Heat capacity and viscosity of basaltic melts with H₂O ± F ± CO₂

Geneviève Robert^{a,b,*}, Jaayke L. Knipping^c, Stefanie Scherbarth^d, Timothy E. Robertson^a, André Stechern^d, Harald Behrens^d, Alan G. Whittington^a

^a*Department of Geological Sciences, University of Missouri, Columbia, Missouri 65211, USA*

^b*Department of Geology, Bates College, Lewiston, Maine 04240, USA*

^c*Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA*

^d*Institut für Mineralogie, Leibniz Universität Hannover, 30167 Hannover, Germany*

Abstract

We determined the viscosity and heat capacity of a series of two basaltic liquids containing H₂O, F, H₂O+CO₂, H₂O+F, and H₂O+CO₂+F. One was a natural calc-alkaline basalt from Fuego volcano, Guatemala, and the other was a Fe-free synthetic analogue. The viscosity measurements were performed in the low-temperature, high-viscosity range ($\sim 10^9$ - 10^{12} Pa s) just above the glass transition, where the kinetics of volatile exsolution are slow. Differential scanning calorimetry measurements were performed at atmospheric pressure from room temperature up to ~ 100 K above the glass transition. The water contents ranged from nominally anhydrous to 3 wt.% H₂O, with F contents up to 2 wt.%, and CO₂ contents up to 0.2 wt.%. Volatiles do not noticeably affect the heat capacity of glasses. The glass transition temperatures obtained from calorimetry and viscometry are in good agree-

*Corresponding author

Email address: grobert@bates.edu (Geneviève Robert)

ment. Water has a strong viscosity-reducing effect on basaltic melts. F has a measurable viscosity-reducing effect in basaltic melts, but it is significantly smaller than that of water. The combined effects of H₂O and F on viscosity appear to be additive on a wt.% basis. Both the effects of H₂O and F on basaltic melts are smaller than for more polymerized melts. Small quantities of CO₂ do not measurably affect basaltic melt viscosity, at least in the presence of >1 wt.% water. Future viscosity models incorporating fluorine need to account for the compositional dependence of its effects on dry and hydrous melts.

Keywords:

heat capacity, viscosity, water, fluorine, carbon dioxide, basalt

1. Introduction

Arc volcanism is characterized by volatile-rich magmas. Water is by far the most abundant volatile, present in amounts up to ~6 wt.% (e.g., Sisson and Layne, 1993; Berlo et al., 2012), but carbon dioxide and fluorine are

5 also present in smaller quantities (Blundy et al., 2010). Fluorine concentra-
 6 tions are typically in the 100-1000 ppm range in subduction-related basalts
 7 (Aiuppa et al., 2009), and CO₂ abundances can be a few thousand ppm (e.g.,
 8 Wallace, 2005). Both H₂O and CO₂ have solubilities that are negligible at
 9 atmospheric pressures, but which increase with increasing pressure (Brooker
 10 and Blank, 1994; Brooker et al., 1999). Moreover, the solubility of CO₂ is
 11 much less than that of H₂O for relevant crustal pressures (e.g., ~3400 ppm
 12 at 500 MPa; Shishkina et al., 2010). In contrast, fluorine is incompatible
 13 in the gas phase, and does not exsolve with the other volatiles upon de-
 14 pressurization of the magma. Indeed, fluorine is quite soluble in melts even
 15 at atmospheric pressure, up to several wt.% (Webster, 1990; Aiuppa et al.,
 16 2009). In silicic systems, the addition of F has even been demonstrated to
 17 increase the solubility of water (Holtz et al., 1993). Water and CO₂, how-
 18 ever, affect each other’s solubilities negatively at equilibrium conditions (e.g.,
 19 Papale, 1999; Behrens et al., 2009; Shishkina et al., 2010; Iacono-Marziano
 20 et al., 2012). Magma degassing paths recovered from the analysis of H₂O and
 21 CO₂ in matrix glasses and melt inclusions typically point to vapour-buffered
 22 conditions, where the magma is in equilibrium with a gas phase of fixed com-
 23 position, perhaps coming from deeper open-system degassing in the system
 24 (e.g., Blundy et al., 2010).

25 There are a number of previous studies that investigated the effects of CO₂
 26 on the viscosity of silicate systems (Brearley and Montana, 1989; White and
 27 Montana, 1990; Bourgue and Richet, 2001; Morizet et al., 2007; Seifert et al.,
 28 2013; Di Genova et al., 2014). In most cases H₂O is present in equal amounts
 29 or in excess of CO₂ in the samples due to the low solubility of CO₂ relative

30 to H_2O and because of hydrogen diffusion through the noble metal capsules
 31 used in synthesis experiments. This makes the effects of CO_2 on viscosity
 32 especially difficult to interpret. Indeed, CO_2 was interpreted to have no effect
 33 on viscosity based on calorimetric measurements of the glass transition on
 34 jadeite ($\text{NBO}/\text{T} = 0$; where NBO/T is the ratio of non-bridging oxygens
 35 to tetrahedrally-coordinated cations in the melt) and phonolite ($\text{NBO}/\text{T} =$
 36 0.18) melts (Morizet et al., 2007), but to have a strong depressing effect,
 37 comparable to that of water, on the viscosity of a potassium silicate ($\text{K}_2\text{O}-$
 38 SiO_2) melt (Bourgue and Richet, 2001, $\text{NBO}/\text{T} \sim 1.5$). Di Genova et al.
 39 (2014) reported that CO_2 causes a further small decrease in the viscosity
 40 of latitic melts ($\text{NBO}/\text{T} = 0.31$), relative to melts containing only H_2O .
 41 The same authors found that there may also be a weak effect of CO_2 on
 42 the viscosity of trachybasalt ($\text{NBO}/\text{T} = 0.65$), based on calorimetric glass
 43 transition measurements. Seifert et al. (2013) extracted viscosity at constant
 44 temperature from the timescale of decompression of glasses. They reported
 45 a very modest effect of CO_2 on viscosity of K_2O -free basalt (~ 0.5 log units
 46 for 3.9 wt.% of CO_2 at 898K; $\text{NBO}/\text{T} = 0.57$), and no measurable effect on
 47 phonolite or rhyolite, even for CO_2 contents as high as 3.4 wt.% (NBO/T of
 48 0.13 and 0.01, respectively). Brearley and Montana (1989) found that CO_2
 49 reduced the viscosity of albite melt ($\text{NBO}/\text{T} = 0$) at high pressures, but
 50 not that of Na-melilite melt ($\text{NBO}/\text{T} = 0.67$). White and Montana (1990)
 51 found that CO_2 had a greater viscosity-reducing effect on sanidine melt than
 52 albite melt, at high pressures. In fact, they found CO_2 to be as efficient
 53 as H_2O in reducing the viscosity of sanidine melt at high temperature and
 54 pressures (1500-1600 °C and 25 kbar). It is important to note that in the

55 latter two studies exact volatiles contents were not measured and that the
56 interpretation is based solely on nominal volatile contents. In summary, the
57 available data for CO₂-bearing melts are frequently contradictory, or at best
58 inconclusive, and the confusion demonstrates the need for thorough sample
59 characterization and accurate measurement of all volatile species that may
60 be present.

61 The effects of fluorine on viscosity have been previously studied in compo-
62 sitions ranging from alkali-rich and silicic melts to diopside melts, with and
63 without water (e.g., Dingwell and Mysen, 1985; Dingwell et al., 1985; Ding-
64 well, 1989; Dingwell and Webb, 1992; Bagdassarov et al., 1993; Baker and
65 Vaillancourt, 1995; Giordano et al., 2004; Zimova and Webb, 2007; Barber,
66 2007; Baasner et al., 2013). Fluorine was always found to decrease the vis-
67 cosity of the samples studied, relative to F-free compositions. The combined
68 effects of F and H₂O were found to be additive in the haplogranitic system by
69 Giordano et al. (2004), but not in the albitic system by Dingwell (1987). The
70 combined effects of H₂O $\pm$ F $\pm$ CO₂ have never been investigated together
71 on the same composition. Moreover, compositions for which the effects of
72 these three volatiles on viscosity and/or heat capacity have been investigated
73 are mostly either Fe-free synthetic analogues or naturally low Fe melts (e.g.,
74 granite, rhyolite).

75 We present viscosity and heat capacity data obtained on natural remelts
76 of a calc-alkaline basalt from Fuego volcano, Guatemala, for samples con-
77 taining water and fluorine, CO₂, or both. Data were also collected on Fe-free
78 synthetic analogues for calc-alkaline basalt containing water and fluorine or
79 only fluorine.

2. Experimental methods

2.1. Sample synthesis

The natural anhydrous glasses (fu06) were obtained by remelting and homogenizing a crystalline sample collected on Fuego volcano, Guatemala, in a high-temperature furnace at 1600 °C under atmospheric conditions, for 30 minutes to 1 hour. Homogenization was achieved by quenching the melt to a glass, crushing it and remelting it, and repeating this process two times. The Fe-free synthetic analogue samples (sb) were obtained by mixing oxide and carbonate powders in the appropriate proportions to reproduce the whole-rock composition of sample GU-4-309 compiled in the Central American volcanic rock geochemistry database (Carr et al., 2014), but replacing the iron, calculated as FeO, by MgO on a molar basis. After slow decarbonation, the CO₂-free mixture was melted and homogenized following the same procedure as for the natural sample. The decarbonation procedure consists of heating the powder mixture at 10 °C/min to 300 °C, holding for 10 minutes, heating at 2 °C/min to 700 °C, holding for 120 minutes, heating at 0.5 °C/min to 950 °C, holding for 60 minutes, and finally heating to 1200 °C at 2 °C/min before shutting power off and cooling to room temperature. Compositions reported in Table 1 represent the average of 30 electron microprobe analyses (see Robert et al., 2013, for details).

