Revision 1

An Updated Calibration of the Plagioclase-Liquid Hygrometer-Thermometer Applicable to Basalts through Rhyolites

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Abstract

20

21   An updated and expanded data set that consists of 214 plagioclase-liquid equilibrium

22 pairs from 40 experimental studies in the literature is used to recalibrate the thermodynamic

23 model for the plagioclase-liquid hygrometer of Lange et al. (2009); the updated model is

24 applicable to metaluminous and alkaline magmas. The model is based on the crystal-liquid

25 exchange reaction between the anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$) components, and

26 all available volumetric and calorimetric data for the pure end-member components are used in

27 the revised model. The activities of the crystalline plagioclase components are taken from

28 Holland and Powell (1992). Of the 214 experiments, 107 are hydrous and 107 are anhydrous.

29 Four criteria were applied for inclusion of experiments in the final data set: (1) crystallinities

30 <30%; (2) pure-H_2O fluid saturated; (3) compositional totals (including H_2O component) of 97–

31 101% for hydrous quenched glasses and 98.5-101 for anhydrous quenched glasses; and (4) melt

32 viscosities $\leq$5.2 $\log_{10}$ Pa s. The final data set spans a wide range in liquid composition (45-80

33 wt% SiO_2; 1-10 wt% Na_2O+K_2O), plagioclase composition (An_{17}-An_{95}), temperature (750-

34 1244°C), pressure (0-350 MPa), and H_2O content (0-8.3 wt%). The water solubility model of

35 Zhang et al. (2007) was applied to all hydrous experiments. The standard error estimate on the

36 hygrometer model is 0.35 wt% H_2O, and all liquid compositions are fitted equally well.

37 Application of the model as a thermometer recovers temperatures to within ±12 degrees, on

38 average. Tests of the hygrometer on anhydrous piston-cylinder experiments in the literature, not

39 included in the regression, show that the model is accurate at all pressures where plagioclase is

40 stable. Applications of the hygrometer are made to natural rhyolites (Bishop Tuff, Katmai and

41 TobaTuff) with reported H_2O analyses in quartz-hosted melt inclusions from the literature; the

42 results show agreement. Applications of the hygrometer/thermometer are additionally made to

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43   natural rhyolites from Iceland and Glass Mountain, CA. The updated model can be downloaded

44   either as a program in Excel format or as a MatLab script from the Data Repository.

45   **Keywords**

46   NEW TECHNIQUE: plagioclase-liquid hygrometer, IGNEOUS PETROLOGY: hygrometer,

47   thermometer, THERMODYNAMICS, PHASE EQUILIBRIA: plagioclase, liquid

48
49   **Introduction**

50   The composition of plagioclase in magmatic liquids is strongly sensitive to temperature

51   and dissolved water concentrations, and therefore plagioclase has the potential to be used as

52   either a hygrometer or thermometer in volcanic rocks (e.g., Kudo and Weill 1970; Mathez 1973;

53   Glazner 1984; Marsh et al. 1990; Housh and Luhr 1991, Sisson and Grove 1993;

54   Panjasawatwong et al. 1995; Danyushevksy et al. 1997; Putirka 2005, 2008). Recently, Lange et

55   al. (2009) developed a thermodynamic model for the plagioclase-liquid exchange reaction

56   involving the anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$) components, in which all published

57   calorimetric and volumetric data on the standard state reaction were incorporated into the model

58   in order to independently constrain the effects of temperature and pressure. This allowed

59   available phase-equilibrium experiments in the literature to constrain the effect of melt

60   composition, including dissolved water, on the exchange reaction, thus permitting a plagioclase-

61   liquid hygrometer to be developed.

62   Application of the Lange et al. (2009) model is restricted to plagioclase more calcic than

63   An_{35} and therefore cannot be applied to most rhyolites, owing to the compositional limitation of

64   the experimental data set upon which that model was calibrated. The 2009 hygrometer was

65   calibrated on 71 plagioclase-liquid experiments, of which 45 were hydrous and 26 anhydrous.

66   Three filters were applied to that phase-equilibrium data set: (1) crystallanities < 30%; (2) pure

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67   H_2O-fluid saturated; and (3) compositional totals (including H_2O component) of 97-101 % for

68   hydrous quenched glasses. In the 2009 calibration, all melt water concentrations were obtained

69   using the water solubility model of Moore et al. (1998). Experiments were included in the

70   calibration if the analyzed anhydrous oxide components in the glass and the H_2O concentration

71   determined by Moore et al. (1998) summed to values between 97 and 101%.

72   Results from the Couch et al. (2003) study on a low-silica rhyolite were included in the

73   calibration, but owing to the application of the three filters, experiments from other studies on

74   silica-rich liquids with more sodic plagioclases ($<An_{35}$) were not included. In some cases,

75   experiments were not included because information on modes or glass totals were not published,

76   but otherwise would have passed all three filters (e.g, Larsen, 2006).

77   Since 2009, there have been several published water-saturated phase-equilibrium

78   experiments on rhyolite, rhyodacite and trachyte liquids that pass all filters (e.g., Martel, 2012;

79   Rader and Larsen, 2013; Martel et al., 2013; Castro et al., 2013; Waters et al., 2014), as well as

80   on basalts (e.g., Parman et al., 2011). Therefore, there is an opportunity to significantly expand

81   the data set upon which the plagioclase-liquid hygrometer/thermometer is calibrated, and to

82   extend its application to a wider range of plagioclase and melt composition, including both

83   rhyolites and alkaline magmas in equilibrium with sodic plagioclase. In addition, the Zhang et

84   al. (2007) water solubility model is used in this study, which is calibrated on the same data set

85   used by Moore et al. (1998) as well as additional data published in the intervening years.

86

87   **Thermodynamic Model of Plagioclase-Liquid Equilibrium**

88   Following Lange et al., (2009), the plagioclase-liquid hygrometer/thermometer is based

89   on the equilibrium exchange reaction of the anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$)

3

90   components between crystalline plagioclase and magmatic liquid:

91           $CaAl_2Si_2O_8{}^{crystal} + NaAlSi_3O_8{}^{liquid} = CaAl_2Si_2O_8{}^{liquid} + NaAlSi_3O_8{}^{crystal}$ (1)
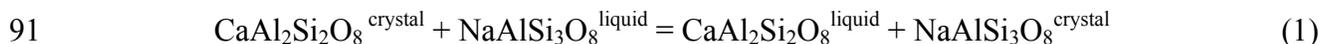
92   At equilibrium:

93           $$\Delta G(T,X,P) = 0 = \Delta H°(T) - T\Delta S°(T) + RTlnK + \int_0^P \Delta V°_T(P)dP,$$ (2)

94   where $\Delta H°(T)$ and $\Delta S°(T)$ are the standard state change in molar enthalpy and entropy,

95   respectively, for the pure crystalline and liquid components, K is the equilibrium constant that

96   accounts for differences in ΔG due to composition, and $\Delta V°_T(P)$ is the change in molar volume

97   for the reaction at temperature T, as a function of pressure, where initial pressure is one bar or

98   0.0001 GPa (shown as 0 in Eq. 2).

