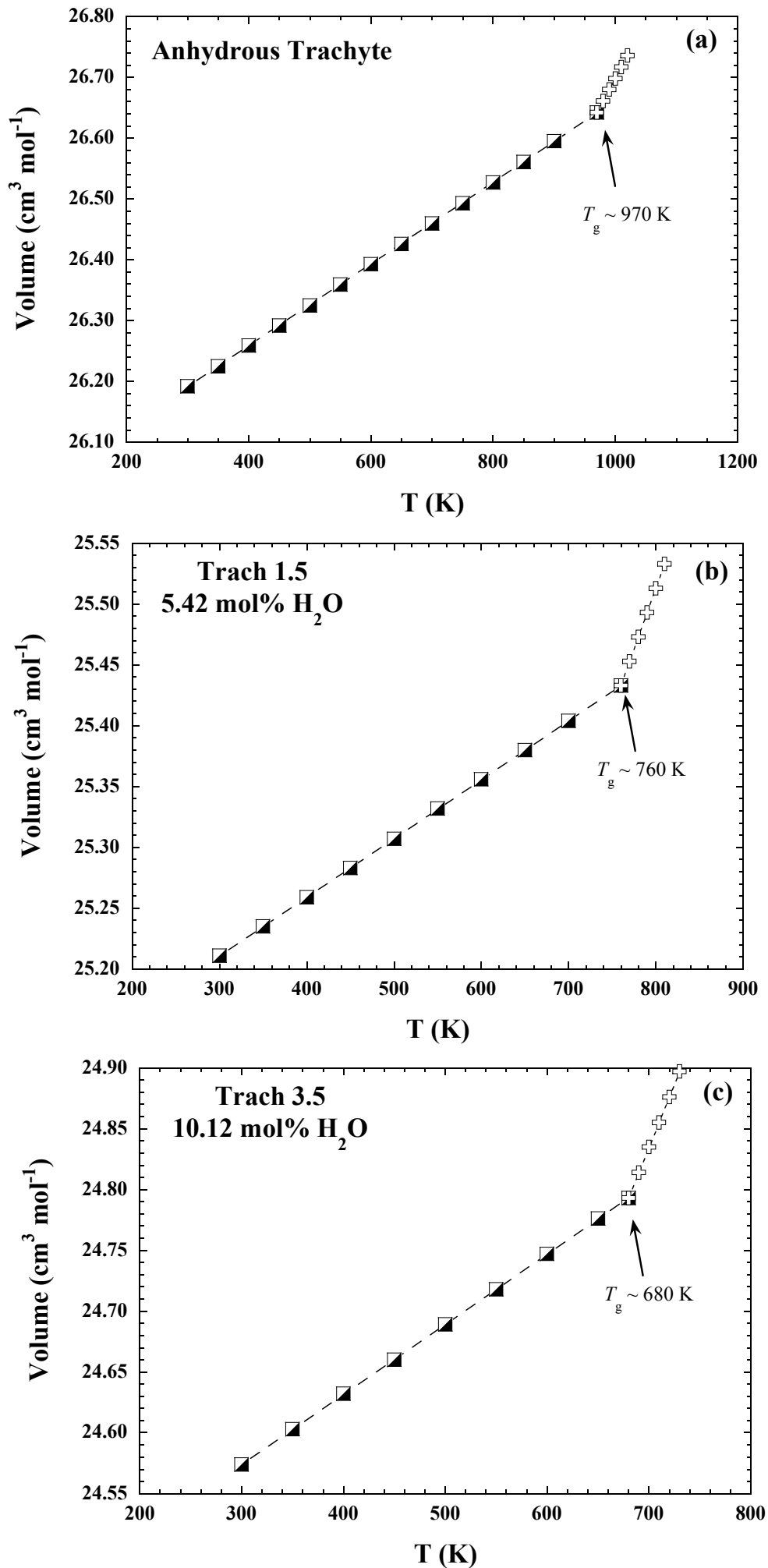


Figure 4.