Volatiles were dissolved in the anhydrous melts under pressure, in internally heated pressure vessels (IHPV) at the Institut für Mineralogie, Leibniz Universität Hannover. The anhydrous glasses were crushed and sieved to obtain size fractions of <100 μm and 100<x<200 μm that were subsequently mixed in a 1:1 ratio. Distilled water was added in a step-wise fashion to

105 the dry powders in AuPd capsules of 6 mm internal diameter and ~ 30 mm
106 in length. The glass powder was compacted at each step using a metal piston.
107 Each sample was brought to 1250 or 1400 °C (sample sb has a higher
108 liquidus temperature and low water content syntheses required high temperatures)
109 and 3 kbar in the IHPV for 16 hours followed by rapid isobaric quench.
110 For samples also containing F and/or CO₂, an aliquot of the anhydrous base
111 composition was mixed with the appropriate amount of F, added as AlF₃,
112 and/or CO₂ as Ag₂C₂O₄. Adding F as AlF₃ ensured that the Al content of
113 the natural base composition, fu06, would be affected only slightly because
114 3 moles of F are added for every mole of Al. Microprobe measurements on
115 the F-bearing samples recorded a ~ 0.5 wt.% increase in Al₂O₃ for samples
116 containing ~ 1.3 wt.% F, relative to the F-free base composition (see Tables
117 1-2). These mixed powders were then loaded in AuPd capsules and water
118 was added in a step-wise fashion. The mixtures containing multiple volatiles
119 were melted at 1250 °C and 5 kbar for 3 hours. After this initial synthesis,
120 the quenched glass was recovered, recrushed and loaded into Pt capsules
121 with flat, circular bottoms of ~ 4 mm in diameter. These were remelted at 5
122 kbar and 1250 °C for only 3 minutes to avoid Fe loss to the Pt capsule wall.
123 Pt capsules are more flexible than AuPd capsules and therefore minimize
124 stresses on the sample during quenching. We were therefore able to produce
125 intact glass cylinders that could simply be unwrapped from the capsules after
126 quenching.

127 Anhydrous samples with F as the only volatile (sb+F, fu06+F) were synthesized
128 at 1 atm in the laboratory at the University of Missouri – Columbia.
129 In the natural samples, F was added to an fu06 remelt as CaF₂ powder. This

130 resulted in an increase in the CaO content of fu06 of ~ 2 wt.% for samples
 131 containing 2.04 wt.% F relative to the F-free base composition. In the syn-
 132 thetic composition sb, calcium is introduced as CaCO_3 , and the compositions
 133 decarbonated to remove all CO_2 . We introduced F in sb by replacing the
 134 appropriate amount of CaCO_3 by CaF_2 in the mixture (one oxygen atom is
 135 exchanged for two fluorine atoms via the exchange operator F_2O_{-1}). We did
 136 not detect a difference in the measured CaO content between the F-bearing
 137 and F-free glasses, within microprobe uncertainty.

138 *2.2. Sample characterization*

139 Backscattered electron images of the samples containing a single volatile
 140 (either H_2O or F) and the synthetic sample sb+ H_2O +F showed they con-
 141 tained no vesicles or crystals and consisted of homogeneous glass. Glasses
 142 of natural basalt, fu06, containing multiple volatiles, however, were always
 143 vesicular (vesicles up to $50\ \mu\text{m}$ in size), with an inhomogeneous vesicle disri-
 144 bution, but they did not contain quench crystals. We interpret the vesicles
 145 to be pockets of trapped air remaining in the glasses because of the short (3
 146 minute) final synthesis step. The most porous samples had bubble fractions
 147 of ~ 0.10 and we therefore do not expect viscosity measurements to be af-
 148 fected significantly by the vesicles at the low strain rates and high viscosities
 149 of the parallel-plate experiments (Mader et al., 2013).

150 The density of the glass cores was measured before and after each viscos-
 151 ity experiment, and before each calorimetry experiment (Table 2). Density
 152 was measured by the Archimedean method, using anhydrous ethanol as the
 153 immersion liquid. The densities of the samples containing multiple volatiles
 154 represent the density of the volatile-bearing glass plus any air bubbles rather

than a true glass density, as is the case for the non-vesicular dry or hydrous samples. Water content of the samples containing no other volatiles was determined by Karl Fischer Titration (KFT). We refer to Robert et al. (2013) for details of the two methods.

The CO₂ content of samples was determined by FTIR in the Middle InfraRed (MIR) range on doubly polished sections of 100 μm thickness at LUH. All samples showed a double peak at 1430 and 1520 cm^{-1} indicating carbon dissolved as carbonate rather than molecular CO₂. This is in agreement with previous studies on tholeiitic basalts (e.g., Pawley et al., 1992; Brooker and Blank, 1994; Dixon et al., 1995; Shishkina et al., 2010). The 1520 cm^{-1} peak overlapped with the 1630 cm^{-1} molecular H₂O peak, and therefore the 1430 cm^{-1} CO₃²⁻ peak was used to extract the CO₂ concentrations. We used the linear absorption coefficients $\varepsilon_{1430} = 317 \pm 23 \text{ Lmol}^{-1}\text{cm}^{-1}$ derived for CO₂ by Shishkina et al. (2010) for tholeiitic basalts, and $\varepsilon_{3550} = 61 \pm 7 \text{ Lmol}^{-1}\text{cm}^{-1}$ for water calibrated based on the KFT measurements of fu06. Water and CO₂ concentrations (C) were then obtained with the following equations:

$$C_{H_2O} = \frac{M_{H_2O} \cdot A_{3550}}{\rho \cdot d \cdot \varepsilon_{3550}} \quad (1)$$

$$C_{CO_2} = \frac{M_{CO_2} \cdot A_{1430}}{\rho \cdot d \cdot \varepsilon_{1430}} \quad (2)$$

where M is the molar mass in gmol^{-1} , A the absorbance at a given wavenumber, ρ the density in gL^{-1} , d the sample thickness in m, and ε the linear molar absorption coefficients in $\text{Lmol}^{-1}\text{cm}^{-1}$. This method is valid only for low water contents measurable in the Middle InfraRed range (MIR).

Fluorine content was measured by electron microprobe at LUH. The instrument is a CAMECA SX 100. We used an acceleration voltage of 15

177 kV, a beam current of 4 nA, a defocused beam diameter of 10 μm , and a
 178 counting time of 20 s. The standard for fluorine was SrF_2 . The $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$
 179 ratio of the Fe-bearing samples was determined by wet chemistry based on
 180 the method of Wilson (1960) and subsequently modified by Schuessler et al.
 181 (2008). Volatile contents and Fe oxidation ratios of the samples are reported
 182 in Table 2.

183 2.3. Viscometry

184 We measured viscosity at low temperatures just above the glass transition
 185 by parallel-plate viscometry on cylindrical samples with polished parallel
 186 ends. Samples had diameters between 4-6 mm and lengths between 4-10 mm.
 187 Details of the technique and calibration of the parallel-plate apparatus can
 188 be found in Whittington et al. (2009). Samples generally underwent less than
 189 10% shortening during the viscosity measurements and the cores maintained
 190 a cylindrical shape. We therefore calculated viscosity from the shortening
 191 rate of the samples at constant load using the perfect slip condition (Dingwell
 192 et al., 1993), using the following equation:

$$\eta_s = \frac{mgh^2}{3V \frac{dh}{dt}} \quad (3)$$

193 where m is the mass applied to the sample (kg), g gravity (ms^{-2}), h the
 194 sample height (m), V the volume of the sample (m^3), and t is time (s).

195 2.4. Calorimetry

196 Calorimetric measurements were made using PerkinElmer DSC8500 and
 197 Netzsch DSC 404 Pegasus F1 Differential Scanning Calorimeters (DSC), the
 198 former up to 750°C and the latter up to a 1495°C. Measurements in the

199 PerkinElmer DSC8500 were performed using a scan rate of 25K/min, 25K
 200 intervals, and 1 minute holds between scanning steps under a nitrogen flow
 201 of 20 ml/min and gold sample and reference pans. Measurements in the
 202 Netzsch 404 Pegasus F1 were performed using continuous scanning at a rate
 203 of 20K/min under a nitrogen flow of 20 ml/min and PtRh alloy sample and
 204 reference pans. Prior to heat capacity measurements, compacted glasses were
 205 relaxed to their equilibrium volume at atmospheric pressure by heating them
 206 to the temperature at which they were expected to have a viscosity of 10^{14} Pa
 207 s following the procedures described above. Each heat capacity measurement
 208 consisted of three runs: a blank run with empty sample and reference pans,
 209 a standard run with empty reference pan but using a pure α -Al₂O₃ disk in
 210 the sample pan, and finally the sample run against an empty reference pan.
 211 Whenever possible, samples were prepared into thin disks of $\sim$ 10-60 mg.
 212 Repeat measurements on the same disk returned the same values of heat ca-
 213 pacity within 2% and glass transition temperature within 5K. Calorimetric
 214 measurements on the α -Al₂O₃ standard disk run as an unknown recovered
 215 values well within 1% of the standard values (Ditmars et al., 1982). These
 216 tests were performed with the same manipulations involved when measur-
 217 ing an unknown and therefore take into account user-introduced errors. An
 218 analysis of the uncertainties in heat capacity can be found in Robert et al.
 219 (2014). The minimum estimate of uncertainty on C_P is ~ 0.36 Jmol⁻¹K⁻¹
 220 based on an evaluation of the mismatch in the heat capacity measured for
 221 α -Al₂O₃ run as an unknown and the accepted standard values of Ditmars
 222 et al. (1982).

223 The calorimetric glass transition was calculated using the methodology

224 defined by Webb and Knoche (1996). A linear fit to liquid heat capacity was
 225 extrapolated to lower temperatures, a Maier-Kelley fit for the glass extrapo-
 226 lated to higher temperatures, and the low temperature and high temperature
 227 intersections of the extrapolated curves with a linear fit of the steepest part
 228 of the heat capacity data through the glass transition defined T_a and T_b
 229 (Figure 1). The calorimetric glass transition temperature is then defined as
 230 $T_g^{cal} = T_a + (T_b - T_a)/2$ (Webb and Knoche, 1996). The glass transition
 231 temperatures obtained by fitting the step scan DSC data obtained in the
 232 PerkinElmer calorimeter and the continuous traces on repeat samples in the
 233 Netzsch calorimeter agree to within 5 degrees.

234 **3. Results**

235 *3.1. Viscometry*

236 Figure 2 shows the viscosity results for the natural basaltic sample, fu06,
 237 and the synthetic analogue, sb. Dotted lines are Tammann-Vogel-Fulcher
 238 (TVF) fits to the data of the form $\log \eta = A + B/(T-C)$ where T is in Kelvin
 239 and A , B , and C are fitting parameters. The data are reported in Tables 3-7,
 240 and TVF fits in Table 8. In Figure 2a, the viscosity of natural basalt fu06
 241 with F, H_2O+F , H_2O+CO_2 , or $H_2O+F+CO_2$ is compared to the viscosity
 242 of hydrous fu06. H_2O reduces the viscometric glass transition temperature
 243 T_{12} defined as the temperature at which the samples have a viscosity of
 244 10^{12} Pa s. Adding 2.3 wt.% H_2O to fu06, reduces T_{12} by 180 K (sample
 245 fu06+2.29H₂O). The addition of ~ 2 wt.% F reduces T_{12} by 32 K relative to
 246 the volatile-free fu06 (fu06+2.02F). In Figure 2b, the viscosity of synthetic
 247 basalt sb with F and H_2O+F are compared to the viscosity of hydrous sb.