99
100   **Standard State Thermodynamic Data**

101   The standard state thermodynamic data used in Equation 2 are listed in Table 1. As

102   stated in Lange et al. (2009), $\Delta H°(T)$, $\Delta S°(T)$ and $\Delta V°_T(P)$ are equivalent to the difference

103   between the enthalpy, entropy and volume of fusion of pure anorthite (An) and pure albite (Ab),

104   respectively (see Eq. 3-5 in Lange et al. 2009). The enthalpy and entropy of fusion for anorthite

105   and albite vary with temperature as follows (where f refers to fusion):

106           $$\Delta H_f(T) = \Delta H_f(T_f) + \int_{T_f}^T \left[C_P^{liq}(T) - C_P^{xtl}(T) \right] dT$$ (3)

107           $$\Delta S_f(T) = \Delta S_f(T_f) + \int_{T_f}^T \left[\frac{C_P^{liq}(T) - C_P^{xtl}(T)}{T} \right] dT$$ (4)

108   In this study, the heat capacity equations of Berman (1988) are used for crystalline anorthite and

109   albite in Equations 3 and 4 (Table 1). Tenner et al. (2007) used the drop calorimetric

110   measurements of Stebbins et al. (1983) and Richet and Bottinga (1984a), together with the heat

111   capacity equations of Berman (1988) and Richet (1987) for albite crystal and glass, respectively,

112   to derive internally consistent values for the enthalpy of fusion for albite at its 1-bar fusion

4

113   temperature and the heat capacity of liquid $NaAlSi_3O_8$ (Table 1). A similar exercise is followed

114   in this study to derive internally consistent values for the 1-bar enthalpy of fusion for anorthite

115   and the heat capacity of liquid $CaAl_2Si_2O_8$ from the drop calorimetric data of Stebbins et al.

116   (1983) and Richet and Bottinga (1984b). The details of this exercise are provided in Appendix

117   A, and the results are given in Table 1.

118   Calculation of $\Delta V°_T(P)$ in Equation 2 requires information on the molar volume, thermal

119   expansion, and compressibility for both liquid and crystalline anorthite and albite (Table 1). The

120   data and equations used in this study are identical to those used in Lange et al. (2009), where a

121   detailed discussion of the volumetric terms is provided. We note, however, that there was a

122   decimal point error in Table 1 of Lange et al. (2009) for the $\delta V/\delta P$ values for albite and anorthite

123   liquid, respectively, which are correct in Table 1 of this study.

124
125   **Activity-Composition Relations**

126   The natural log of the equilibrium constant in Equation 2 is equal to:

$$\ln(K) = \ln\left(\frac{a_{CaAl_2Si_2O_8}^{liquid}}{a_{NaAlSi_3O_8}^{liquid}}\right) + \ln\left(\frac{a_{NaAlSi_3O_8}^{crystal}}{a_{CaAl_2Si_2O_8}^{crystal}}\right). \tag{5}$$

128   The activity terms in Equation 5 are further broken down to the mole fractions (X) and activity

129   coefficients (γ) for the crystalline and liquid components in Equations 6a and 6b, respectively:

$$\ln\left(\frac{a_{NaAlSi_3O_8}^{crystal}}{a_{CaAl_2Si_2O_8}^{crystal}}\right) = \ln\left(\frac{\gamma_{NaAlSi_3O_8}^{crystal}}{\gamma_{CaAl_2Si_2O_8}^{crystal}}\right) + \ln\left(\frac{X_{NaAlSi_3O_8}^{crystal}}{X_{CaAl_2Si_2O_8}^{crystal}}\right) \tag{6a}$$

$$\ln\left(\frac{a_{CaAl_2Si_2O_8}^{liquid}}{a_{NaAlSi_3O_8}^{liquid}}\right) = \ln\left(\frac{\gamma_{CaAl_2Si_2O_8}^{liquid}}{\gamma_{NaAlSi_3O_8}^{liquid}}\right) + \ln\left(\frac{X_{CaAl_2Si_2O_8}^{liquid}}{X_{NaAlSi_3O_8}^{liquid}}\right). \tag{6b}$$

132   The mole fraction of anorthite and albite in the plagioclase crystal is based on the abundance of

133   Ca and Na in the A site alone and is determined from microprobe analyses. In both the

134   hygrometer of Lange et al. (2009) and the updated hygrometer in this study, the activity

5

135   coefficient (γ) terms for the crystalline components are obtained from the THERMOCALC

136   program (http://www.earthscii.unimelb.edu.au/tpg/thermocalc/), which is based on the Holland

137   and Powell (1992) model for plagioclase. In this study, the activity coefficient terms for

138   crystalline plagioclase have been parameterized for a range of compositions (0 to 100 mol% An)

139   and a range of temperatures (600 to 1350°C); the details of the parameterization are given in

140   Appendix B.

141   The activity-composition relations for the liquid components (Equation 6b), forms the

142   basis of the hygrometer of both Lange et al. (2009) and this study. The mole fractions of the

143   *liquid* anorthite and albite components are defined following Carmichael (1977):

$$X_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{ideal liquid}} = 64.0\left(X_{\text{CaO}}^{\text{liq}}\right)\left(X_{\text{Al}_2\text{O}_3}^{\text{liq}}\right)\left(X_{\text{SiO}_2}^{\text{liq}}\right)^2 \tag{7a}$$

$$X_{\text{NaAlSi}_3\text{O}_8}^{\text{ideal liquid}} = 18.963\left(X_{\text{Na}_2\text{O}}^{\text{liq}}\right)^{0.5}\left(X_{\text{Al}_2\text{O}_3}^{\text{liq}}\right)^{0.5}\left(X_{\text{SiO}_2}^{\text{liq}}\right)^3 \tag{7b}$$

146   The coefficients in Equations 7a and 7b ensure that the mole fraction of pure anorthite and pure

147   albite liquid, respectively, each take the value of one. The ratio of the activity coefficient terms

148   (γ) in Equation 6b is modeled as a linear function of liquid composition, including the dissolved

149   H_2O component:

$$\ln\left(\frac{\gamma_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{liquid}}}{\gamma_{\text{NaAlSi}_3\text{O}_8}^{\text{liquid}}}\right) = a + \frac{b}{T} + \sum d_i X_i + d_{\text{H}_2\text{O}} X_{\text{H}_2\text{O}} \tag{8}$$

151   The terms *a*, *b* and d_i are parameters to be fitted from the calibration of plagioclase-liquid

152   equilibrium experiments, X_{H2O} is the mole fraction of dissolved H_2O in the melt, and X_i the mole

153   fraction of other oxide components (e.g., SiO_2, Al_2O_3, etc.), where "i" is defined as i=1 to n,

154   where n is the number of oxide components in Equation 8. A temperature term (*b*/T) is added to

155   account for the dependence of H_2O speciation (e.g., OH^- groups and molecular H_2O) on

156   temperature, which is discussed extensively in Lange et al. (2009).

6

157
158 **Calibration Equation**

159   Because the goal is to calibrate a plagioclase-liquid hygrometer, a regression equation is

160 developed with X_{H2O} as the dependent variable on the left side of the equation. To accomplish

161 this, first the equilibrium reaction is shown in Equation 9, where x (defined in Equation 10)

162 includes all of the standard-state thermodynamic data, crystalline activity terms, and the ideal

163 contributions to the liquid anorthite and albite activities.