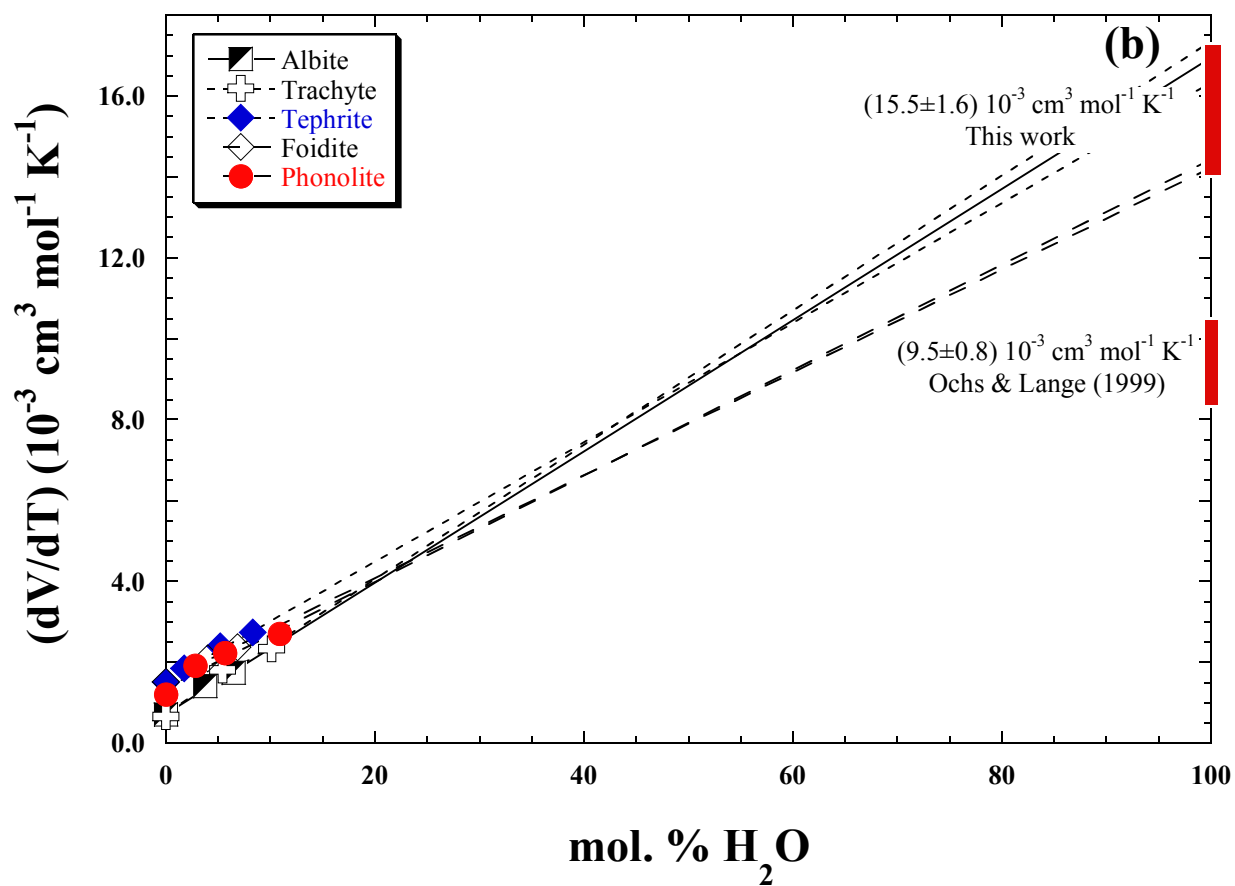
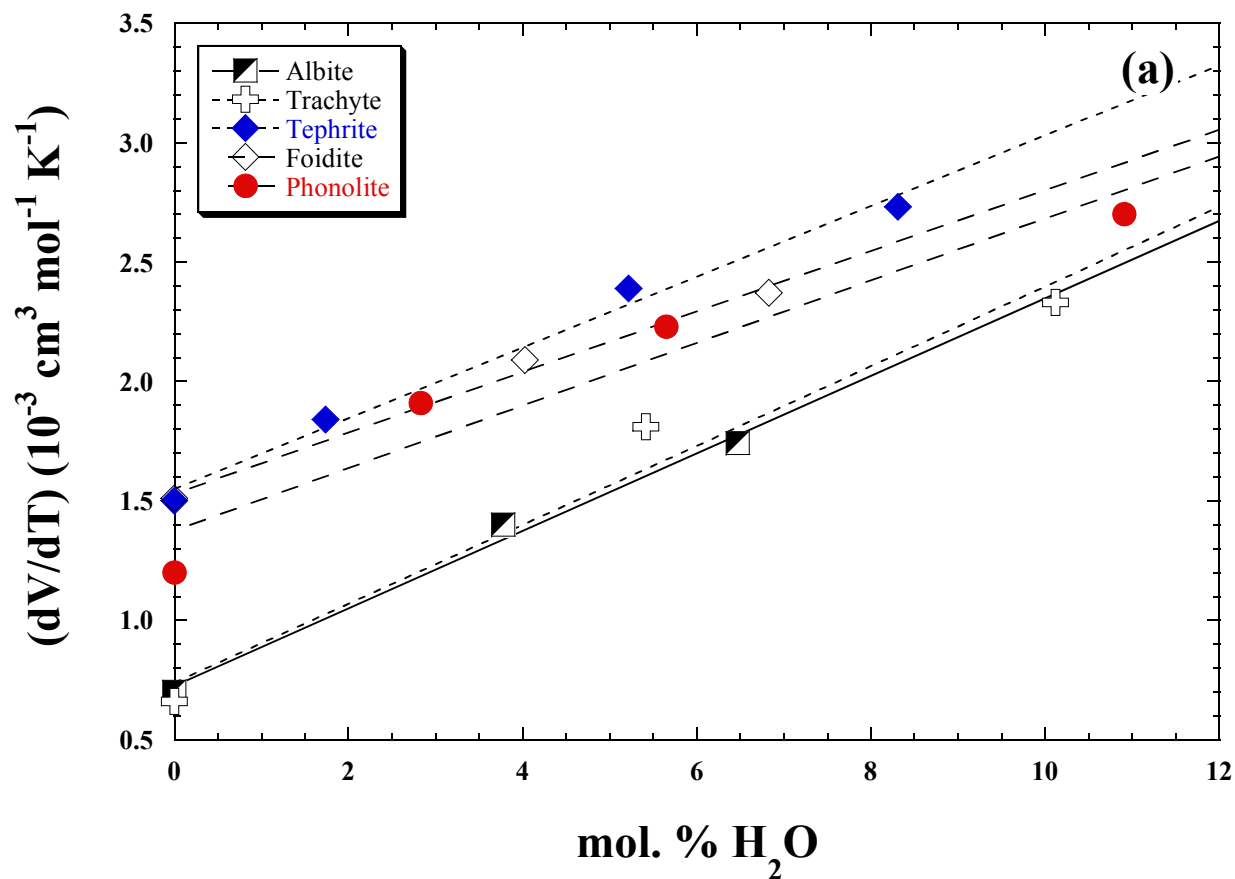


Figure 5.