248 Adding 3.0 wt.% H₂O to sb reduces T₁₂ by 210 K, and ~1.3 wt.% reduces
 249 T₁₂ by 105 K (sb+3.02H₂O and sb+1.31H₂O, respectively). The addition of
 250 ~1 wt.% F to sb results in a reduction of T₁₂ by 27 K.

251 3.2. Calorimetry

252 The data are reported in Tables 9-12b. Heat capacity data obtained on
 253 samples containing only H₂O have been previously published in Robert et al.
 254 (2014). The data on hydrous samples are compared here to heat capacity
 255 data for samples containing only fluorine or multiple volatiles (Figure 3). In
 256 the rare cases where samples underwent degassing or crystallization during
 257 the measurements, as confirmed by a heat capacity decrease below glass
 258 values at high temperatures, sample weight change, or visual inspection, the
 259 data in Figure 3 are only plotted up to the glass transition and these data
 260 are annotated (e.g., Table 10). Volatiles have no discernible effect on the
 261 heat capacity of the glasses. Indeed, heat capacity curves below the glass
 262 transition do not vary in a systematic way with respect to volatile content.

263 Samples containing F only, or containing multiple volatiles, behave sim-
 264 ilarly to water-only samples. That is, all samples with a given total volatile
 265 content undergo a similar increase in heat capacity at the glass transition
 266 ($\Delta C_P(T_g)$), defined as the configurational heat capacity. Fluorine does not
 267 seem to affect the configurational heat capacity at the glass transition of the
 268 samples any differently than water does. The same reduction in the glass
 269 transition temperature is observed in the heat capacity data as in the viscos-
 270 ity data (see Figure 4), although in most cases $T_g^{cal} > T_{12}$ and instead closer
 271 to T₁₁ because of the shorter experimental timescales in the calorimetry ex-
 272 periments.

273 4. Discussion

274 4.1. Effect of a single volatile on the glass transition

275 Water has a much stronger effect on the glass transition than fluorine,
276 on a molar basis, when the volatiles are considered individually (Figure 2,
277 and see sb+F vs. sb+H₂O and fu06+F vs. fu06+H₂O in Figure 5b, d).
278 This observation supports the conclusions from some previous authors that
279 fluorine is not as efficient at reducing viscosity as water is, on a molar basis
280 (e.g., Giordano et al., 2004), and that the effect of fluorine decreases with
281 decreasing SiO₂ content (e.g., Dingwell et al., 1985).

282 4.2. Combined effects of volatiles on the glass transition

283 We were unable to synthesize samples containing multiple volatiles with
284 exactly the same water contents as samples containing only H₂O, but al-
285 though direct comparisons are impossible, some conclusions may still be
286 drawn. The viscosity data show that CO₂ may have a small viscosity-
287 reducing effect at low water contents (<1 wt.% H₂O). For example, samples
288 fu06+1.18H₂O and fu06+0.84H₂O+0.09CO₂ have a similar viscosity, even
289 though the latter has a lower water content and would be expected to have a
290 higher viscosity if not for the effect of CO₂. This can also be seen in Figure
291 5c, where the CO₂-bearing sample at ~3 mol.% H₂O has a lower T₁₂ than a
292 sample containing the same amount of only H₂O would have. A CO₂ content
293 of 0.09 wt.% represents only 0.13 mol.%, because CO₂ has a higher molar
294 mass than the other two volatiles (44.01 vs. 18.02 and 38.00 g for H₂O and
295 F₂, respectively), and could imply that CO₂ has a greater effect than H₂O on
296 a molar basis, at least at low water contents. There seems to be little to no

297 effect of CO₂ at higher water contents or in the presence of water and fluorine
 298 (e.g., fu06+1.62H₂O+0.22CO₂, fu06+1.77H₂O+1.31F+0.23CO₂; Figure 2).
 299 The uncertainties on these low CO₂ and H₂O content samples are relatively
 300 large (Table 2, and shown on the lower panels in Figure 5), however, and
 301 caution should be used in the interpretation of the viscosity results. Since
 302 it is difficult to synthesize a melt containing CO₂ without H₂O also being
 303 present (see Bourgue and Richet, 2001; Morizet et al., 2007; Seifert et al.,
 304 2013; Di Genova et al., 2014), we cannot comment on potential CO₂/H₂O
 305 interactions at higher CO₂ contents. We can conclude that the effect of CO₂
 306 on melt viscosity should be negligible in shallow basaltic magmas.

307 The addition of fluorine to a hydrous melt clearly reduces viscosity fur-
 308 ther, but its effects appear to be smaller than those of water. For example,
 309 samples fu06+2.29H₂O and fu06+1.59H₂O+1.31F have similar viscosities,
 310 whereas a sample with 2.29 wt.% total volatiles, sample fu06+1.04H₂O+1.25F,
 311 has a higher viscosity (Figure 2). When only the water content of the samples
 312 is taken into consideration, one sees that the samples containing a significant
 313 amount of fluorine in addition to water deviate from the trend defined by
 314 the water-only or water+CO₂ samples (Figure 5a,c). Indeed, samples con-
 315 taining both volatiles show T_g^{cal} lower than that of samples containing the
 316 same amount of water alone (Figure 5a). When considering the total volatile
 317 content, samples containing water and fluorine show the same T_g reduction
 318 as samples with more H₂O, on a molar basis, and with fluorine expressed as
 319 F₂ (e.g., 4.04 mol%H₂O and 3.47 mol%H₂O+1.98 mol%F₂).

320 Viscosity results for sb show that ΔT_{12} is 7 K for the addition of 0.34
 321 wt.%F, 78 K from the addition of 0.63 wt.%H₂O, and 82 K for the addition of

0.55 wt%H₂O+0.34 wt.%F. Viscosity results for fu06 show that the addition of 1.14 wt.%F results in ΔT_{12} of 27 K, the addition of 1.18 wt.%H₂O in ΔT_{12} of 94 K and the addition of 1.04 wt.%H₂O+1.25 wt.%F in a ΔT_{12} of 110 K. These results suggest the effects of F and H₂O on viscosity and the glass transition temperature to be nearly additive, on a wt.% basis, but more data are needed to be conclusive. In any case, our data do not suggest a strong departure from additivity such as was observed in the system NaAlSi₃O₈-H₂O-F₂O₋₁ studied by Dingwell (1987).

4.3. Comparison with literature data

Several previous studies have investigated the effect of CO₂ or F on the viscosity near the glass transition or calorimetric glass transition temperature of melts (Bourgue and Richet, 2001; Morizet et al., 2007; Zimova and Webb, 2007; Barber, 2007; Baasner et al., 2013; Seifert et al., 2013; Di Genova et al., 2014). Only the K₂O-SiO₂ melts of Bourgue and Richet (2001) show a nearly vertical trend indicative of a significant additional effect of CO₂ on viscosity relative to H₂O-only samples when the glass transition temperature of melts containing both volatiles is plotted against only the water content of the sample (Figure 6a). A detailed look at the data of Bourgue and Richet (2001) shows that the glass transition temperature clearly decreases with increasing CO₂ as H₂O stays nearly constant for all samples. All other compositions investigated show little to no deviation from a trend defined by samples containing only H₂O, including latite and trachybasalt melts (D14; Di Genova et al., 2014), jadeite and phonolite melts (M07; Morizet et al., 2007), and the basalt melts of this study (sb and fu06). Seifert et al. (2013) found a very modest effect of CO₂ on the viscosity of basalt, and no effect

of CO₂ on phonolite or rhyolite, although the unusual way they obtained viscosity data through glass decompression timescales precludes it from being represented on Figure 6a.

The effect of F on T₁₂ depression is clearly a strong function of polymerization, as can be seen in Figure 6b comparing our data with those from dacitic (Barber, 2007), Na₂O-Fe₂O₃-Al₂O₃-SiO₂ (Zimova and Webb, 2007), and (Al₂O₃)-Na₂O-CaO-SiO₂ systems (Baasner et al., 2013). The T₁₂ of sample NCS with ~2 mol.% of F (NBO/T = 0.68) is similar to what is measured for fu06 (NBO/T = 0.64) for roughly the same F content, and follows the trend of T₁₂ depression defined by the basaltic samples. More polymerized samples have much larger ΔT_{12} as F is added. For example, the sample of Zimova and Webb (2007) with NBO/T = 0.06 falls on the trend defined by the dacite samples of Barber (2007) (NBO/T = 0.10). This may suggest that the dissolution mechanisms of F in polymerized melts cause more depolymerization, although the behaviour of the two peraluminous melts from Zimova and Webb (2007) is inconsistent with the overall trend. Indeed, the NBO/T ratio does not give any information about the proportions of the different network formers (e.g., SiO₂ vs. Al₂O₃) and the ratios of alkali to alkaline earth cations in a specific melt, which are needed to assess the possible interactions volatiles may have in the melt structure.

4.4. *Effect of iron*

By comparing our results for the Fe-free melt sb and Fe-bearing melt fu06, we see that F affects both melts more or less equally (Figure 5). Ferrous iron represents 0.46Fe_{total} in the remelted fu06 dry glasses synthesized in air. Fe-bearing fu06 samples containing multiple volatiles were synthesized in IHPV

372 with reducing conditions (QFM at water saturation; Berndt et al., 2002),
 373 resulting in $\text{Fe}^{2+}/\text{Fe}_{total}$ ratios ranging from ~ 0.80 - 0.90 (Table 2). Sample
 374 fu06-04 is the only sample containing only H_2O for which reducing conditions
 375 were used during synthesis. All other hydrous samples were not synthesized
 376 under reducing conditions, and the iron oxidation ratios in these samples
 377 is controlled by their H_2O contents and the intrinsic buffer of the IHPV
 378 (QFM+3.3; Schuessler et al., 2008) via the reaction $\text{Fe}_2\text{O}_3 + \text{H}_2 \rightleftharpoons 2\text{FeO}$
 379 $+ \text{H}_2\text{O}$. As water content increases for the hydrous samples, $\text{Fe}^{2+}/\text{Fe}_{total}$
 380 decreases from ~ 0.8 to 0.6 . The hydrogen pressure is roughly constant during
 381 synthesis, without the addition of hydrogen to the pressure medium. All
 382 hydrous samples are more reduced than the anhydrous fu06 remelt.