164
$$0 = x + a + \frac{b}{T} + \sum X_i d_i + X_{H_2O}\left(d_{H_2O}\right) \tag{9}$$

165 where

166
$$x = \frac{\Delta H°(T)}{RT} - \frac{\Delta S°(T)}{R} + \frac{\int_1^P \Delta V_T°(P)dP}{RT} + \ln\left(\frac{X_{CaAl_2Si_2O_8}^{ideal\,liquid}}{X_{NaAlSi_3O_8}^{ideal\,liquid}}\right) + \ln\left(\frac{a_{NaAlSi_3O_8}^{crystal}}{a_{CaAl_2Si_2O_8}^{crystal}}\right) \tag{10}$$

167 Equation 9 is then rearranged so that X_{H2O} is the dependent variable in Equation 11.

168
$$X_{H_2O}\left(-d_{H_2O}\right) = x + a + \frac{b}{T} + \sum X_i d_i \tag{11}$$

169 Both sides of Equation 11 are divided through by $-d_{H2O}$, which leads to:

170
$$X_{H_2O} = mx + a' + \frac{b'}{T} + \sum X_i d_i' \tag{12}$$

171 where

172
$$m = -\frac{1}{d_{H_2O}}, \quad a' = \frac{a}{-d_{H_2O}}, \quad b' = \frac{b}{-d_{H_2O}}, \quad d_i' = \frac{d_i}{-d_{H_2O}} \tag{13}$$

173 Lange et al. (2009) found that the most advantageous form of the regression equation was made

174 by substituting wt% H_2O for X_{H2O}, which allows for the calculation of wt% H_2O without having

175 prior information about the concentration of dissolved melt H_2O. This empirical change does not

176 diminish the quality of the final calibration.   Thus, the final form of the regression equation is:

177
$$\text{wt\% } H_2O = m'x + a'' + \frac{b''}{T} + \sum X_i d_i''. \tag{14}$$

178
179 **Plagioclase-Liquid Phase Equilibrium Data**

180   In order to perform a regression on Equation 14, plagioclase-liquid equilibrium

181   experiments from the literature are required. A final data set of 214 plagioclase-liquid

182   equilibrium pairs (107 hydrous; 107 anhydrous) was chosen from an initially larger set of

183   experiments, after application of the following four filters: (1) pure-H_2O fluid saturated; (2)

184   compositional totals (including H_2O component) of 97–101% for hydrous quenched glasses and

185   98.5-101 for anhydrous quenched glasses; (3) crystallinities ≤ 30%; and (4) melt viscosities ≤5.2

186    $\log_{10}$ Pa s. The purpose of these filters is to exclude experiments where analytical uncertainties

187   may be too high and/or where equilibrium may not have been attained. Lange et al. (2009)

188   provide a detailed explanation of the first three filters. The last filter is new to this study

189   (although it applies to the data set used in Lange et al. 2009) and it is another mechanism to

190   exclude experiments where equilibrium may not have been obtained owing to slow diffusion in

191   the melt phase. The four filters were applied uniformly to experiments from the literature, and

192   although some experiments may have been excluded that achieved equilibrium and/or had small

193   analytical uncertainties, the uniform application of all four filters prevented several

194   disequilibrium experiments and/or those with low analytical totals from being included in an

195   unbiased manner. In this study, the H_2O solubility model of Zhang et al. (2007) is used to

196   calculate the water concentration in all experimental liquids; the model has a 1σ error of 0.34

197   wt% H_2O.

198   The final data set of 214 plagioclase-liquid equilibrium experiments is obtained from 40

199   studies (Aigner-Torres et al., 2007; Bartels et al., 1991; Berndt et al., 2005; Blatter and

200   Carmichael, 2001; Blundy, 1997; Botcharnikov et al., 2008; Brugger et al., 2003; Castro et al.,

201   2013; Couch et al., 2003; Costa et al., 2004; Gardner et al., 1995; Grove et al., 1982, 1997, 2003;

202   Grove and Bryan, 1983; Grove and Juster, 1989; Holtz et al., 2005; Juster et al., 1989; Larsen,

8

203   2006; Luhr, 1990; Mahood and Baker, 1986; Martel et al., 1999, 2013; Martel, 2012; Moore and

204   Carmichael, 1998; Parman et al., 2011; Rader and Larsen, 2013; Sack et al., 1987; Sisson et al.

205   (1993a,b); Snyder et al., 1993; Takagi et al., 2005; Thy et al., 2006; Toplis et al., 1994; Toplis

206   and Carroll, 1995; Tormey et al., 1987; Wagner et al., 1995; Waters et al., (in review); Vander

207   Auwera et al., 1998; Yang et al., 1996) and greatly expands the compositional range relative to

208   the data set used by Lange et al. (2009). The final hydrous data set (Appendix C) spans a wide

209   range of liquid composition (45-80 wt% SiO_2), plagioclase composition (An_{17-95}), temperature

210   (750-1125°C), pressure (48-350 MPa), and water concentration (1.4-8.3 wt%), which is

211   illustrated in Fig 1A and 1B. The anhydrous data set (Appendix C) is dominated by basaltic melt

212   compositions, but extends to 70 wt% SiO_2 (Brugger et al., 2003), which marks the limit of the

213   melt viscosity filter. The plagioclase compositions in anhydrous melts are also more restricted

214   (An_{51-90}), as well as the temperature range (1072-1244°C). The 214 experiments include several

215   alkaline liquids (as defined by Irvine and Baragar, 1971; Fig. 2) in equilibrium with plagioclase

216   from the studies of Sack et al. (1987), Luhr (1990), Martel et al. (2013), and Waters et al. (in

217   review).

218   Another illustration of the compositional range of the calibration data set is seen in a plot

219   of plagioclase composition (mol% An) vs. the An-number of the equilibrium melt composition

220   (Fig. 3). An-number is defined as $X_{CaAl_2Si_2O_8}^{liquid}\left/\left(X_{NaAlSi_3O_8}^{liquid} + X_{CaAl_2Si_2O_8}^{liquid}\right)\right.$, using Equations 7a and 7b.

221   Figure 3 shows that for each liquid An-number there is a wide range of plagioclase compositions

222   that can crystallize under equilibrium conditions, depending on other compositional components

223   in the melt, especially dissolved water concentration, as well as temperature and pressure. The

224   effect of dissolved water is clearly seen; plagioclase is systematically more calcic in hydrous vs.

225   anhydrous liquids. What is most striking is the wide range in plagioclase compositions (An_{17-60})

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226   at melt An-numbers ≤ 20, and the question is whether a multiple linear regression of Equation 14

227   can adequately model the data in Figure 3. The calibration data set is projected onto the

228   anhydrous and hydrous binary loop phase diagrams to further illustrate the effect of temperature

229   and melt composition on plagioclase composition in the supplemental material (Appendix D).

230
231   **RESULTS**

232   **Hygrometer/Thermometer Regression Results**

233   A series of un-weighted, least squares, multiple linear regressions of Equation 14 were

234   performed using the backward stepwise method. The initial regression included 11 fitted terms

235   (m', a'', b'' and d_i'', where i = SiO_2, TiO_2, Al_2O_3, FeO^T, MgO, CaO, Na_2O and K_2O). The only

236   component that did not pass the t-test was TiO_2, but all others were statistically significant,

237   leading to 10 fitted terms. However, the magnitude of the fitted K_2O term was anomalously

238   large, and so a new term ($K_2Al_2O_4$) was constructed, where the moles of K_2O in each sample

239   were subtracted from the moles of Al_2O_3, leading to a revised Al_2O_3* term. This change

240   improved the regression results, whereas a similar approach to construct a $Na_2Al_2O_4$ term did

241   not. The results of the final regression are shown in Table 2; the fit has an R^2 value of 0.98 and a

242   standard error on the estimate of 0.35 wt% H_2O, which is comparable to the 1σ error of $\pm$ 0.34

243   wt% on the H_2O solubility model of Zhang et al. (2007). Therefore the hygrometer recovers the

244   wt% H_2O in each experimental liquid within the uncertainty of its value in the calibration data

245   set. Attempts to reduce the standard error estimate in half, to levels well below the

246   1σ uncertainty in the water contents of the experimental liquids by more than doubling the

247   number of fitted terms (e.g., 26 fitted terms in Zeng et al., 2014), should be viewed with caution

248   as this can lead to an over fit to the experimental data set. A plot of measured vs. calculated H_2O

249   concentrations is shown in Figure 4A, along with a histogram of residuals in Figures 4B. The

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250   residuals plotted in Figure 5A-F show that the quality of the fit is equally good for all melt

251   compositions (wt% SiO_2, wt% Na_2O+K_2O, An-number), as well as plagioclase composition,

252   temperature and melt viscosity.   Also shown in Figure 5 are the residuals when the model of

253   Lange et al. (2009) is applied. This former model breaks down when the An-number of the

254   liquid is < 15, which is also when SiO_2 concentrations exceed 70 wt% and total alkalis exceed 8

255   wt%.