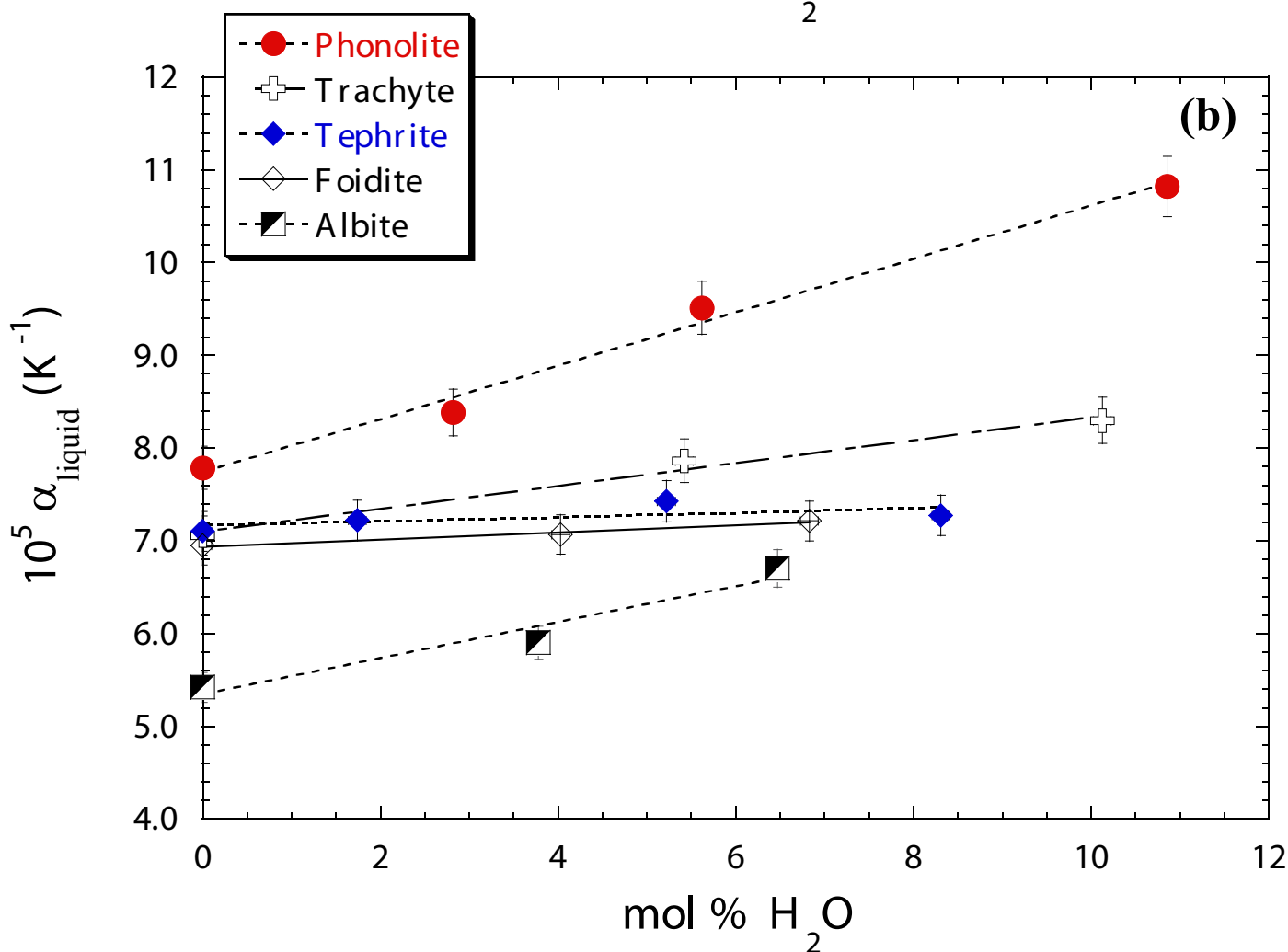
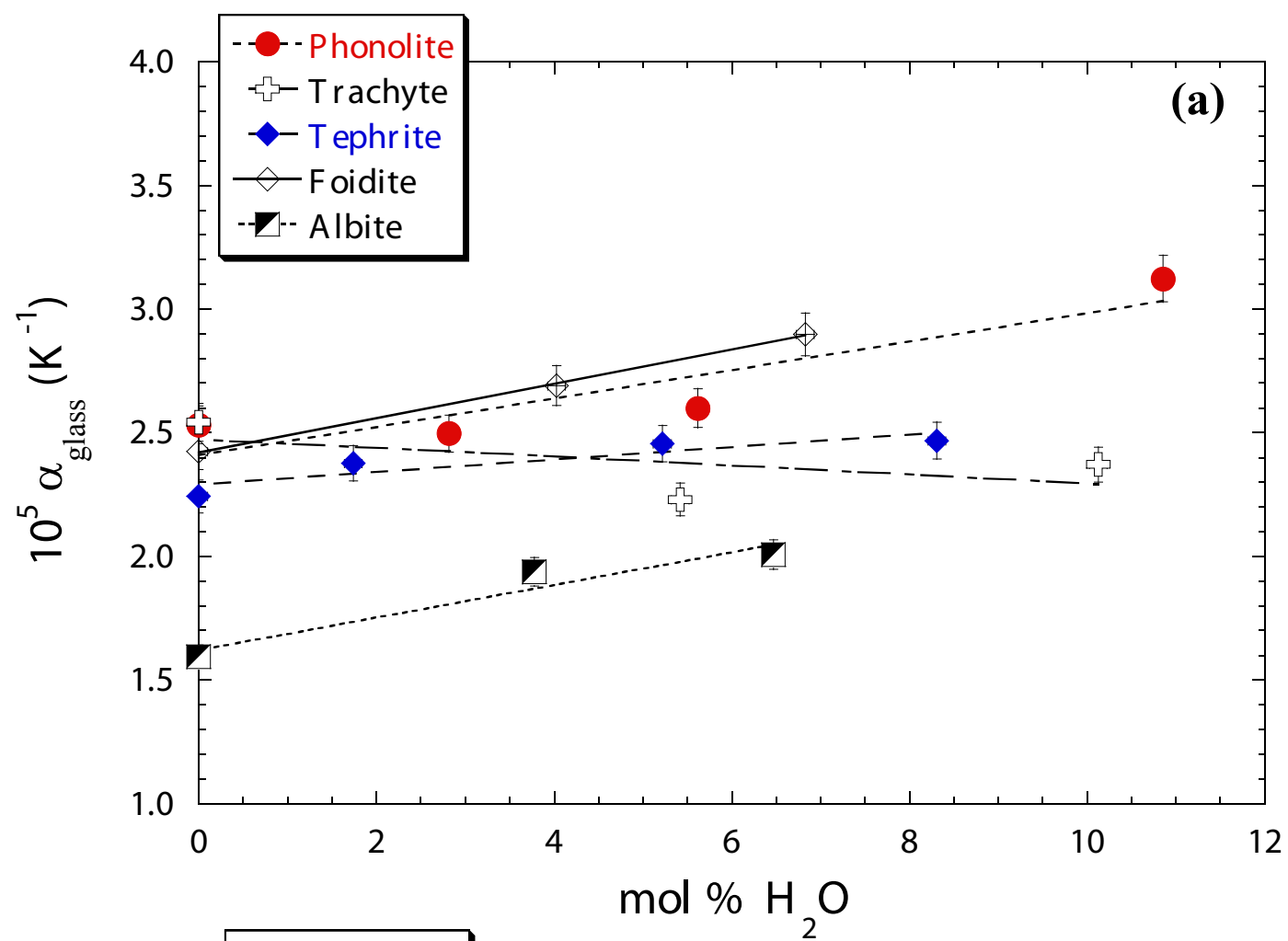