383 Previous studies on the effect of iron oxidation on viscosity agree that
 384 reduction of Fe from oxidized conditions reduces viscosity, with minimal or
 385 no further effect once $\text{Fe}^{2+}/\text{Fe}_{total}$ is greater than 0.5 (e.g., Dingwell and
 386 Virgo, 1987; Dingwell, 1991; Liebske et al., 2003; Chevrel et al., 2013). All of
 387 the water-bearing samples investigated in this study have $\text{Fe}^{2+}/\text{Fe}_{total}$ ratios
 388 between ~ 0.60 - 0.90 . We therefore expect little effect on viscosity due to
 389 the different iron oxidation ratios between the water-bearing samples. The
 390 main effect should be between the dry, more oxidized samples synthesized
 391 in air and the water-bearing samples. Comparison of the effects of H_2O
 392 only on the Fe-free sb and Fe-bearing fu06 melts, however, shows essentially
 393 the same magnitude of viscosity decrease for the first ~ 2 mol.% H_2O added,
 394 and parallel trends in glass transition temperature depression with increasing
 395 water content (see Figure 5). We therefore conclude that the Fe oxidation
 396 ratio of samples has no significant effect on the viscosity of hydrous melts

397 within the range $0.6-0.9\text{Fe}^{2+}/\text{Fe}_{\text{total}}$.

398 4.5. *Solution mechanisms of volatiles*

399 Studies of the influence of F on viscosity may be categorized in the fol-
400 lowing ways: (i) studies of polymerized, silica-rich systems, that are alumina-
401 bearing (Dingwell and Mysen, 1985; Dingwell et al., 1985; Zimova and Webb,
402 2007; Bagdassarov et al., 1993; Barber, 2007; Baasner et al., 2013) or alumina-
403 free (Dingwell and Hess, 1998) (ii) studies of depolymerized, silica-poor sys-
404 tems (Dingwell, 1989, alumina-free), and (iii) studies of Fe-bearing melts
405 (Zimova and Webb, 2007; Dingwell and Hess, 1998). Of those studies, only
406 that of Barber (2007) is a complex, multi-component melt close in compo-
407 sition to a natural melt. The melts we studied are calc-alkaline, relatively
408 high-Al depolymerized melts, with one Fe-bearing natural melt (fu06) and
409 one Fe-free analogue (sb). Direct comparisons of the magnitude of the influ-
410 ence of F on viscosity between the different systems are difficult. In many
411 of the studies, the effects of F cannot be separated from the metal cation in
412 the added fluoride used to introduce F in the melt (e.g., CaF_2 or AlF_3 in this
413 study). In others, water and F are both present in all melts. However, in
414 all systems studied, F was always found to reduce the viscosity of the melt
415 relative to an F-free equivalent.

416 Dingwell et al. (1985) and Dingwell (1989) studied the effects of F on
417 viscosity at superliquidus temperatures in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, rel-
418 evant to polymerized, alkali-bearing high-silica natural melts, and on diop-
419 side, as an analogue for very depolymerized (i.e., low SiO_2 – but alumina-free)
420 melts. The effects of fluorine on viscosity were found to be much greater in
421 SiO_2 -rich melts. The correlation of the magnitude of the viscosity-reducing

422 effect of F with SiO_2 can be interpreted as F primarily dissolving in polymer-
 423 ized silicate melts by substituting for bridging oxygens in the Si-O-Si network
 424 and forming non-bridging F or ‘terminal F’. Alternatively, F can dissolve in
 425 fully-polymerized melts ($\text{NBO}/\text{T} = 0$) by forming Na-F and/or Al-F com-
 426 plexes independent of the network (Mysen and Virgo, 1985). A recent NMR
 427 spectroscopic study on fluorine-bearing $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ polymerized
 428 glasses found F associated only with network-forming cations Al and Si in
 429 peraluminous glasses via Si-F-Na, Al-F-Ca, Al-F-Al and Al-F-Na complexes
 430 (Baasner et al., 2014).

431 In peralkaline glasses, however, F also bonds with network-modifying
 432 cations via F-Ca and F-Na complexes, with F-Ca being the most abundant
 433 (Baasner et al., 2014). The weak effect of F on the viscosity of (Al-free) diop-
 434 side and Raman spectroscopic studies of the structure of F-bearing glasses
 435 in which the metal cation is Ca or Na (Mysen and Virgo, 1985; Luth, 1988)
 436 that show little interaction between Si and F, suggested F may dissolve in the
 437 diopside melts by forming charge-neutral (Ca,Mg)- F_2 complexes, effectively
 438 removing some network modifying cations from that role and increasing the
 439 proportion of O that can bridge between tetrahedrally-coordinated Si cations.
 440 In this scenario, the (Ca,Mg)- F_2 complexes are envisaged to be the control
 441 on viscosity and outweigh the effects of increasing polymerization, as F is
 442 always observed to reduce the viscosity of the melts it is added to (Dingwell,
 443 1989).

444 Recent NMR spectroscopic studies confirm that when alkali or alkaline-
 445 earth cations are present in an aluminosilicate glasses, the cations with higher
 446 field strength are preferred by F, with cations such as Mg^{2+} becoming in-

creasingly able to compete for F with Al^{3+} (e.g., Kiczenski and Stebbins, 2006; Kiczenski et al., 2004; Zeng and Stebbins, 2000). As recently corroborated by Baasner et al. (2014), Kiczenski and Stebbins (2006) had found F associated in greater proportion with metal cations in glasses with $\text{M}/\text{Al} > 1$, whereas F-Al environments dominate when $\text{M}/\text{Al} \sim 0.5$. These more recent studies, however, also detect a small proportion of Si-F environments, suggesting the Si-F interaction may be present in all silicate melts (Kiczenski et al., 2004). Moreover, the proportion of Si-F environments increases with increasing fictive temperature, making the proportions of Si-F bonding detected in glasses minimum estimates for what would exist in the melt (Kiczenski and Stebbins, 2006).

In the high-alumina, high-Mg melts studied here, we expect any depolymerization caused by F to occur via F-Al complexes that remove Al from tetrahedral coordination, in addition to a small proportion of Si-F probably present in all F-bearing silicate melts. Baasner et al. (2014) found that water in peralkaline NCAS glasses had a strong influence on F speciation by promoting F-Ca over F-Al environments, and interpreted this as indicating that OH-Al complexes are much more favourable than F-Al complexes. This could help explain our observation that F has a smaller viscosity-reducing power relative to water in increasingly depolymerized melts.

The nature of the interactions of CO_2 with the silicate network and their effects on overall polymerization is more nebulous. In the K_2O - SiO_2 melts studied by Bourgue and Richet (2001), CO_2 is dissolved primarily as carbonate CO_3^{2-} , as determined by Raman spectroscopy. The authors suggested unspecified “special interactions” between CO_2 and potassium to explain the

strong effects of CO_2 on the viscosity of such depolymerized melts (NBO/T
 ~ 1.5). Special interaction of CO_2 with potassium seem to corroborate the
results of Brearley and Montana (1989) and White and Montana (1990) who
found CO_2 affected the viscosity of KAlSi_3O_8 more than that of $\text{NaAlSi}_3\text{O}_8$
melt, and had no effect on $\text{NaCaAlSi}_2\text{O}_7$ melt at superliquidus temperatures.
It is important to note that the CO_2 and H_2O contents were not measured
in the latter two studies and definitive conclusions cannot be made.

We did not observe a measurable effect of CO_2 on viscosity in the presence
of H_2O , therefore we cannot comment further on CO_2 's interactions with
the silicate network, but the “special interactions” invoked by Bourgue and
Richet (2001) could potentially have detectable effects in high-alkali basalts,
and especially lamprophyres, which are strongly enriched in both potassium
and CO_2 compared to typical magmas.

4.6. Comparison with available viscosity models

The viscosity model by Giordano et al. (2008) is currently the only
one that attempts to predict the viscosity of silicate melts containing wa-
ter and/or fluorine. The model is empirical and its accuracy dependent
on the quantity and quality of the viscosity data in its database. Figure
7 shows the measured sample viscosity vs. the calculated sample viscosity
for all dry, water-, fluorine-, and water- and fluorine-bearing samples using
the model of Giordano et al. (2008). Only the viscosity of the dry natu-
ral remelt is well predicted by the model. The viscosities of all volatile-
bearing natural melts are underestimated except for fu06+2.70H₂O and
fu06+1.59H₂O+1.31F which are overestimated. The viscosities of all Fe-free
synthetic melts are underestimated. The mismatch between the measured

497 and calculated viscosities is not systematic, and most of the viscosity data is
498 underestimated by the Giordano et al. (2008) model by more than one order
499 of magnitude, and up to 3 orders of magnitude in some cases. The model
500 overestimates the effect of F alone on viscosity (see fu06+F and sb+F), and
501 because it treats the effects of H₂O and F as additive, this results in the
502 underestimation of the viscosity of mixed volatiles melts. Viscosity measure-
503 ments on volatile-bearing depolymerized compositions are scarce in the low
504 temperature range, near the glass transition, and empirical viscosity mod-
505 els strongly rely on them. We therefore do not find the mismatch between
506 the measured and calculated viscosities surprising. The discrepancies instead
507 highlight the need for more viscosity measurements to be made on complex,
508 multi-component geologic melts.

509 **Acknowledgements**

510 We thank A. Sehlke (MU) and S. Wilke at Leibniz Universität Hannover
511 (LUH) for help with IR and Fe redox measurements, and O. Dietrich at LUH
512 for impeccable sample preparation. This research is supported by the Na-
513 tional Science Foundation through grant EAR-0748411 (AGW). Calorimetry
514 facilities at MU are supported by the National Science Foundation through
515 EAR-1220051 and by NASA through award PGG-NNX12A044G (AGW).
516 Additional support by the German DFG grant BE 1720/24-1,2 (HB) and
517 DAAD and NSERC fellowships (GR) is acknowledged. Comments by three
518 anonymous reviewers, the Special Volume guest editors and Klaus Mezger
519 helped improve this paper.

520 **Figure captions**

521 Figure 1. Graphical representation of the definition of the calorimetric glass
522 transition.

523

524 Figure 2. Viscosity data for the natural basaltic melts (a) containing H₂O
525 (open black circles), H₂O+F (open triangles), H₂O+CO₂ (open diamonds),
526 H₂O+CO₂+F (crosses), and F only (open squares), and for Fe-free synthetic
527 basaltic analogue melts (b) containing H₂O (closed circles), H₂O+F (closed
528 triangles), and F only (closed squares). Water contents in wt.% for water-
529 only samples are in black boxes next to each data set. Fluorine contents
530 in wt.% for F-only samples are in grey boxes next to each data set. Other
531 samples as marked in legend; sample volatile content increases from high
532 temperature to low temperature within each series. There are no exceptions
533 to this trend. Lines are TVF fits to the viscosity data (see Table 8). H₂O-
534 only: solid lines, F-only: dashed lines, multiple volatiles: dotted lines.