256   It is also possible to use the plagioclase-liquid model as a thermometer rather than a

257   hygrometer. When melt composition, plagioclase composition, pressure and wt% H_2O are all

258   inputs, temperature can be varied until the calculated wt% H_2O value matches the input wt%

259   H_2O. A plot of measured vs. calculated temperatures is shown in Figure 6A, along with a

260   histogram of residuals in Figures 6B.   Figure 7 illustrates that the model (Equation 14; Tables 1

261   and 2) recovers temperatures equally well for all experimental temperatures (750-1244°C) and

262   all melt compositions (45-80 wt% SiO_2). The average difference between the reported and

263   calculated temperature for the 214 experiments is 12 degrees (10 and 14 degrees, respectively,

264   for anhydrous and hydrous experiments). The excellent recovery in temperature is notable

265   because the regression of Equation 14 did not minimize residuals for temperature, but for wt%

266   H_2O. Therefore, the advantage of this thermometer is that it is not based on a separate regression

267   from the hygrometer, but is the exact same model. We attribute the internal consistency to the

268   incorporation of thermodynamic data on the standard-state reaction (Table 1). For comparison,

269   the plagioclase-liquid thermometer presented by Putirka (2008) yields calculated temperatures

270   for our calibration data set that are within 18°C, on average (12 and 23 degrees, respectively, for

271   anhydrous and hydrous experiments), as shown in Figure 7.

272
273   **Tests of the Accuracy of the Hygrometer/Thermometer Model**

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274   The newly calibrated plagioclase-liquid hygrometer/thermometer can be tested against

275   several experimental studies not included in the regression. For example, anhydrous piston-

276   cylinder experiments on plagioclase-liquid equilibrium pairs at 1.0-1.2 GPa (Bartels et al., 1991;

277   Draper and Johnston, 1992; Appendix E) allow an examination of how well the volumetric terms

278   in the hygrometer/thermometer model capture the effect of increasing pressure on plagioclase-

279   liquid equilibrium, independent of melt water concentration. The model outputs water

280   concentrations that range from -0.4 to 0.5 wt% for these anhydrous high-pressure experiments,

281   which is well within the range of residuals for the 1-bar anhydrous experiments used in the

282   calibration (see Figure 4B). Therefore, the results demonstrate that the hygrometer can be

283   applied to all pressures where plagioclase is stable.

284   A similar test can be made on hydrous plagioclase-liquid experiments on basalts

285   conducted under H_2O-undersaturated conditions (Hamada and Fujii, 2008) and on rhyolites

286   conducted under mixed H_2O-CO_2 fluid conditions (Almeev et al., 2012), where the quenched

287   glasses in the run products were all analyzed directly for dissolved H_2O concentration using

288   FTIR (Fourier Transform Infrared) spectroscopy (Appendix E). The average difference between

289   analyzed and calculated wt% H_2O is 0.6 and 0.4, respectively, for the basalt and rhyolite

290   experiments (Fig. 8), again indicating good agreement within the combined uncertainties of the

291   hygrometer model (see residuals in Fig. 4) and the experiments (including analyzed water and

292   reported temperature; an uncertainty of five degrees can lead to an uncertainty in calculated

293   water of $\pm$ 0.2 wt% H_2O).

294   Another test of the hygrometer, in terms of its ability to be extrapolated to rhyolitic melts

295   (72-77 wt% SiO_2) under anhydrous conditions, is made by applying it those experiments in

296   Brugger et al. (2003) not included in the calibration data set because melt viscosities ranged from

12

297   5.3 to 6.6 $\log_{10}$ Pa-s (Note that three experiments from that study with lower melt viscosities

298   were included in the regression; Appendix C.) Experiments with high viscosities (>5.3 $\log_{10}$ Pa-

299   s) were excluded from the calibration, as the high viscosities may prevent achievement of

300   equilibrium due to low melt diffusivity. The Brugger et al. (2003) rhyolite experiments were held

301   for seven days and the starting material was 100% glass. The plagioclase compositions that

302   crystallized from these experiments lead to calculated wt% H_2O values that range from -0.3 to +

303   0.3 wt% H_2O (Fig. 9), which is well the within the range of residuals for anhydrous experiments

304   used to calibrate this hygrometer (see Fig. 4). These results suggest that is it is possible to attain

305   equilibrium plagioclase compositions at high melt viscosities if the samples are held long enough

306   and the starting material is glass. The good agreement further indicates that the updated

307   hygrometer model accurately captures the effect of variable melt composition (from basalt to

308   rhyolite) on plagioclase composition, independent of the effects of dissolved water

309   concentration, temperature and pressure.

310
311   **The Effects of Melt composition, Dissolved Water Concentration, Temperature and**

312   **Pressure on Plagioclase Composition**

313   The effect of melt composition, temperature, pressure and dissolved water concentration

314   on the composition of plagioclase is illustrated in Fig. 10.   In that diagram, calculated values of

315   wt% H_2O in melt vs. equilibrium plagioclase composition are plotted at constant 100 MPa for

316   three different melt compositions, at temperatures that each is reasonably found in nature. The

317   compositions of the basalt (50.5 wt% SiO_2; 1200°C), andesite (61.8 wt% SiO_2; 1000°C), and

318   rhyolite (75.4 wt% SiO_2; 800°C) used for this figure are given in Table 3. Not surprisingly, for a

319   given plagioclase composition (e.g., An_{50}), the rhyolite at lower temperature requires a higher

320   dissolved water concentration than a basalt at higher temperature, in order to be in equilibrium

13

321   with the same plagioclase composition. What is also illustrated in Figure 10 is the strong

322   sensitivity of plagioclase composition to dissolved water concentration. An increase of just 0.5

323   wt% dissolved H_2O leads to an increase in the anorthite component of ~20 mol% in the

324   equilibrium plagioclase, with the effect of water strongest at high temperature. Additionally,

325   temperature exerts a strong influence on calculated values of wt% H_2O, as seen in the dashed

326   lines associated with a change of ± 20 degrees in the input temperature for each melt

327   composition (Fig. 10). At relatively low and high temperatures, (800 and 1200 °C), a variation

328   of ±20 degrees in the input temperature leads to a variation in calculated water of ±0.5 and ±0.2

329   wt%, respectively. This result underscores the necessity of evaluating temperature

330   independently and accurately (e.g., through Fe-Ti oxide thermometry) in order to apply the

331   plagioclase-liquid hygrometer.

332   In stark contrast to the effect of temperature, pressure exerts little influence on the

333   plagioclase-liquid hygrometer. This is illustrated in Fig. 11, where the effect of increasing

334   pressure on the calculated wt% H_2O is shown for rhyolite, andesite and basalt melts (at 800,

335   1000, and 1200°C, respectively) for the same plagioclase composition of An_{50}. The results show

336   a weak pressure dependence on the calculated value of wt% H_2O, where an increase from 0 to

337   1.2 GPa leads to a small increase of 0.3 and 0.2 wt% H_2O, at 800 and 1200°C, respectively. The

338   slight temperature dependence on the magnitude of the pressure effect is due to the fact that the

339   volume change for the exchange reaction varies with temperature. Nonetheless, the reason for

340   the nearly negligible effect of pressure on the hygrometer, which contrasts with the very large

341   effect of temperature, is due to the small magnitude of the volume change for the exchange

342   reaction, particularly when compared to the large magnitude of the enthalpy of the exchange

343   reaction, all of which is discussed at length in Lange et al. (2009).