Figure 6.

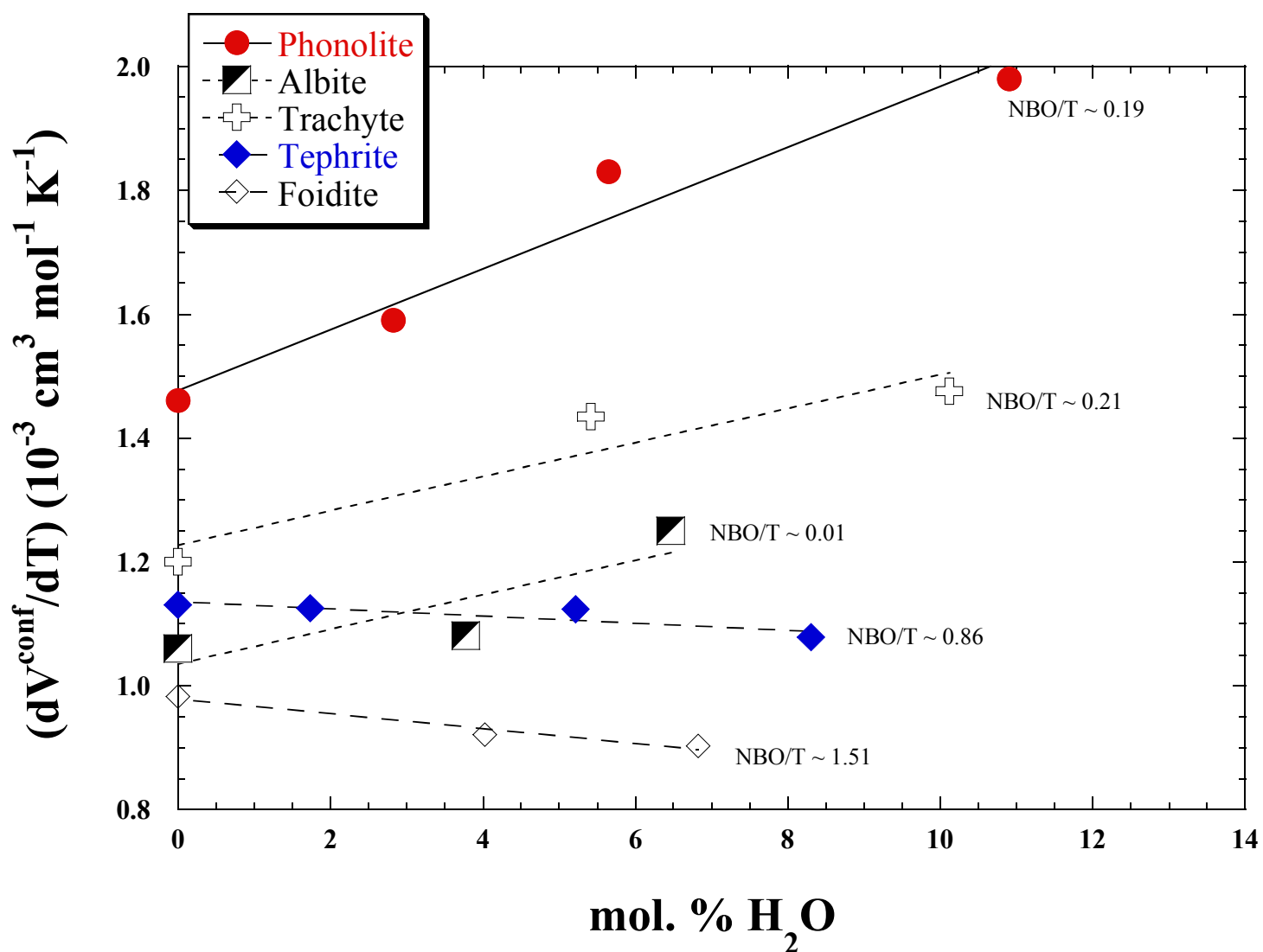


Table 1. Starting anhydrous compositions normalized to mole percent (mol%).