535

536 Figure 3. Heat capacity data for the natural basaltic melts (a), and Fe-free
537 synthetic analogues (b). Symbols as in Figure 2, but symbols for samples
538 containing H₂O only alternate between black and grey circle outlines for the
539 natural samples or solid grey and black circles for the analogue samples. As
540 in Figure 2, sample volatile content increases from high temperature to low
541 temperature within each series. Data shown as continuous lines collected in
542 the Netzsch calorimeter for samples sb-dry, sb+0.34F, and sb+1.06F that go
543 through the glass transition near or at higher temperatures than 950K. Hor-
544 izontal dashed line marks the Dulong-Petit harmonic limit of heat capacity

545 of $3R$, where R is the gas constant (Haggerty et al., 1968).

546

547 Figure 4. Comparison of the change in the viscometric glass transition
548 temperature (taken as T_{12}) vs. the change in the calorimetric glass transi-
549 tion temperature due to the addition of volatiles relative to a volatile-free
550 sample (see Table 8). Dashed line marks the perfect 1:1 relationship between
551 the two metrics. Thinner dashed lines on either side mark a $\pm 10K$ deviation.

552

553 Figure 5. (a) Calorimetric glass transition temperature vs. sample water
554 content in mol.%. Numbers next to each symbol indicate F_2 or CO_2 con-
555 tents. (b) Total volatile content in mol.%, where fluorine is reported as mol.%
556 F_2 . Numbers next to each symbol refer to water content. Grey labels refer
557 to fu06, black labels refer to sb. Bottom panels c and d show the viscometric
558 glass transition T_{12} vs. sample water content only (c) or total volatile content
559 (d). Grey dashed lines highlight the natural samples, and black dashed lines
560 the synthetic samples. Error bars for volatile contents are shown on lower
561 panels. Error bars for F-only samples are smaller than symbol size.

562

563 Figure 6. (a) Comparison of literature data with data from this study. Sym-
564 bols for data from this study as in previous figures. K_2O-SiO_2 melts from
565 Bourgue and Richet (2001) (BR01), jadeite and haplophonolite from Morizet
566 et al. (2007) (M07), and latite and trachybasalt melts from Di Genova et al.
567 (2014) and Giordano and Dingwell (2003) (D14). The calorimetric glass tran-
568 sition is reported for fu06, sb, and M07. The viscometric T_{12} is reported for
569 BR01 and D14. (b) F-bearing samples from this study and highly polymer-

570 ized melts in the system $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ from Zimova and Webb
 571 (2007) (ZW07), depolymerized melts in the system $(\text{Al}_2\text{O}_3)-\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$
 572 from Baasner et al. (2013) (B13), and dacitic melts from Barber (2007) (B07).
 573 Labels next to symbols are NBO/T of the volatile-free composition. Fluorine
 574 data reported as mol.% F.

575

576 Figure 7. Comparison of the measured viscosity in our experiments with
 577 the calculated viscosity obtained using the model of Giordano et al. (2008).
 578 Central long-dashed line represents a perfect match between the predicted
 579 and measured values, and the shaded area represents ± 1 log units. Each
 580 data set is labelled with the volatile content on the right. Grey labels for
 581 natural samples, and black labels for synthetic samples.

582

583 References

- 584 Aiuppa, A., Baker, D.R., Webster, J.D., 2009. Halogens in volcanic systems.
 585 Chemical Geology 263, 1–18.
- 586 Baasner, A., Schmidt, B.C., Dupree, R., Webb, S.L., 2014. Fluorine specia-
 587 tion as a function of composition in peralkaline and peraluminous $\text{Na}_2\text{O}-$
 588 $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses: a multinuclear NMR study. *Geochimica et Cos-*
 589 *mochimica Acta* 132, 151–169.
- 590 Baasner, A., Schmidt, B.C., Webb, S.L., 2013. Compositional dependence of
 591 the rheology of halogen (F, Cl) bearing aluminosilicate melts. *Chemical*
 592 *Geology* 346, 172–183.

- 593 Bagdassarov, N., Dingwell, D., Webb, S., 1993. Effect of boron, phosphorus
594 and fluorine on shear stress relaxation in haplogranite melts. *European*
595 *Journal of Mineralogy* 5, 409–425.
- 596 Baker, D.R., Vaillancourt, J., 1995. The low viscosities of F+ H₂O-bearing
597 granitic melts and implications for melt extraction and transport. *Earth*
598 *and Planetary Science Letters* 132, 199–211.
- 599 Barber, N., 2007. The effects of fluorine on the viscosity of dacitic melts.
600 Undergraduate senior thesis. University of Missouri - Columbia.
- 601 Behrens, H., Misiti, V., Freda, C., Vetere, F., Botcharnikov, R.E., Scarlato,
602 P., 2009. Solubility of H₂O and CO₂ in ultrapotassic melts at 1200 and
603 1250 °C and pressure from 50 to 500 MPa. *American Mineralogist* 94,
604 105–120.
- 605 Berlo, K., Stix, J., Roggensack, K., Ghaleb, B., 2012. A tale of two magmas,
606 Fuego, Guatemala. *Bulletin Of Volcanology* 74, 377–390.
- 607 Berndt, J., Liebske, C., Holtz, F., Freise, M., Nowak, M., Ziegenbein,
608 D., Hurkuck, W., Koepke, J., 2002. A combined rapid-quench and H₂-
609 membrane setup for internally heated pressure vessels: Description and
610 application for water solubility in basaltic melts. *American Mineralogist*
611 87, 1717.
- 612 Blundy, J., Cashman, K.V., Rust, A., Witham, F., 2010. A case for CO₂-rich
613 arc magmas. *Earth and Planetary Science Letters* 290, 289–301.
- 614 Bourgue, E., Richet, P., 2001. The effects of dissolved CO₂ on the density

615 and viscosity of silicate melts: a preliminary study. *Earth and Planetary*
616 *Science Letters* 193, 57–68.

617 Brearley, M., Montana, A., 1989. The effect of CO₂ on the viscosity of silicate
618 liquids at high pressure. *Geochimica et Cosmochimica Acta* 53, 2609–2616.

619 Brooker, R.A., Blank, J.G., 1994. Experimental studies of carbon dioxide in
620 silicate melts: solubility, speciation, and stable carbon isotope behavior, in:
621 Carroll, M.R., Holloway, S.R. (Eds.), *Volatiles in Magmas*. Mineralogical
622 Society of America. volume 30, pp. 157–186.

623 Brooker, R.A., Kohn, S.C., Holloway, J.R., McMillan, P.F., Carroll, M.R.,
624 1999. Solubility, speciation and dissolution mechanisms for CO₂ in melts
625 on the NaAlO₂-SiO₂ join. *Geochimica et Cosmochimica Acta* 63, 3549–
626 3565.

627 Carr, M.J., Feigenson, M.D., Bolge, L.L., Walker, J.A., Gazel, E., 2014.
628 RU_CAGeochem, a database and sample repository for Central American
629 volcanic rocks at Rutgers University. *Geoscience Data Journal* , 6pp.

630 Chevrel, M.O., Giordano, D., Potuzak, M., Courtial, P., Dingwell, D.B.,
631 2013. Physical properties of CaAl₂Si₂O₈-CaMgSi₂O₆-FeO-Fe₂O₃ melts:
632 analogues for extra-terrestrial basalt. *Chemical Geology* 346, 93–105.

633 Di Genova, D., Romano, C., Alletti, M., Misiti, V., Scarlato, P., 2014. The
634 effect of CO₂ and H₂O on Etna and Fondo Riccio (Phlegrean Fields) liq-
635 uid viscosity, glass transition temperature and heat capacity. *Chemical*
636 *Geology* 377, 72–86.

- 637 Dingwell, D., Bagdassarov, N., Bussod, G., Webb, S., 1993. Magma rhe-
638 ology, in: Luth, R.W. (Ed.), Short Course Handbook On Experiments
639 at High Pressure and Applications to the Earth's Mantle. Mineralogical
640 Association of Canada, Edmonton, Alberta. volume 21, pp. 131–196.
- 641 Dingwell, D., Mysen, B., 1985. Effects of water and fluorine on the viscosity
642 of albite melt at high pressure: a preliminary investigation. Earth and
643 Planetary Science Letters 74, 266–274.
- 644 Dingwell, D., Scarfe, C., Cronin, D., 1985. The effect of fluorine on viscosities
645 in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$: implications for phonolites, trachytes and
646 rhyolites. American Mineralogist 70, 80–87.
- 647 Dingwell, D., Webb, S., 1992. The fluxing effect of fluorine at magmatic
648 temperatures (600–800 °C): A scanning calorimetric study. American Min-
649 eralogist 77, 30–33.
- 650 Dingwell, D.B., 1987. Melt viscosities in the system $\text{NaAlSi}_3\text{O}_8-\text{H}_2\text{O}-\text{F}_2\text{O}_{-1}$,
651 in: Mysen, B.O. (Ed.), Magmatic Processes: Physicochemical Principles.
652 The Geochemical Society, pp. 423–431.
- 653 Dingwell, D.B., 1989. Effect of fluorine on the viscosity of diopside liquid.
654 American Mineralogist 74, 333–338.
- 655 Dingwell, D.B., 1991. Redox viscometry of some Fe-bearing silicate melts.
656 American Mineralogist 76, 1560–1562.
- 657 Dingwell, D.B., Hess, K.U., 1998. Melt viscosities in the system Na-Fe-
658 Si-O-F-Cl: contrasting effects of F and Cl in alkaline melts. American
659 Mineralogist 83, 1016–1021.

660 Dingwell, D.B., Virgo, D., 1987. The effect of oxidation state on the viscosity
661 of melts in the system Na_2O - FeO - Fe_2O_3 - SiO_2 . *Geochimica et Cosmochim-*
662 *ica Acta* 51, 195–205.

663 Ditmars, D.A., Ishihara, S., Chang, S.S., Bernstein, G., West, E.D., 1982.
664 Enthalpy and heat-capacity standard reference material: Synthetic sap-
665 phire ($\alpha\text{-Al}_2\text{O}_3$) from 10 to 2250K. *Journal of Research of the National*
666 *Bureau of Standards* 87, 1–5.