14

344

345   **Discussion**

346   **Application of the Hygrometer to Natural Rhyolites with Analyzed Melt Inclusion Water**

347   **Contents**

348   In the following section, the plagioclase-liquid hygrometer is applied to rhyolites from:

349   (1) the Bishop Tuff, California; (2) the Katmai 1912 eruption, Alaska; and (3) the Toba Tuff,

350   Sumatra, Indonesia. The rhyolites from these three localities permit a test of the plagioclase-

351   liquid hygrometer against reported H_2O contents measured in quartz-hosted melt inclusions (MI)

352   from the literature.

353
354   **Bishop Tuff.**

355   The Bishop Tuff is the product of a >600 km^3 Plinian eruption of rhyolite magma, which

356   was saturated in nine to twelve mineral phases: quartz + plagioclase + sanidine + biotite +

357   titanomagnetite + ilmenite + apatite + zircon ± allanite ± orthopyroxene ± monazite ± augite ±

358   pyrrhotite.   Whole-rock compositions are reported for 14 samples (75.3-77.6 wt% SiO_2) in

359   Hildreth (1977), for which plagioclase (An_{13}-An_{24}), titanomagnetite and ilmenite compositions

360   are also provided. The Fe-Ti oxide analyses from Hildreth (1977) were input into the Ghiorso

361   and Evans (2008) thermometer, leading to pre-eruptive temperatures that range between ~700-

362   810°C. Application of the plagioclase-liquid hygrometer to these samples results in H_2O

363   contents that range from 3.9-6.8 wt% (Fig. 12), with water concentrations increasing

364   systematically with decreasing temperature. Also shown in Fig. 12 are the range of H_2O contents

365   measured in quartz-hosted melt inclusions from Wallace et al. (1999) and Anderson et al. (2000)

366   for the Early (Ig1Eb), Middle (Ig2Ea) and Late (Ig2NWa; Ig2NWb) units of the Bishop Tuff,

367   which are plotted as a function of Fe-Ti oxide temperatures reported for those units by Hildreth

15

368   and Wilson (2007). The H_2O contents calculated with the plagioclase-liquid hygrometer broadly

369   match the H_2O contents measured in quartz-hosted melt inclusions from the Early, Middle and

370   Late Bishop Tuff (Fig. 12).

371

372   **Katmai 1912 Eruption.**

373   The Katmai 1912 eruption produced 11-15 km^3 of magma ranging from 58-75 wt% SiO_2.

374   The rhyolitic end-member is a crystal-poor (0.5-2%), high-silica rhyolite (76.9 wt% SiO_2) that is

375   saturated with up seven mineral phases: quartz + plagioclase + titanomagnetite + ilmenite +

376   hypersthene + pyrrhotite ± amphibole.   Analyzed H_2O concentrations in quartz-hosted melt

377   inclusions range from 3.0-5.2 wt% (Lowenstern, 1993) and 4.2-4.7 wt% H_2O (Wallace, 2005).

378   For comparison, application of the plagioclase-liquid hygrometer using whole-rock compositions

379   (76.6-77.4 wt% SiO_2), plagioclase compositions (An_{25-29}), and pre-eruptive temperatures (805-

380   850°C; recalculated with Ghiorso and Evans, 2008) obtained from Fe-Ti oxide analyses reported

381   in Hildreth (1983) lead to values that range from 3.9-5.0 wt% H_2O. This result shows that the

382   plagiclase-liquid hygrometer is fully consistent with the published melt inclusion analyses

383   reported in Lowenstern (1993) and Wallace (2005).

384   This consistency further suggests that plagioclase and quartz were co-liquidus phases in

385   the Katmai rhyolite. This inference is confirmed by some of the phase-equilibrium experiments

386   reported for Katmai rhyolite in Coombs and Gardner (2001), although at 800-850°C the

387   plagioclase-in and quartz-in curves are both located at P_{H2O} = 100-40 MPa, which leads to a

388   maximum H_2O concentration in the melt during crystallization of these phases of $\leq$ 4.1 wt%.

389   This discrepancy of ~1 wt% H_2O between the results from the phase-equilibrium experiments

390   and those from the melt inclusion analyses and the plagioclase-liquid hygrometer may be

391   attributable to the relatively high viscosity of the liquids (>5.5 log_{10} Pa-s) in the phase-

16

392   equilibrium experiments at $P_{H2O} \leq 100$ MPa.

393
394   **Toba Tuff.**

395   The youngest unit of the Toba tuff (YTT) is 2,800 km^3 (Chesner, 1998) of zoned rhyolite

396   (68-76 wt% SiO$_2$) (Chesner and Rose, 1991), which is saturated in ten mineral phases: quartz,

397   plagioclase, sanidine, biotite, amphibole, orthopyroxene, titanomagnetite, allanite, zircon, and

398   ilmenite. The compositions of Fe-Ti oxides reported in Chesner (1998) are incorporated into the

399   geothermometer of Ghiorso & Evans (2008) to calculate three pre-eruptive temperatures for the

400   YTT (687, 722, and 732 °C). The plagioclase-liquid hygrometer is applied to pre-eruptive

401   temperatures, the average plagioclase composition found in the YTT (An$_{34}$) and the bulk

402   composition of the more evolved end member of the YTT (sample #54; Chesner 1998) to

403   calculate melt H$_2$O contents of 6.6 to 7.9 wt% H$_2$O (Fig. 13). Using the water solubility model

404   of Zhang et al. (2007), these H$_2$O contents (6.6-7.9 wt%) correspond to P_{H2O}(total) values

405   ranging from ~230 to 330 MPa for the YTT melt composition. The water contents derived from

406   the plagioclase-liquid hygrometer are compared to the results of phase equilibrium experiments

407   on the Toba Tuff conducted by Gardner et al. (2002) in Figure 13. The water contents obtained

408   by appling the hygrometer to plagioclase from the natural sample match the water contents at the

409   plagioclase-in curve experimentally determined by Gardner et al. (2002), which implies that the

410   plagioclase-hygrometer accurately predicts-pre-eruptive melt H$_2$O contents for the average of the

411   reported plagioclase compositions.

412   Pre-eruptive melt H$_2$O and CO$_2$ contents measured by FTIR in quartz hosted melt

413   inclusions from the Younger Toba Tuff reported by Chesner and Luhr (2010) range from 3.9-6.4

414   wt% and 10-175 ppm, respectively. The plagioclase-liquid hygrometer calculates a maximum

415   melt H$_2$O content of 7.9 wt% at 687°C, which is ~1.5 wt% higher than the maximum value

17

416   obtained from melt inclusions (Chesner and Luhr, 2010). The discrepancy between the

417   plagioclase hygrometer and the melt inclusion analyses can be accounted for by the observation

418   that plagioclase crystallizes at higher P_{H2O} than quartz in this rhyolite composition at any given

419   temperature at upper crustal conditions, according to the experimental phase diagram of Gardner

420   et al. (2002) in Fig. 13. Therefore, the H_2O contents measured in quartz-hosted melt inclusions

421   are not always applicable to the conditions of plagioclase growth, which is seen in liquids

422   (typically those with An-numbers >4) where quartz saturates at a lower P_{H2O} value lower than

423   that for plagioclase.

424
425   **Application of the hygrometer to rhyolites for which H_2O and/or temperature is unknown**

426   The plagioclase-liquid hygrometer/thermometer provides an opportunity to obtain pre-

427   eruptive intensive variables for samples where data from melt inclusions are not available or

428   where geo-thermometers may not be applied. Here, melt water contents are calculated for lavas

429   from Glass Mountain, Long Valley, CA and Thingmuli Volcano, Iceland, and pre-eruptive

430   temperatures are calculated for rhyolites from the Torfajökull volcanic complex, Iceland.