	Albite	Tephrite	Trachyte	Foidite	Phonolite ^a
SiO ₂	75.30	51.32	69.00	42.98	65.40
Al ₂ O ₃	12.07	8.39	10.54	5.92	12.72
Na ₂ O	12.62	6.93	6.95	7.26	10.03
K ₂ O	0.01	1.95	2.30	0.60	5.28
CaO		16.31	6.15	27.55	2.80
MgO		13.30	4.66	13.48	3.10
TiO ₂		1.79	0.40	2.20	0.66
gfw (g) ^b	65.381	61.468	64.324	59.573	66.810
<i>N</i> ^c	3.242	2.872	3.103	2.708	3.196
NBO/T ^d	0.01	0.86	0.21	1.51	0.19

^aThe experimental results for phonolite hydrous compositions are reported in Bouhifd et al. (2001).

^bGram formula weight on the basis of one mole of oxides.

^c*N* is the number of atoms per gfw.

^dNon-Bridging Oxygen per Tetrahedra cations ratio.

Table 2. Hydration conditions, water contents and densities of hydrated albite, tephrite, trachyte and foidite glasses.

Sample	H ₂ O ^a mol%	P (kbar)	T (°C)	t (h)
Albite				
Alb 0.				
Albite-1.3	3.78	2	1200	65
Albite-2.2	6.47	2	1200	65
Tephrite				
Teph 0.				
Teph 0.3	1.74	2	1300	18
Teph 1.5	5.22	3	1300	48
Teph 3	8.31	3	1300	45
Trachyte				
Trach 0.				
Trach 1.5	5.42	2	1300	18
Trach 3.5	10.12	3	1300	48
Foidite				
NIQ 0.				
NIQ 1.2	4.03	3	1300	18
NIQ 2.3	6.83	3	1300	18

^aWater content measured by Karl-Fischer titration (Whittington *et al.*, 2000).

Table 3. Water contents (mol%), gram formula weight on the basis of one mole of oxides, densities of compacted and relaxed glasses, and the corresponding 1 bar volumes.

Sample	H ₂ O mol%	gfw (g)	ρ_{comp} (g/cm ³)	V ₀ (comp) (cm ³ /mol)	ρ_{relax} (g/cm ³)	V ₀ (relax) (cm ³ /mol)	^a Diff%
Albite							
Alb 0.	0.0	65.385			2.371	27.577	
HAB0.6	2.39	64.249	2.387	26.916	2.376	27.041	0.46
Albite-1.3	3.78	63.596	2.384	26.676	2.373	26.800	0.46
Albite-2.2	6.47	62.322	2.375	26.241	2.366	26.341	0.38
HAB5.2	15.75	57.920	2.345	24.699	2.335	24.805	0.43
Tephrite							
Teph 0.	0.0	61.468			2.677	22.962	
Teph 0.3	1.74	60.712	2.686	22.603	2.677	22.679	0.34
Teph 0.8	2.92	60.200	2.682	22.446	2.671	22.538	0.41
Teph 1.8	4.46	59.530	2.674	22.263	2.661	22.371	0.49
Teph 1.5	5.22	59.201	2.677	22.115	2.664	22.223	0.49
Teph 2.2	7.29	58.301	2.661	21.909	2.644	22.050	0.64
Teph 3	8.31	57.855	2.656	21.783	2.644	21.882	0.45
Trachyte							
Trach 0.	0.0	64.328			2.456	26.192	
Trach 50	2.01	63.399	2.477	25.595	2.466	25.709	0.44
Trach 0.83	2.90	62.985	2.468	25.521	2.452	25.687	0.65
Trach 1.19	4.12	62.419	2.461	25.363	2.429	25.697	1.30
Trach 1.5	5.42	61.818	2.467	25.058	2.452	25.211	0.61
Trach 2.2	7.40	60.901	2.457	24.787	2.429	25.072	1.14
Trach 3.5	10.12	59.641	2.437	24.473	2.427	24.574	0.41
Trach 5	15.59	57.121	2.412	23.682	2.398	23.820	0.58
Foidite							
NIQ 0.	0.0	59.573			2.808	21.215	
NIQ 0.7	2.20	58.658	2.815	20.838	2.806	20.904	0.32
NIQ 1.	3.22	58.237	2.806	20.754	2.795	20.836	0.39
NIQ 1.2	4.03	57.899	2.801	20.671	2.790	20.752	0.39
NIQ 1.8	5.93	57.110	2.791	20.462	2.791	20.462	0.0
NIQ 2.3	6.83	56.736	2.789	20.343	2.766	20.512	0.83
Phonolite							
Phon 0.	0.0	66.810			2.457	27.192	
Phon 0.5B	0.78	65.428	2.472	24.468	2.464	26.554	0.32
Phon 1.6	5.65	64.052	2.460	26.037	2.458	26.059	0.08
Phon 2.2	7.53	63.135	2.458	25.686	2.450	25.769	0.33
Phon 3.2	10.91	61.486	2.438	25.220	2.433	25.272	0.21
Phon 5	15.49	59.251	2.412	24.565	2.406	24.626	0.25

^a Diff% corresponds to $(V_0(\text{relax}) - V_0(\text{comp})) \times 100 / V_0(\text{relax})$.

ρ_{comp} : densities of compacted glasses.

ρ_{relax} : relaxed glass densities measured after first thermal expansion measurements up to T_{13} (temperature at which the viscosity is 10^{13} Pa.s).