667 Dixon, J.E., Stolper, E.M., Holloway, J.R., 1995. An experimental study of
668 water and carbon dioxide solubilities in Mid-Ocean Ridge basaltic liquids.
669 Part I: Calibration and solubility models. *Journal of Petrology* 36, 1607–
670 1631.

671 Giordano, D., Dingwell, D.B., 2003. Viscosity of hydrous Etna basalt: im-
672 plications for Plinian-style basaltic eruptions. *Bulletin Of Volcanology* 65,
673 8–14.

674 Giordano, D., Romano, C., Dingwell, D.B., Poe, B., Behrens, H., 2004. The
675 combined effects of water and fluorine on the viscosity of silicic magmas.
676 *Geochimica et Cosmochimica Acta* 68, 5159–5168.

677 Giordano, D., Russell, J.K., Dingwell, D.B., 2008. Viscosity of magmatic
678 liquids: a model. *Earth and Planetary Science Letters* 271, 123–134.

679 Haggerty, J.S., Cooper, A.R., Heasley, J.H., 1968. Heat capacity of three in-
680 organic glasses and supercooled liquids. *Physics and Chemistry of Glasses*
681 5, 130–136.

- 682 Holtz, F., Dingwell, D., Behrens, H., 1993. Effects of F, B₂O₃ and P₂O₅ on
683 the solubility of water in haplogranite melts compared to natural silicate
684 melts. *Contributions to Mineralogy and Petrology* 113, 492–501.
- 685 Iacono-Marziano, G., Morizet, Y., Le Trong, E., Gaillard, F., 2012. New ex-
686 perimental data and semi-empirical parameterization of H₂OCO₂ solubility
687 in mafic melts. *Geochimica et Cosmochimica Acta* 97, 1–23.
- 688 Kiczenski, T., Du, L.S., Stebbins, J., 2004. F-19 NMR study of the ordering
689 of high field strength cations at fluoride sites in silicate and aluminosilicate
690 glasses. *Journal of Non-Crystalline Solids* 337, 142–149.
- 691 Kiczenski, T., Stebbins, J., 2006. The effect of fictive temperature on the
692 structural environment of fluorine in silicate and aluminosilicate glasses.
693 *Journal of the American Ceramic Society* 89, 57–64.
- 694 Liebske, C., Behrens, H., Holtz, F., Lange, R., 2003. The influence of pres-
695 sure and composition on the viscosity of andesitic melts. *Geochimica et*
696 *Cosmochimica Acta* 67, 473–485.
- 697 Luth, R., 1988. Raman spectroscopic study of the solubility mechanisms
698 of F in glasses in the system CaO-CaF₂-SiO₂. *American Mineralogist* 73,
699 297–305.
- 700 Mader, H.M., Llewellyn, E.W., Mueller, S.P., 2013. The rheology of two-phase
701 magmas: A review and analysis. *Journal of Volcanology and Geothermal*
702 *Research* 257, 135–158.
- 703 Morizet, Y., Nichols, A.R.L., Kohn, S.C., Brooker, R.A., Dingwell, D.B.,
704 2007. The influence of H₂O and CO₂ on the glass transition temperature:

insights into the effects of volatiles on magma viscosity. *European Journal of Mineralogy* 19, 657–669.

Mysen, B., Virgo, D., 1985. Structure and properties of fluorine-bearing aluminosilicate melts: the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}$ at 1 atm. *Contributions to Mineralogy and Petrology* 91, 205–220.

Papale, P., 1999. Modeling of the solubility of a two-component $\text{H}_2\text{O}+\text{CO}_2$ fluid in silicate liquids. *American Mineralogist* 84, 477–492.

Pawley, A.R., Holloway, J.R., McMillan, P.F., 1992. The effect of oxygen fugacity on the solubility of carbon-oxygen fluids in basaltic melt. *Earth and Planetary Science Letters* 110, 213–225.

Robert, G., Whittington, A.G., Stechern, A., Behrens, H., 2013. The effect of water on the viscosity of a synthetic calc-alkaline basaltic andesite. *Chemical Geology* 346, 135–148.

Robert, G., Whittington, A.G., Stechern, A., Behrens, H., 2014. Heat capacity of hydrous basaltic glasses and liquids. *Journal of Non-Crystalline Solids* *Under Review*.

Schuessler, J.A., Botcharnikov, R.E., Behrens, H., Misiti, V., Freda, C., 2008. Oxidation state of iron in hydrous phono-tephritic melts. *American Mineralogist* 93, 1493–1504.

Seifert, R., Malfait, W.J., Lerch, P., Sanchez-Valle, C., 2013. Partial molar volume and compressibility of dissolved CO_2 in glasses with magmatic compositions. *Chemical Geology* 358, 119–130.

- 727 Shishkina, T.A., Botcharnikov, R.E., Holtz, F., Almeev, R.R., Portnyagin,
728 M.V., 2010. Solubility of H₂O- and CO₂-bearing fluids in tholeiitic basalts
729 at pressures up to 500 MPa. *Chemical Geology* 277, 115–125.
- 730 Sisson, T., Layne, G., 1993. H₂O in basalt and basaltic andesite glass inclu-
731 sions from four subduction-related volcanoes. *Earth and Planetary Science*
732 *Letters* 117, 619–635.
- 733 Wallace, P., 2005. Volatiles in subduction zone magmas: concentrations and
734 fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanol-*
735 *ogy and Geothermal Research* 140, 217–240.
- 736 Webb, S., Knoche, R., 1996. The glass-transition, structural relaxation and
737 shear viscosity of silicate melts. *Chemical Geology* 128, 165–183.
- 738 Webster, J., 1990. Partitioning of F between H₂O and CO₂ fluids and topaz
739 rhyolite melt. *Contributions to Mineralogy and Petrology* 104, 424–438.
- 740 White, B.S., Montana, A., 1990. The effect of H₂O and CO₂ on the viscosity
741 of sanidine liquid at high pressures. *Journal of Geophysical Research* 95,
742 15683–15693.
- 743 Whittington, A.G., Hellwig, B.M., Behrens, H., Joachim, B., Stechern, A.,
744 Vetere, F., 2009. The viscosity of hydrous dacitic liquids: implications
745 for the rheology of evolving silicic magmas. *Bulletin of Volcanology* 71,
746 185–199.
- 747 Wilson, A.D., 1960. The micro-determination of ferrous iron in silicate min-
748 erals by a volumetric and a colorimetric method. *Analyst* 85, 823–827.

- 749 Zeng, Q., Stebbins, J.F., 2000. Fluoride sites in aluminosilicate glasses: high-
750 resolution ^{19}F NMR results. *American Mineralogist* 85, 863–867.
- 751 Zimova, M., Webb, S., 2007. The combined effects of chlorine and fluorine on
752 the viscosity of aluminosilicate melts. *Geochimica et Cosmochimica Acta*
753 71, 1553–1562.

Figure 1: *Calculation of the calorimetric glass transition temperature*

Figure 2: *Viscosity*

Figure 3: *Heat capacity*

Figure 4: *Comparison of T_g*

Figure 5: *Calorimetric glass transition*

Figure 6: *Literature data*

Figure 7: *Viscosity models*

Table 1: Compositions (wt.%) of the samples used in this study

Sample Description	sb synthetic basalt	fu06 Fuego basalt
SiO ₂	51.46(0.35)	49.40(0.50)
TiO ₂	1.16(0.06)	0.96(0.05)
Al ₂ O ₃	18.62(0.92)	17.57(0.21)
FeO _{total}	<d.l.	10.56(0.38)
MnO	<d.l.	<d.l.
MgO	14.87(0.60)	7.46(0.16)
CaO	9.33(0.24)	8.97(0.21)
Na ₂ O	3.28(0.36)	3.10(0.25)
K ₂ O	0.71(0.04)	0.60(0.05)
P ₂ O ₅		0.16(0.07)
TOTAL	99.44	98.79
NBO/T	0.67	0.64
gfw (g) ^a	60.28	63.48
n ^b	2.897	2.908

Standard deviation on 30 measurements in parentheses.

^a Gram formula weight for one mole of oxides, assuming 0.01 wt.% H₂O.

^b Number of atoms per gram formula weight.

Table 2: Volatile content, density, and iron oxidation ratio of the samples used in this study

sample	H ₂ O KFT ^a (wt.%)	H ₂ O IR ^b (wt.%)	CO ₂ IR ^b (wt.%)	F ^c (wt.%)	ρ pre ^d (kgm ⁻³)	ρ post ^d (kgm ⁻³)	Fe ²⁺ /Fe _{total} pre
sb-01	dry				2679(1)	2683(1)	
sb-02	dry				2677(1)	2684(1)	
sb-11	0.63(0.16)				2692(1)	2672(1)	
sb-12	1.31(0.17)				2682(1)	2659(1)	
sb-16	1.98(0.15)				2661(1)	2647(1)	
sb-14	3.02(0.16)				2641(2)	2629(1)	
sbF-1	0.55(0.16)			0.34(0.03)	2687(2)	2658(2)	
sbF-3	3.70(0.17)			0.34(0.03)	n.a.	n.a.	
sb1Ftr				0.30(0.02)	2681(2)	2684(2)	
sbFgr				0.34(0.03)	2674(1)	2681(2)	
sb3Ftr				1.06(0.04)	2673(2)	2693(2)	
fu06-01	dry				2770(1)	2776(1)	0.46
fu06-02	dry				2771(1)	n.a.	0.46
fu06-07	1.18(0.16)				2773(1)	2755(2)	n.a.
fu06-06	1.44(0.16)				2769(1)	2750(2)	0.78
fu06-03	2.29(0.16)				2755(3)	2732(3)	0.72
fu06-04	2.70(0.15)				2714(1)	2696(2)	0.84 ^f
fu06-10	3.10(0.20)				2737(1)	n.d.	0.65
fu06-11	3.98(0.23)				2710(2)	n.d.	0.64
fu06-0.5H ₂ O-CO ₂ ^e		0.72(0.09)	0.16(0.01)	0.11(0.02)	2785(15)	2588(10)	0.88 ^f
fu06-1H ₂ O-CO ₂ ^e		0.84(0.10)	0.09(0.01)		2811(9)	2478(15)	0.92 ^f
fu06-1.5H ₂ O-CO ₂ ^e		1.62(0.19)	0.22(0.02)		2796(24)	1905(6)	0.82 ^f
fu06-0.5H ₂ O-F ^e		1.04(0.13)		1.25(0.02)	2802(6)	2654(14)	0.84 ^f
fu06-1H ₂ O-F ^e		1.28(0.17)		1.34(0.02)	2742(8)	2453(16)	0.83 ^f
fu06-1.5H ₂ O-F ^e		1.59(0.18)		1.31(0.02)	2779(17)	2509(15)	0.86 ^f
fu06-0.5H ₂ O-CO ₂ -F ^e		0.98(0.12)	0.04(0.01)	1.29(0.02)	2748(18)	2446(90)	n.a.
fu06-1.5H ₂ O-CO ₂ -F ^e		1.77(0.21)	0.23(0.02)	1.31(0.02)	2780(11)	2613(13)	0.88 ^f
fu06-dry		dry		0.12(0.02)	2766(10)	2770(11)	n.d. ^g
fu06-0.35F		dry		0.61(0.02)	2771(11)	2785(7)	n.d. ^g
fu06-1F		dry		1.14(0.01)	2789(10)	2792(5)	n.d. ^g
fu06-2F		dry		2.04(0.03)	2800(13)	2798(7)	n.d. ^g

n.d.: non determined; n.a.: not available

^a Average of KFT measurements on top and bottom of synthesis cylinder. Error in parentheses.