431
432   **Glass Mountain Rhyolites, Long Valley, CA.**

433   The hygrometer is applied to rhyolites from Glass Mountain, Long Valley, CA to obtain

434   the first estimates of their pre-eruptive water contents. Glass Mountain is composed of high-

435   silica (76.8-77 wt% SiO_2) rhyolite lavas that are saturated in $\geq$ seven mineral phases: plagioclase

436   + sanidine + ilmenite + titanomagnetite + zircon + allanite + apatite $\pm$ biotite (Metz & Mahood,

437   1991). Compositions of coexisting ilmenite and titanomagnetite phenocrysts are reported for

438   eight obsidian lavas in Metz & Mahood (1991) and input into the thermometer of Ghiorso &

439   Evans (2008) to obtain pre-eruptive temperatures that range from 698-725°C. Application of the

18

440   plagioclase-liquid hygrometer using these temperatures with the plagioclase (An_9-An_{22}) and

441   liquid compositions reported in Metz & Mahood (1991) results in pre-eruptive water contents

442   that range from 6.6-7.7 wt% H_2O for the Glass Mountain rhyolites. The fact that lower water

443   contents are not recorded by the plagioclase in these degassed obsidian samples, with LOI (loss

444   on ignition) of <0.4 wt% (Metz and Mahood, 1991), suggests that magma ascent was sufficiently

445   rapid that the loss of dissolved water led to a rapid increase in melt viscosity and decrease in

446   chemical diffusivity, similar to the effects of rapid cooling, leading to a termination in

447   plagioclase nucleation and growth, which is experimentally demonstrated in Waters et al. (in

448   review).

449

450   **Icelandic Rhyolites: Thingmuli and Torfajökull Volcanic Complexes.**

451   Thingmuli Volcano in eastern Iceland erupted a suite of lavas that span a range of

452   compositions from tholeiitic basalt to rhyolite (47.1-75.7 wt% SiO_2; Carmichael, 1964).

453   Compositions are reported for whole rocks (Carmichael, 1964), as well as for mineral phases,

454   including plagioclase, ilmenite, and titanomagnetite (Carmichael, 1967). Here, we re-calculate

455   temperatures (917 and 865°C, respectively) for two silicic lavas (59 and 70 wt% SiO_2) (#16 and

456   #18; Carmichael, 1964), using the Fe-Ti oxide thermometer of Ghiorso and Evans (2008).

457   Application of the plagioclase-liquid hygrometer to these two samples, which crystallized sparse

458   plagioclase phenocrysts (An_{42} and An_{38}, respectively), leads to melt water concentrations of 3.5

459   and 3.6 wt%, respectively, at the time of phenocryst crystallization.

460   In contrast to the case for Thingmuli silicic lavas, where pre-eruptive temperatures are

461   known from two Fe-Ti oxides, rhyolites from the Torfajökull volcanic complex contain a mineral

462   assemblage that does not permit thermometry to be applied. The Torfajökull rhyolites are

19

463   saturated with ≥ four mineral phases: plagioclase +alkali feldspar + clinopyroxene +

464   titanomagnetite ± olivine ± apatite ± zircon ± biotite ± amphibole; neither ilmenite nor

465   orthpyroxene is found (MacDonald et al., 1990). Although pre-eruptive temperatures are not

466   known for these rhyolites, Owens et al. (2013) analyzed water concentrations in feldspar-hosted

467   melt inclusions in several samples; the highest value of 4.8 wt% was found in an explosively

468   erupted unit. This maximum value for the melt water concentration in the Torfajökull rhyolites

469   provides an opportunity to use the plagioclase-liquid thermometer from this study to constrain

470   pre-eruptive temperatures. Given the range of plagioclase (An_{27-15}) observed in the Torfajökull

471   rhyolites, along with the range of whole-rock compositions (MacDonald et al., 1990), the

472   calculated pre-eruptive temperatures ranges from 780-830°C. These are minimum values, as

473   melt water concentrations ≤ 4.8 wt% were measured in some of the units, and lower water

474   concentrations will lead to higher calculated temperatures. Nonetheless, the collective data

475   reveal that Icelandic rhyolites are surprisingly hydrous, with ≤ 4.8 wt% H_2O in the Torfajökull

476   rhyolites (Owens et al., 2013) and ~3.5-3.6 wt% H_2O in the Thingmuli rhyolites (this study).

477
478   **Implications and Recommended Applications**

479   The plagioclase thermometer/hygrometer presented in this study is calibrated on a data

480   set that spans a wide range of liquid compositions (45-78 wt% SiO_2), including high-SiO_2

481   rhyolites and both metaluminous and alkaline liquids. In addition, the compositional range of

482   plagioclase in the calibration has been extended to values as sodic as An_{17}. It is demonstrated

483   that the updated hygrometer accurately reproduces plagioclase-liquid equilibrium experiments

484   that were conducted in a piston-cylinder apparatus at 1.0-1.2 GPa (Bartels et al., 1991), although

485   these experiments were not included in the calibration. This result shows that the updated

486   plagioclase-liquid hygrometer/thermometer in this study can be applied to all pressures

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487   throughout the crustal column, and that the volumetric terms in the thermodynamic model

488   accurately account for the minor effect of pressure. Application of the revised plagioclase-liquid

489   hygrometer/thermometer is recommended for liquids that range from 45-78 wt% SiO_2,

490   plagioclase compositions that range from An_{15-95}, temperatures of 700-1300°C, and pressures of

491   0-1.2 GPa.   The updated model can be downloaded in Excel format from the data repository or

492   obtained directly from the authors. The program is also availabe as a script formated for MatLab

493   that may be obtained directly from the authors.

494

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796 **Figure Captions**
797
798 **Figure 1:** (A) Histogram of hydrous (light grey) and anhydrous (black) liquid compositions used
799 in the calibration of the hygrometer as a function of wt% SiO_2 in the melt. (B) A histogram of
800 plagioclase compositions used in the calibration of the hygrometer as a function of mol% An.
801
802 **Figure 2:** Plot showing the range in total alkali content (wt% Na_2O + wt% K_2O) as a function of
803 wt% SiO_2 for liquids used in the calibration of the hygrometer, along with the proposed
804 boundary between alkaline and calc-alkaline liquids from Irvine & Baragar (1972). Water-
805 saturated experiments are shown as hollow circles, anhydrous experiments are shown as black
806 diamonds, and the experiments used in the calibrations Lange et al. (2009) are shown as grey
807 circles.
808
809 **Figure 3:** (A) Plot showing the experiments used in the calibration of the hygrometer as a
810 function of liquid An-number and mol% An in plagioclase. (B) Plot showing the experiments
811 used in the calibration of the hygrometer as a function of wt% SiO_2 in the liquid and mol%An in
812 plagioclase. The dashed lines highlight the limits of the calibration of Lange et al. (2009), which
813 does not adequately cover the liquids with low An-numbers (rhyolitic). Symbols the same as in
814 Fig. 2.
815
816 **Figure 4:** (A) A plot of measured water contents from the calibration v. the predicted water
817 contents derived from the hygrometer, with a 1:1 correspondence line, and dashed lines
818 reflecting two standard errors (±0.7 wt% H_2O). (B) Results of the plagioclase-liquid hygrometer
819 show as a function of residuals (measured wt% H_2O – predicted wt% H_2O). With the exception
820 of three experiments, the hygrometer predicts melt water contents for the calibration data set
821 within <1 wt%.
822
823 **Figure 5:** The residuals (measured – predicted wt% H_2O) of the hygrometer plotted against (A)
824 wt% SiO_2, (B) Total Alkalis (wt% Na_2O + wt% K_2O), (C) liquid An-number, (D) plagioclase
825 composition (mol% An), (E) temperature (°C), and (F) melt viscosity (log_{10} Pa s). In all plots
826 (A-F), water saturated experiments are shown as hollow circles, anhydrous experiments are
827 shown as black diamonds. For comparison, results from the model of Lange et al. (2009) are
828 shown as grey circles.
829
830 **Figure 6:** (A) Comparison of measured vs. predicted temperature (°C) using a 1:1
831 correspondence line. The average difference is 12°C (14°C and 10°C for hydrous and anhydrous
832 experiments, respectively). Also shown are dashed lines marking ±40°C, which highlights that
833 the model recovers temperatures within ≤40°C for 210 of 214 experiments. (B) The difference in
834 measured vs. predicted temperature for the calibration data set, shown as a histogram.
835
836 **Figure 7:** The difference between measured and predicted temperature for the calibration data
837 set plotted against (A) wt% SiO_2, (B) temperature, and (C) wt% H_2O. In all plots (A-C), water
838 saturated experiments are shown as hollow circles, and anhydrous experiments are shown as
839 black diamonds. For comparison, results from the thermometer of Putirka (2008) are shown as
840 grey diamonds in A-C.
841