Table 4. Experimental length (L in mm) of super-cooled liquids as a function of temperature.

T (K)	L(mm)	T (K)	L(mm)	T(K)	L(mm)	T(K)	L(mm)
<u>Anhy. Albite</u>		<u>Albite-1.3</u>		<u>Albite-2.2</u>			
995.6	4.7421	715.5	6.2238	650.3	4.2749		
1005.5	4.7429	725.5	6.2251	660.4	4.2759		
1015.6	4.7436	725.5	6.2250	670.4	4.2769		
1015.6	4.7438	735.5	6.2263	670.5	4.2770		
1025.6	4.7447	745.5	6.2275	680.4	4.2778		
1035.6	4.7455	755.5	6.2286	690.2	4.2788		
1035.7	4.7455						
1045.6	4.7464						
<u>Anhy. Tephrite</u>		<u>Teph 0.3</u>		<u>Teph 1.5</u>		<u>Teph 3</u>	
880.3	8.8040	820.1	6.8025	750.3	4.9377	680.3	4.6249
890.4	8.8061	820.2	6.8024	760.4	4.9388	690.4	4.6259
890.3	8.8057	830.1	6.8041	770.4	4.9402	700.5	4.6269
900.4	8.8081	840.2	6.8058	780.3	4.9412	700.5	4.6272
900.4	8.8078	840.2	6.8056	790.3	4.9426	710.5	4.6283
900.5	8.8080	850.1	6.8076	800.3	4.9438	720.4	4.6291
910.6	8.8102	850.2	6.8075			720.5	4.6294
910.6	8.8101	860.1	6.8092			730.5	4.6305
920.8	8.8124	860.2	6.8091			740.5	4.6316
<u>Anhy. Trachyte</u>		<u>Trach 1.5</u>		<u>Trach 3.5</u>			
916.1	9.8768	730.4	4.2140	650.5	9.1137		
926.1	9.8792	740.3	4.2153	660.5	9.1162		
936.0	9.8815	740.3	4.2149	670.5	9.1185		
936.2	9.8809	750.4	4.2163	680.5	9.1211		
946.1	9.8838	760.3	4.2173	690.5	9.1238		
946.1	9.8832	770.1	4.2185				
956.1	9.8857						
956.1	9.8862						
966.1	9.8887						
966.1	9.8882						
<u>Anhy. Foidite</u>		<u>NIQ 1.2</u>		<u>NIQ 2.3</u>			
850.3	12.8889	760.3	4.0331	680.5	4.5551		
860.2	12.8919	770.1	4.0340	690.5	4.5563		
870.2	12.8947	780.3	4.0350	700.4	4.5574		
880.4	12.8980	800.2	4.0369	700.5	4.5572		
890.1	12.9009			710.4	4.5586		
900.3	12.9038			710.4	4.5583		
				720.3	4.5595		

Table 5. Thermal expansion of the liquids and glasses (compacted and relaxed ones) and temperature intervals of the thermal expansion of liquids.

Sample	H ₂ O mol%	α_{glass}^* (10 ⁻⁵ K ⁻¹)	$\alpha_{\text{glass}}^{**}$ (10 ⁻⁵ K ⁻¹)	Diff. %	α_{liquid} (10 ⁻⁵ K ⁻¹)	ΔT (K)
Albite						
Alb 0.	0.		1.594		5.418	990 - 1050
Albite-1.3	3.78	2.036	1.937	+ 5%	5.900	715 - 755
Albite-2.2	6.47	2.109	2.006	+ 5%	6.701	650 - 690
Tephrite						
Teph 0.	0.		2.242		7.100	880 - 920
Teph 0.3	1.74	2.317	2.376	- 2%	7.220	820 - 860
Teph 1.5	5.22	2.602	2.455	+ 6%	7.424	750 - 800
Teph 3	8.31	2.525	2.467	+ 2%	7.271	670 - 740
Trachyte						
Trach 0.	0.		2.542		7.055	915 - 965
Trach 1.5	5.42	2.335	2.230	+ 5%	7.859	730 - 770
Trach 3.5	10.12	2.505	2.371	+ 7%	8.296	650 - 690
Foidite***						
NIQ 0.	0.		2.422		6.946	850 - 900
NIQ 1.2	4.03		2.690		7.064	760 - 800
NIQ 2.3	6.83		2.897		7.212	680 - 720

*Thermal expansion coefficient of compacted glasses as synthesized (*cf.* Table 2).

**Thermal expansion coefficient of relaxed glasses.

***Only thermal expansion experiments on relaxed glasses were performed.

Diff.% corresponds to $(\alpha_{\text{glass}}^* - \alpha_{\text{glass}}^{**}) / \alpha_{\text{glass}}^*$.

Table 6. Comparison between measured and calculated hydrous liquid volumes (cm³/mol).