^b Error on IR measurements calculated by propagation of standard deviation on absorbance (A), uncertainty on absorbance measurement, IR wafer thickness, glass density, and extinction coefficient (ε).

^c Standard deviation on 15 measurements in parentheses.

^d Standard deviation on 5 measurements in parentheses.

^e Samples contain $\sim 10\%$ vesicles.

^f Synthesized in reducing environment.

^g Synthesized in air, Fe²⁺/Fe_{total} ratio likely 0.45-0.50.

Table 3: Viscosity data – sb+H₂O

sb dry			sb-16 top		
0.01 wt.%; 0.04 mol%			1.98 wt.%; 6.33 mol%		
T (K)	log η	order	T (K)	log η	order
947.4	13.62	6b	807.4	12.22	7
974.8	12.33	9a	826.6	11.52	8
979.5	12.03	8a	832.7	11.24	10
982.8	12.10	4b	836.9	11.01	5
991.8	11.67	3b	846.4	10.64	6
994.3	11.50	11a	855.6	10.23	4
998.8	11.39	7b	864.7	9.95	9
1006	11.10	8b			
1009	10.91	12a	sb-14 top		
1014	10.77	9b	3.02 wt.%; 9.43 mol%		
1019	10.53	13a	T (K)	log η	order
1025	10.33	1b	784.2	11.53	12
1029	10.14	14a	789.0	11.36	14
1035	9.97	2b	791.2	11.14	11
1039	9.78	15a	797.7	10.95	13
			798.6	11	15
sb-11 top					
0.63 wt.%; 2.08 mol%					
T (K)	log η	order			
900.0	12.16	6			
915.7	11.61	10			
926.8	11.10	5			
937.4	10.75	9			
941.2	10.47	4			
951.0	10.20	8			
sb-12 top					
1.31 wt.%; 4.25 mol%					
877.3	11.98	9			
887.0	11.56	11			
896.9	11.18	13			
901.1	11.03	10			
906.3	10.80	7			
915.8	10.44	8			
920.3	10.33	12			
933.5	9.67	6			

Table 4: Viscosity data – fu06+H₂O

fu06 dry			fu06-03 centre		
0.01 wt.%; 0.04 mol%			2.29 wt.%; 7.63 mol%		
T (K)	log η	order	T (K)	log η	order
912.4	13.13	9	783.3	11.37	12
922.9	12.49	8	788.2	11.18	14
932.5	11.93	7	794.0	10.89	10
947.6	11.22	6	797.7	10.76	11
958.0	10.80	5	803.3	10.55	13
968.0	10.40	4	806.4	10.25	8
978.2	10.04	3	811.3	10.14	9
984.0	9.80	1	fu06-04 centre		
994.3	9.48	2	2.70 wt.%; 8.90 mol%		
fu06-07 top			T (K)	log η	order
1.18 wt.%; 4.04 mol%			757.0	11.13	6
T (K)	log η	order	773.4	10.47	4
845.5	11.60	8	778.1	10.34	5
855.3	11.13	6	782.6	10.01	3
862.7	10.92	7			
865.5	10.64	4			
871.2	10.51	5			
882.8	9.93	3			
888.8	9.87	9			
fu06-06 top					
1.44 wt.%; 4.89 mol%					
T (K)	log η	order			
826.5	11.56	7			
836.2	11.26	5			
841.2	11.03	3			
845.7	10.81	6			
850.4	10.72	4			
854.4	10.28	2			
864.7	9.81	8			

Table 5: Viscosity data – sb+F±H₂O

sb-1Ftr			sb-3Ftr		
0.30 wt.%F; 0.95 mol%F			1.06 wt.%F; 3.29 mol%F		
T (K)	log η	order	T (K)	log η	order
997.8	11.43	7	965.8	11.50	10
1014	10.93	6	981.4	10.85	8
1020	10.61	5	989.2	10.52	9
1022	10.44	9	998.1	10.17	11
1045	9.72	3	1001	10.04	6
1050	9.51	2	1003	9.98	7
1066	8.84	8	1006	9.82	4
			1017	9.48	5
sbFgr			sbF-1		
0.34 wt.%F; 1.07 mol%F			wt. %: 0.55H ₂ O+0.34F mol%: 1.80H ₂ O+1.06F		
T (K)	log η	order	T (K)	log η	order
954.5	13.00	6			
973.6	12.09	5	904.0	11.83	9
983.8	11.69	4	925.6	10.94	7
993.7	11.26	3	936.1	10.50	5
1010	10.60	8	937.7	10.47	8
1016	10.39	1	942.4	10.27	6
1026	10.04	2	951.3	9.91	4
1035	9.70	9	953.0	9.91	11
1045	9.34	10	961.1	9.63	10

Table 6: Viscosity data – fu06+F

fu06-0.35F			fu06-2F		
0.60 wt.%F; 1.98 mol%F			2.02 wt.%F; 6.43 mol%F		
T (K)	log η	order	T (K)	log η	order
929.1	11.39	6	926.1	10.65	3a
935.4	11.14	4	930.5	10.61	6a
946.3	10.68	2	934.0	10.35	2b
953.6	10.40	3	935.5	10.36	4a
963.3	10.05	5	937.9	10.41	8b
967.5	9.91	7	939.2	10.32	5a
971.8	9.74	8	939.7	10.32	7a
972.3	9.71	1	941.0	10.10	4b
			944.5	9.95	2a
			945.5	9.92	3b
			948.9	9.69	1b
fu06-1F					
1.14 wt.%F; 3.71 mol%F					
T (K)	log η	order			
914.8	11.53	6b			
919.5	11.39	7b			
925.2	11.09	4b			
938.0	10.61	7a			
940.0	10.49	5b			
943.0	10.32	5a			
944.8	10.33	2b			
948.4	10.10	3a			
948.8	10.15	3b			
949.6	10.17	10a			
953.2	10.03	8a			
955.5	9.97	8b			

Table 7: Viscosity data – fu06+H₂O±F±CO₂

fu06-0.5H ₂ O-F			fu06-1.5H ₂ O-CO ₂		
wt.%: 1.04H ₂ O+1.25F			wt.%: 1.62H ₂ O+0.22CO ₂		
mol%: 3.47H ₂ O+3.96F			mol%: 5.48H ₂ O+0.30CO ₂		
T (K)	log η	order	T (K)	log η	order
836.5	11.02	6	828.4	10.99	6
841.3	10.79	4	837.8	10.60	5
846.0	10.70	7	840.6	10.58	3
850.8	10.46	5	844.8	10.36	7
856.7	10.14	2	849.5	10.20	4
860.7	10.05	3			
868.0	9.67	1			
fu06-1.5H ₂ O-F			fu06-0.5H ₂ O-F-CO ₂		
wt.%: 1.59H ₂ O+1.31F			wt.%: 0.98H ₂ O+1.29F+0.04CO ₂		
mol%: 5.23H ₂ O+4.09F			mol%: 3.27H ₂ O+4.08F+0.05CO ₂		
T (K)	log η	order	T (K)	log η	order
787.7	11.02	4	832.8	11.43	5
794.9	10.82	6	842.2	11.00	6
802.1	10.40	2	847.6	10.45	3
803.6	10.35	5	856.0	10.07	2
807.3	10.24	7	861.6	10.12	4
812.0	10.04	3			
fu06-0.5H ₂ O-CO ₂			fu06-1.5H ₂ O-F-CO ₂		
wt.%: 0.72H ₂ O+0.11F+0.16CO ₂			wt.%: 1.77H ₂ O+1.31F+0.23CO ₂		
mol%: 2.48H ₂ O+0.36F+0.23CO ₂			mol%: 5.79H ₂ O+4.07F+0.31CO ₂		
T (K)	log η	order	T (K)	log η	order
861.1	11.52	5	787.1	11.21	8
870.5	11.17	6	794.3	10.88	6
875.7	10.86	3	801.6	10.38	7
885.1	10.54	4	807.3	10.36	4
898.7	9.88	2	810.1	10.13	2
			816.2	10.00	5
fu06-1H ₂ O-CO ₂					
wt.%: 0.84H ₂ O+0.09CO ₂					
mol%: 2.90H ₂ O+0.13CO ₂					
T (K)	log η	order			
843.1	11.79	8			
855.1	11.23	6			
864.7	10.73	4			
871.1	10.58	5			
873.0	10.33	2			
882.9	10.01	3			

Table 8: TVF fits to the viscosity data

sample	A ^a	B	C	T ₁₂ (K)	T ₁₁ (K)	T ^{cal} (K)
fu06-01, fu06-02, fu06-dry	-8.82	8998.3	500.5	932	954	950
fu06-07	-8.64	8997.6	400.6	838	859	842
fu06-06	-9.63	8997.7	404.4	821	840	819
fu06-03	-9.41	8995.9	350.8	771	792	775
fu06-04	-8.72	8994.8	304.2	751	766	753
fu06-0.5H2O-F	-5.58	6002.3	475.5	822	838	840
fu06-1.5H2O-F	-5.28	5984.6	421.4	770	789	791
fu06-0.5H2O-CO2	-10.00	9866.3	403.3	852	873	871
fu06-1H2O-CO2	-5.33	5822.1	503.1	839	860	
fu06-1.5H2O-CO2	-4.65	6244.2	429.2	804	828	800
fu06-0.5H2O-CO2-F	-4.18	4416.3	549.1	817	840	
fu06-1.5H2O-CO2-F	-4.00	4975.2	459.2	768	791	784
fu06-0.35F	-5.88	6964.7	525.8	915	938	942
fu06-1F	-4.00	5409.7	566.9	905	928	924
fu06-2F	-4.00	4893.1	594.7	901	921	919
sb1Ftr	-4.00	5335.2	653.9	987	1010	1015
sbFgr	-4.02	5672.0	621.8	976	999	1002
sb3Ftr	-4.00	5256.8	626.9	955	977	989
sbF-1	-4.00	5547.3	553.7	900	924	929
sb-01, sb-02	-5.24	6860.4	584.5	983	1006	1005
sb-11	-4.00	5865.3	538.1	905	929	936
sb-12	-4.63	6008.7	516.5	878	901	895
sb-16	-4.04	5647.9	461.6	814	837	836
sb-14	-4.00	5877.9	405.2	773	797	795

^a A constrained to ≤ -4.00 .