842   **Figure 8:** A comparison of H_2O contents calculated by the plagioclase-liquid hygrometer on
843   H_2O under-saturated experiments in the studies of Almeev et al. (2012), Bartels et al. (1991) and
844   Hamada and Fujii (2008), where H_2O contents were measured using FTIR. Experiments of
845   Almeev et al. (2012) and Hamada and Fugii (2008) were conducted under mixed CO_2-H_2O
846   conditions on a rhyolite and basalt, respectively. Bartels et al. (1991) performed anhydrous
847   experiments on a basalt and in a piston cylinder at pressures ≥1 GPa. See text for discussion.
848

849   **Figure 9:** Measured minus predicted wt% H_2O, using the the plagioclase-liquid hygrometer, for
850   the anhydrous experiments on rhyolite liquid of Brugger et al. (2003) plotted as a function of
851   wt% SiO_2.
852

853   **Figure 10:** A plot showing the effect of wt% H_2O in melt on equilibrium plagioclase
854   composition for rhyolite, andesite and basalt (see text for discussion).
855

856   **Figure 11:** A plot showing the effect of pressure (MPa) on the wt% H_2O value calculated with
857   the plagioclase-liquid hygrometer for three liquids (rhyolite, andesite, and basalt). Horizontal
858   light-grey isopleths of 2, 4 and 6 wt% H_2O highlight the small effect of pressure. See text for
859   discussion.
860

861   **Figure 12:** (A) A plot of plagioclase composition (mol% An) as a function of temperature for 13
862   samples from the Bishop Tuff using the data reported in Hildreth (1977). (B) A plot showing
863   water contents for the Bishop Tuff calculated using the plagioclase-liquid hygrometer, using
864   plagioclase compositions from (A) and temperatures from Hildreth and Wilson (2007). Also
865   shown are reported water contents in melt inclusions from the Early (Ig1Eb), Middle (Ig2Ea) and
866   Late (Ig1NWa and Ig1NWb) units of the Bishop Tuff from Wallace et al. (1999) (black crosses)
867   and Anderson et al. (2000) (grey diamonds). The width of the grey boxes reflects the range of
868   reported temperatures for each unit in Hildreth and Wilson (2007).   See text for discussion.
869

870   **Figure 13:** Application of the plagioclase-liquid hygrometer to the Youngest Toba Tuff (YTT),
871   using the plagioclase compositions, and bulk compositions reported in Chesner (1998). The pre-
872   eruptive temperatures presented for the YTT have been recalculated using the oxide
873   compositions presented in Chesner (1998) and the geo-thermometer of Ghiorso and Evans
874   (2008). The results of the hygrometer are shown as stars. Also shown are the phase equilibrium
875   experiments (grey circles) and mineral-in curves of Gardner et al. (2002), along with isopleths of
876   H_2O solubility (in wt %) for the YTT calculated with Zhang et al. (2007). The water contents
877   derived from the plagioclase-liquid hygrometer are consistent with the plagioclase-in curve of
878   Gardner et al. (2002). Also shown on the phase diagram is a grey field that shows the range of
879   reported water contents, 3.9-6.4 wt%, in quartz-hosted melt inclusions from Chesner and Luhr
880   (2010). The grey field is defined by pre-eruptive temperatures presented in Chesner (1998) and
881   the quartz-in curve as determined by Gardner et al. (2002). The water contents recorded by the
882   melt inclusions and the plagioclase-liquid hygrometer are consistent with the phase equilibrium
883   experiments. See text for discussion.
884

885   **Figure 14:** A plot showing estimates of minimum pre-eruptive temperatures (°C) that are
886   calculated by applying the plagioclase-liquid thermometer to 19 rhyolite lavas from the
887   Torfajökull Volcanic Complex, for which water contents (≤4.8wt%) have been measured in melt

30

888   inclusions (Owen et al. 2013). Plagioclase compositions (An_{15}-An_{27}) are from MacDonald et al.

889   (1990). See text for discussion.

Table 1A. *Summary of albite thermodynamic data used in the hygrometer model*

Parameter	Value	Reference
T_f	1373 K	Boettcher et al. (1982)
$\Delta H_{fus}(T_f)$	64.5 kJ/(mol·K)	Tenner et al. (2007)
$\Delta S_{fus}(T_f)$	47.0 J/(mol·K)	Tenner et al. (2007)
C_p crystal	$393.64 - 2415.5T^{-0.5} - 7.8928\ 10^6 T^{-2} + 1.07064\ 10^9\ T^{-3}$	Berman (1988)
C_p liquid	359 J/(mol·K)	Tenner et al. (2007)
V_{298K} crystal	100.57 cm^3/mol	Wruck et al. (1991)
α (T) crystal	2.68×10^{-5} K^{-1}	Fei (1995)
$(\delta V/\delta P)^{crystal}$	-1.67 cm^3/GPa	Tenner et al. (2007); Lange et al. (2009)
$V(T)$ liquid	$112.72 + 0.00382\ (T-1373)$ cm^3/mol	Lange (1996)
$(\delta V/\delta P)^{liquid}$	$-6.379 - 0.00055\ (T-1673)$ cm^3/GPa	Kress and Carmichael (1988)

Table 1B. *Summary of anorthite thermodynamic data used in the hygrometer model*

Parameter	Value	Reference
T_f	1830 K	Rankin and Wright (1915)
$\Delta H_{fus}(T_f)$	142.4 kJ/(mol·K)	This study (Appendix A)
$\Delta S_{fus}(T_f)$	77.8 J/(mol·K)	This study (Appendix A)
C_p crystal	$439.37 - 3734.1T^{-0.5} + 0.317024\ 10^9\ T^{-3}$	Berman (1988)
C_p liquid	433.6 J/(mol·K)	This study (Appendix A)
V_{298K} crystal	100.61 cm^3/mol	Wainright and Starky (1971)
α (T) crystal	1.41×10^{-5} K^{-1}	Fei (1995)
$(\delta V/\delta P)^{crystal}$	-1.16 cm^3/GPa	Angel (2004); Lange et al. (2009)
$V(T)$ liquid	$106.3 + 0.00371\ (T-1673)$ cm^3/mol	Lange (1997)
$(\delta V/\delta P)^{liquid}$	$-5.182 - 0.00101\ (T-1673)$ cm^3/GPa	Ai and Lange (2008)

1

Table 2: Model Parameters	*Fitted Values ± 1σ*	*t-statistic*
a"	-17.3 ± 2.53	-6.86
m'	0.39 ± 0.12	3.40
b"	2.99 ± 0.07	39.9
d" (SiO_2)	7.83 ± 2.52	3.11
d" (Al_2O_3*)	-50.1 ± 3.53	-14.2
d" (FeO^T)	14.1 ± 3.30	4.27
d" (MgO)	24.0 ± 3.05	7.86
d" (CaO)	-15.9 ± 3.45	-4.61
d" (Na_2O)	18.6 ± 4.32	4.31
d" ($K_2Al_2O_4$)	24.0 ± 6.73	3.57