Sample	<i>T</i> (K)	<i>V</i> _{exp}	<i>V</i> _{cal} (1) ^a O-L (99)	^b Diff%	<i>V</i> _{cal} (2) ^a This work	^b Diff%
Albite						
Anhydrous	1030	27.90±0.20	27.72	0.65		
Albite	1040	27.91±0.20	27.73	0.65		
	1050	27.93±0.20	27.74	0.69		
	1060	27.95±0.20	27.75	0.73		
	1070	27.96±0.20	27.76	0.73		
	1080	27.98±0.20	27.77	0.76		
Albite-1.3	780	27.05±0.19	27.13	-0.28	27.11	-0.21
	790	27.06±0.19	27.14	-0.27	27.12	-0.20
	800	27.08±0.19	27.15	-0.26	27.14	-0.20
	810	27.10±0.19	27.17	-0.25	27.15	-0.20
	820	27.11±0.19	27.18	-0.24	27.10	-0.20
	830	27.13±0.19	27.19	-0.22	27.18	-0.19
Albite-2.2	710	26.56±0.19	26.77	-0.78	26.70	-0.55
	720	26.58±0.19	26.78	-0.78	26.72	-0.56
	730	26.59±0.19	26.80	-0.77	26.74	-0.56
	740	26.61±0.19	26.81	-0.76	26.76	-0.56
	750	26.63±0.19	26.83	-0.74	26.78	-0.57
	760	26.65±0.19	26.84	-0.73	26.80	-0.57
Tephrite						
Anhydrous	930	23.29±0.16	23.06	0.97		
Tephrite	940	23.30±0.16	23.08	0.93		
	950	23.32±0.16	23.10	0.94		
	960	23.33±0.16	23.12	0.92		
	970	23.35±0.17	23.14	0.91		
	980	23.37±0.17	23.16	0.92		
Teph 0.3	880	22.99±0.16	22.91	0.37	22.91	0.36
	890	23.01±0.16	22.93	0.35	22.93	0.34
	900	23.02±0.16	22.95	0.34	22.95	0.32
	910	23.05±0.16	22.97	0.33	22.97	0.31
	920	23.06±0.16	22.99	0.31	22.99	0.29
	930	23.08±0.16	23.01	0.30	23.01	0.27
Teph 1.5	810	22.50±0.16	22.62	-0.54	22.61	-0.46
	820	22.52±0.16	22.65	-0.56	22.63	-0.50
	830	22.54±0.16	22.67	-0.59	22.66	-0.54
	840	22.55±0.16	22.69	-0.61	22.68	-0.58
	850	22.57±0.16	22.71	-0.63	22.71	-0.61
	860	22.59±0.16	22.74	-0.66	22.73	-0.65
Teph 3	750	22.13±0.15	22.34	-0.95	22.28	-0.69
	760	22.14±0.16	22.36	-1.00	22.31	-0.75
	770	22.16±0.16	22.39	-1.04	22.34	-0.82
	780	22.17±0.16	22.41	-1.07	22.37	-0.87
	790	22.19±0.16	22.44	-1.11	22.40	-0.93
	800	22.21±0.16	22.46	-1.15	22.43	-1.00
Trachyte						
Anhydrous	970	26.64±0.19	26.30	1.28		
Trachyte	980	26.66±0.19	26.31	1.31		
	990	26.68±0.19	26.33	1.31		
	1000	26.70±0.19	26.34	1.35		
	1010	26.72±0.19	26.35	1.38		

	1020	26.74±0.19	26.36	1.42		
Trach 1.5	760	25.47±0.18	25.62	-0.58	25.58	-0.44
	770	25.49±0.18	25.64	-0.57	25.60	-0.44
	780	25.51±0.18	25.65	-0.55	25.62	-0.44
	790	25.53±0.18	25.67	-0.54	25.64	-0.44
	800	25.55±0.18	25.69	-0.53	25.66	-0.44
	810	25.57±0.18	25.70	-0.51	25.68	-0.44
Trach 3.5	680	24.80±0.17	25.08	-1.13	24.79	-0.65
	690	24.82±0.17	25.10	-1.12	24.81	-0.67
	700	24.84±0.18	25.12	-1.12	25.01	-0.70
	710	24.86±0.18	25.14	-1.12	25.04	-0.72
	720	24.88±0.18	25.16	-1.12	25.06	-0.75
	730	24.90±0.18	25.18	-1.12	25.09	-0.77
Foidite*						
Anhydrous	920	21.54±0.15	21.10	2.04	21.57	-0.13
Foidite	930	21.55±0.15	21.12	1.99	21.59	-0.17
	940	21.57±0.15	21.14	1.98	21.61	-0.17
	950	21.58±0.15	21.16	1.93	21.63	-0.22
	960	21.60±0.15	21.18	1.92	21.65	-0.22
	970	21.61±0.15	21.21	1.87	21.67	-0.26
NIQ 1.2	800	21.03±0.15	20.75	1.33	21.15	-0.57
	810	21.05±0.15	20.78	1.29	21.18	-0.60
	820	21.06±0.15	20.80	1.25	21.20	-0.67
	830	21.08±0.15	20.82	1.20	21.23	-0.70
	840	21.09±0.15	20.85	1.16	21.25	-0.77
	850	21.11±0.15	20.87	1.11	21.28	-0.80
NIQ 2.3	750	20.78±0.15	20.55	1.12	20.87	-0.44
	760	20.80±0.15	20.57	1.07	20.90	-0.48
	770	20.81±0.15	20.60	1.01	20.93	-0.57
	780	20.83±0.15	20.63	0.96	20.96	-0.62
	790	20.84±0.15	20.65	0.91	20.99	-0.71
	800	20.86±0.15	20.68	0.85	21.02	-0.76
Phonolite						
Anhydrous	920	27.62±0.19	27.37	0.90		
Phonolite	930	27.65±0.19	27.39	0.95		
	940	27.67±0.19	27.40	0.96		
	950	27.69±0.19	27.42	0.98		
	960	27.71±0.19	27.44	0.99		
	970	27.73±0.19	27.45	1.00		
Phon 0.8	850	26.92±0.19	26.99	-0.27	26.99	-0.26
	860	26.94±0.19	27.01	-0.25	26.01	-0.25
	870	26.97±0.19	27.03	-0.23	27.03	-0.24
	880	26.99±0.19	27.05	-0.22	27.05	-0.23
	890	27.01±0.19	27.07	-0.20	27.07	-0.22
	900	27.03±0.19	27.08	-0.19	27.09	-0.21
Phon 1.6	730	26.35±0.18	26.51	-0.61	26.47	-0.43
	740	26.38±0.19	26.53	-0.60	26.49	-0.43
	750	26.40±0.19	26.56	-0.58	26.51	-0.43
	760	26.43±0.19	26.58	-0.56	26.54	-0.42
	770	26.45±0.19	26.60	-0.55	26.56	-0.42
	780	26.48±0.19	26.62	-0.53	26.59	-0.42
Phon 3.2	620	25.53±0.18	25.75	-0.89	25.60	-0.23
	630	25.55±0.18	25.78	-0.88	25.62	-0.24
	640	25.58±0.18	25.80	-0.86	25.65	-0.26
	650	25.61±0.18	25.83	-0.85	25.68	-0.27