T₁₂ is the temperature at which the viscosity is equal to 10¹² Pa s.

T^{cal} is the calorimetric glass transition.

Table 9: Heat capacity data – sb+F

sbFgr			sb-1Ftr			sb-3Ftr		
Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)
g	340.1	50.29	g	340.1	50.33	g	340.1	49.78
g	365.2	52.21	g	365.2	52.27	g	365.2	51.67
g	390.2	53.95	g	390.2	54.02	g	390.2	53.38
g	415.2	55.51	g	415.2	55.56	g	415.2	54.91
g	440.2	56.92	g	440.2	56.98	g	440.2	56.30
g	465.2	58.22	g	465.2	58.25	g	465.2	57.56
g	490.2	59.40	g	490.2	59.45	g	490.2	58.73
g	515.2	60.52	g	515.2	60.60	g	515.2	59.83
g	540.2	61.41	g	540.2	61.51	g	540.2	61.48
g	565.2	62.26	g	565.2	62.34	g	565.2	61.46
g	590.2	63.11	g	590.2	63.17	g	590.2	62.28
g	615.2	64.13	g	615.2	63.98	g	615.2	63.08
g	640.2	64.49	g	640.2	64.63	g	640.2	63.90
g	665.2	65.09	g	665.2	65.45	g	665.2	64.04
g	690.2	66.05	g	690.2	65.96	g	690.2	64.90
g	715.2	66.83	g	715.2	66.53	g	715.2	65.67
g	740.2	67.35	g	740.2	67.49	g	740.2	66.29
g	765.2	67.64	g	765.2	67.72	g	765.2	66.87
g	790.2	68.18	g	790.2	68.34	g	790.2	67.47
g	815.2	68.98	g	815.2	69.01	g	815.2	68.11
g	840.2	69.70	g	840.2	69.58	g	840.2	68.75
gt	865.2	70.17	g	865.2	70.08	g	865.2	69.31
gt	890.2	70.81	gt	890.2	70.66	gt	890.2	70.11
gt	915.2	71.52	gt	915.2	71.37	gt	915.2	71.11
gt	940.2	72.57	gt	940.2	72.26	gt	940.2	72.55
gt	965.2	74.12	gt	965.1	73.46	gt	965.2	74.49
gt	990.2	77.91	gt	990.2	75.21	gt	990.2	86.45
l	1015	95.36	gt	1015	85.62	gt	1015	96.23

g: glass; gt: glass transition; l: supercooled liquid.

Table 10: Heat capacity data – sb+H₂O+F

sbF-1			sbF-3		
Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)
g	340.2	50.58	g	340.2	49.77
g	365.2	52.50	g	365.2	51.72
g	390.2	54.27	g	390.2	53.47
g	415.2	55.82	g	415.2	55.07
g	440.2	57.26	g	440.2	56.58
g	465.2	58.56	g	465.2	57.95
g	490.2	59.74	g	490.2	59.22
g	515.2	60.89	g	515.2	60.46
g	540.2	61.80	g	540.2	61.49
g	565.3	62.71	g	565.3	62.51
g	590.3	63.56	g	590.3	63.49
g	615.2	64.30	g	615.2	64.50
g	640.3	65.08	g	640.3	65.67
g	665.3	65.74	gt	665.3	66.94
g	690.2	66.51	gt	690.2	68.18
g	715.2	67.28	gt	715.2	69.87
g	740.3	68.01	gt	740.3	73.52
g	765.2	68.58	gt	765.2	84.47
g	790.2	69.35	l ^a	790.2	97.21
g	815.2	70.10	l ^a	815.2	85.51
gt	840.3	71.09	l ^a	840.3	67.49
gt	865.2	72.33			
gt	890.2	73.85			
gt	915.3	76.73			
gt	940.2	91.76			
l	965.2	97.52			
l	990.2	95.62			
l	1015	95.23			

g: glass; gt: glass transition; l: supercooled liquid.

^a Crystallization.

Table 11: Heat capacity data – fu06+F

fu06-0.35F			fu06-1F			fu06-2F		
Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C_P (Jmol ⁻¹ K ⁻¹)
g	340.1	50.75	g	340.2	50.28	g	340.2	49.58
g	365.2	52.66	g	365.2	52.12	g	365.2	51.39
g	390.2	54.39	g	390.2	53.81	g	390.2	53.03
g	415.2	55.95	g	415.2	55.33	g	415.2	54.53
g	440.2	57.38	g	440.2	56.73	g	440.2	55.88
g	465.2	58.69	g	465.2	57.99	g	465.2	57.11
g	490.2	59.85	g	490.2	59.14	g	490.2	58.23
g	515.2	60.99	g	515.2	60.22	g	515.2	59.31
g	540.2	61.95	g	540.2	61.17	g	540.2	60.20
g	565.2	62.84	g	565.3	62.07	g	565.2	61.08
g	590.2	63.67	g	590.2	62.91	g	590.2	61.89
g	615.2	64.49	g	615.2	63.69	g	615.2	62.65
g	640.2	65.23	g	640.3	64.44	g	640.2	63.41
g	665.2	65.98	g	665.2	65.02	g	665.2	64.01
g	690.2	66.64	g	690.2	65.73	g	690.2	64.71
g	715.2	67.41	g	715.2	66.49	g	715.2	65.29
g	740.2	68.69	g	740.3	67.11	g	740.2	66.08
g	765.2	69.02	g	765.2	67.89	g	765.2	67.05
g	790.2	69.80	gt	790.2	68.78	gt	790.2	67.91
gt	815.2	70.58	gt	815.2	69.72	gt	815.2	68.71
gt	840.2	71.41	gt	840.2	70.59	gt	840.2	69.90
gt	865.2	72.40	gt	865.2	71.95	gt	865.2	71.52
gt	890.2	73.88	gt	890.2	73.80	gt	890.2	73.80
gt	915.2	75.99	gt	915.2	78.11	gt	915.2	80.91
gt	940.2	84.42	gt	940.2	95.40	l	940.2	96.67
l	965.2	98.15	l	965.2	96.73	l	965.2	95.04
l	990.2	96.07	l	990.2	95.11	l	990.2	94.76
l	1015	95.25	l	1015	94.30			

g: glass; gt: glass transition; l: supercooled liquid.

Table 12a: Heat capacity data – fu06+H₂O+F±CO₂

fu06-0.5H2O-F			fu06-1.5H2O-F			fu06-0.5H2O-CO2		
Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)
g	340.1	49.43	g	340.2	49.68	g	340.2	50.52
g	365.2	51.29	g	365.2	51.57	g	365.2	52.42
g	390.2	52.95	g	390.2	53.50	g	390.2	54.16
g	415.2	54.42	g	415.2	54.81	g	415.2	55.71
g	440.2	55.79	g	440.2	56.26	g	440.2	57.16
g	465.2	57.11	g	465.2	57.57	g	465.2	58.46
g	490.2	58.26	g	490.2	58.75	g	490.2	59.68
g	515.2	59.34	g	515.2	59.92	g	515.2	60.83
g	540.2	60.26	g	540.2	60.87	g	540.2	61.81
g	565.3	61.22	g	565.3	61.87	g	565.3	62.75
g	590.2	62.16	g	590.2	62.90	g	590.3	63.62
g	615.2	63.32	g	615.2	63.83	g	615.2	64.49
g	640.3	64.26	g	640.3	64.77	g	640.3	65.34
g	665.3	64.34	gt	665.2	66.12	g	665.3	66.13
gt	690.2	65.71	gt	690.2	67.46	g	690.2	67.20
gt	715.2	66.79	gt	715.2	68.82	g	715.2	67.94
gt	740.3	67.98	gt	740.3	70.61	g	740.3	68.65
gt	765.2	69.18	gt	765.2	73.06	g	765.2	69.65
gt	790.2	70.62	gt	790.2	82.58	gt	790.2	70.81
gt	815.3	72.96	l	815.2	96.81	gt	815.2	72.39
gt	840.3	82.66	l	840.2	95.14	gt	840.3	74.52
l	865.2	95.57	l	865.2	92.96	gt	865.2	81.35
l	890.2	93.63				l	890.2	97.67
l	915.3	92.09				l	915.3	96.47
l	940.2	90.05				l	940.2	92.73

g: glass; gt: glass transition; l: supercooled liquid.

Table 12b: Heat capacity data – fu06+H₂O+F±CO₂, continued

fu06-1.5H2O-CO2			fu06-1.5H2O-CO2-F		
Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)	Phase	T (K)	C _P (Jmol ⁻¹ K ⁻¹)
g	340.1	50.62	g	340.2	49.44
g	365.2	52.51	g	365.2	51.32
g	390.2	54.25	g	390.2	53.00
g	415.2	55.83	g	415.2	54.54
g	440.2	57.26	g	440.2	55.96
g	465.2	58.60	g	465.2	57.27
g	490.2	59.87	g	490.2	58.49
g	515.2	61.06	g	515.2	59.65
g	540.2	62.02	g	540.2	60.65
g	565.3	63.06	g	565.3	61.64
g	590.2	64.09	g	590.3	62.64
g	615.2	65.02	g	615.2	63.61
g	640.3	66.09	g	640.3	64.61
g	665.2	66.88	gt	665.3	65.73
gt	690.2	68.08	gt	690.2	66.92
gt	715.2	69.07	gt	715.2	68.35
gt	740.3	70.41	gt	740.3	70.82
gt	765.2	73.48	gt	765.2	74.23
gt	790.2	78.68	gt	790.2	85.85
gt	815.2	95.35	l	815.3	97.54
l	840.2	97.82	l	840.3	95.03
l	865.2	94.52	l	865.2	92.13
l	890.2	88.33			

g: glass; gt: glass transition; l: supercooled liquid.