660	25.64±0.18	25.85	-0.84	25.72	-0.29
670	25.66±0.18	25.88	-0.83	25.74	-0.30

^a V_{cal} (1) is calculated using the model of Lange (1997) and Ochs and Lange (1999). V_{cal} (2) is calculated using the model of Lange (1997) and our new values for $\bar{V}_{\text{H}_2\text{O}}$ and $\frac{d\bar{V}_{\text{H}_2\text{O}}}{dT}$. For the foidite serie V_{cal} (2) is calculated using the following equation:

$$V_{\text{liquid}}(T) = \sum X_i \times \left[\bar{V}_i(T_{\text{ref}}) + \frac{d\bar{V}_i}{dT} \times (T - T_{\text{ref}}) \right] + X_{\text{SiO}_2} X_{\text{CaO}} \left[\bar{V}_{\text{SiO}_2\text{-CaO}}(T_{\text{ref}}) + \frac{d\bar{V}_{\text{SiO}_2\text{-CaO}}}{dT} \times (T - T_{\text{ref}}) \right]$$

^b Diff% corresponds to $(V_{\text{exp}} - V_{\text{cal}}) \times 100 / V_{\text{exp}}$.

Table 7. Parameters of the liquid volume equation (9)

Oxide	\bar{V}_i (cm ³ /mol)	$d\bar{V}_i / dT$ (cm ³ /mol K)	Reference
$T_{\text{ref}} = 1073$ K			
SiO ₂	26.86	0.	Lange (1997)
Al ₂ O ₃	37.42	0.	Lange (1997)
MgO	9.57	$3.27 \cdot 10^{-3}$	Lange (1997)
CaO	14.10	$3.74 \cdot 10^{-3}$	Lange (1997)
Na ₂ O	23.88	$7.68 \cdot 10^{-3}$	Lange (1997)
K ₂ O	38.22	$12.08 \cdot 10^{-3}$	Lange (1997)
TiO ₂ *	28.32	0.	Lange and Carmichael (1987)
TiO ₂ *	23.87	0.	Lange and Carmichael (1987)
$T_{\text{ref}} = 1273$ K			
H ₂ O	22.89	$9.55 \cdot 10^{-3}$	Ochs and Lange (1999)
H ₂ O	23.80	$15.85 \cdot 10^{-3}$	This work
$T_{\text{ref}} = 1873$ K			
SiO ₂	27.297	$1.157 \cdot 10^{-3}$	Courtial and Dingwell (1999)
Al ₂ O ₃	36.666	$-1.184 \cdot 10^{-3}$	Courtial and Dingwell (1999)
MgO	12.662	$1.041 \cdot 10^{-3}$	Courtial and Dingwell (1999)
CaO	20.664	$3.756 \cdot 10^{-3}$	Courtial and Dingwell (1999)
SiO ₂ -CaO	-7.105	$-2.138 \cdot 10^{-3}$	Courtial and Dingwell (1999)

*The partial molar volume of TiO₂ is 28.32 cm³/mol and 23.87 cm³/mol in sodium and calcium silicate liquids, respectively (Lange and Carmichael, 1987).

Table 8. Linear fits of the molar volume (cm^3/mol) of glasses and liquids and thermal expansivity of glasses and liquids in the albite, tephrite, trachyte and foidite hydrous compositions.

Sample	a_{glass}	$(dV/dT)_{\text{glass}}$ ($10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$)	$\Delta T \text{ (K)}^a$	a_{liquid}	$(dV/dT)_{\text{liquid}}$ ($10^{-3} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$)	$\Delta T \text{ (K)}^a$	$T_{12} \text{ (K)}^b$
Albite							
Alb 0.	27.444	0.44	300-1000	26.353	1.50	990-1050	1032
Albite-1.3	26.644	0.52	300-700	25.802	1.60	715-755	784
Albite-2.2	26.181	0.53	300-640	25.191	1.79	650-690	712
Tephrite							
Teph 0.	22.806	0.52	300-860	21.754	1.65	880-920	933
Teph 0.3	22.516	0.54	300-810	21.526	1.67	820-860	878
Teph 1.5	22.058	0.55	300-740	21.149	1.67	750-800	814
Teph 3	21.719	0.54	300-660	20.910	1.62	670-740	750
Trachyte							
Trach 0.	25.990	0.67	300-900	24.824	1.87	915-965	970
Trach 1.5	25.041	0.57	300-720	23.951	2.00	730-770	760
Trach 3.5	24.398	0.58	300-640	23.396	2.06	650-690	680
Foidite							
NIQ 0.	21.059	0.52	300-830	20.156	1.50	850-900	916
NIQ 1.2	20.583	0.56	300-740	19.848	1.48	760-800	800
NIQ 2.3	20.333	0.60	300-670	19.656	1.50	680-720	750

^a Temperature interval for the experiments for the glasses and super-cooled liquids.

^b $T_{12} \text{ (K)}$ is the temperature at which the viscosity is 10^{12} Pa.s .