Number of cases = 214; SEE =0.35 wt% H_2O; R^2= 0.98

*Al_2O_3 is moles Al_2O_3 minus the moles of K_2O

1
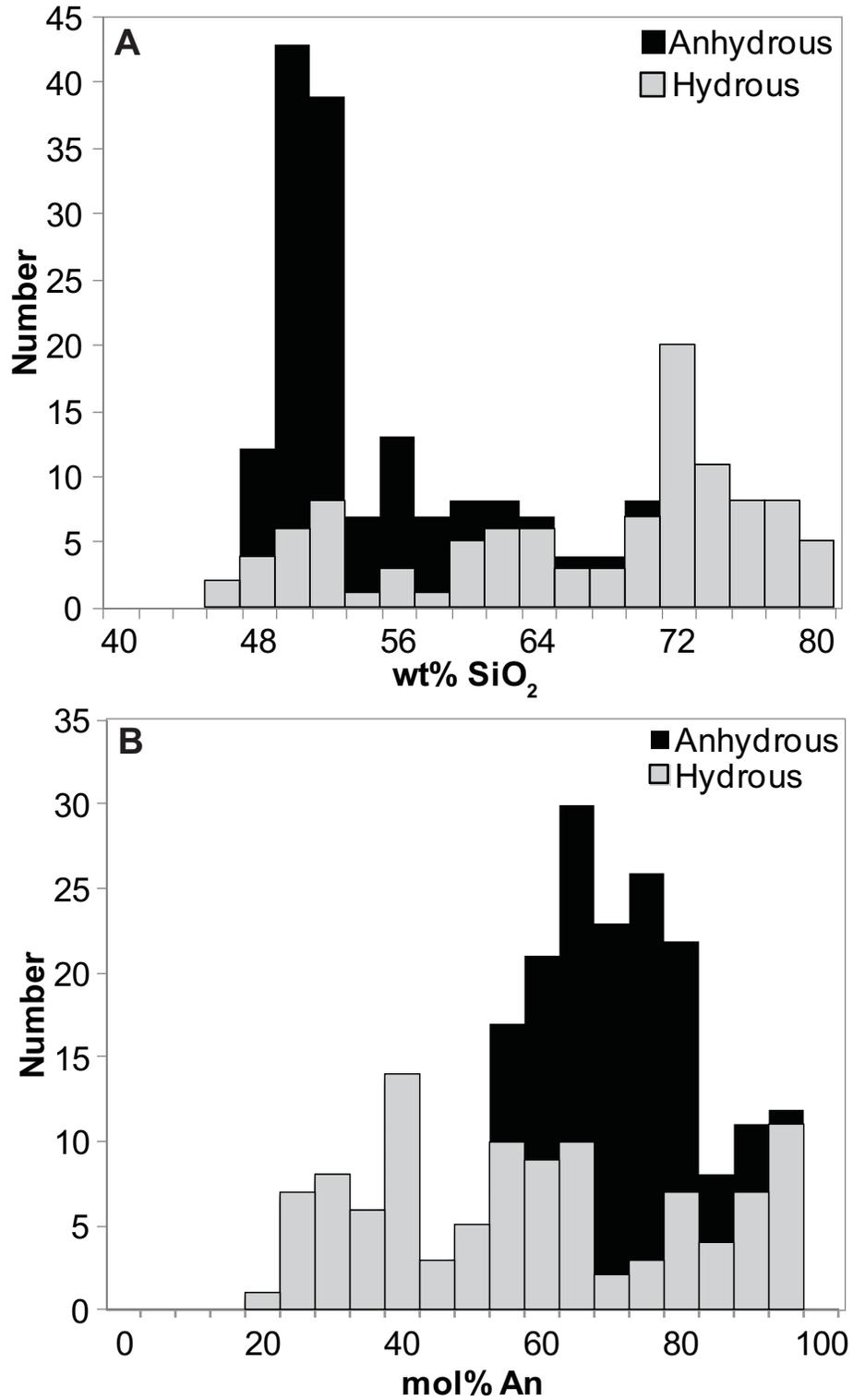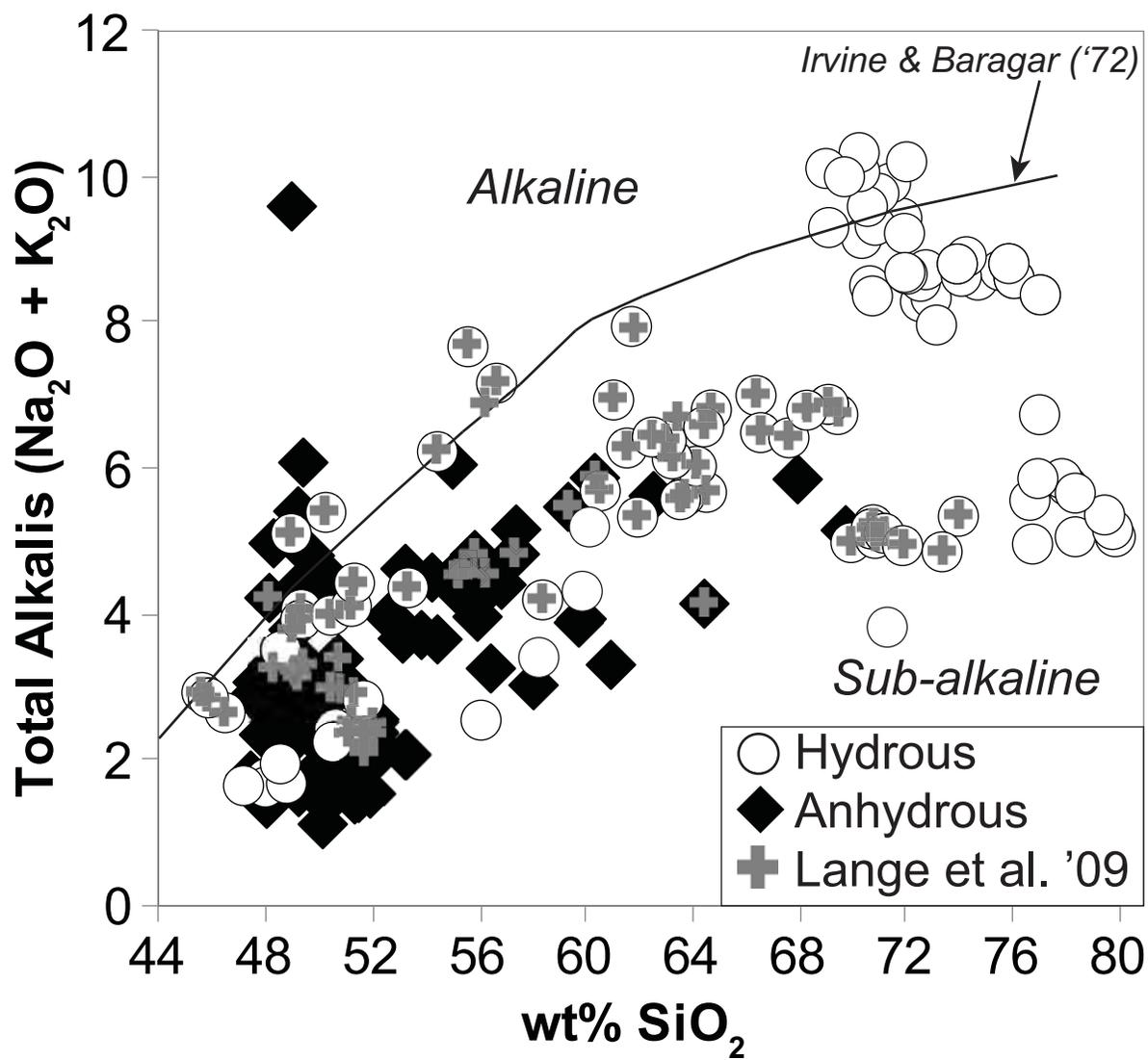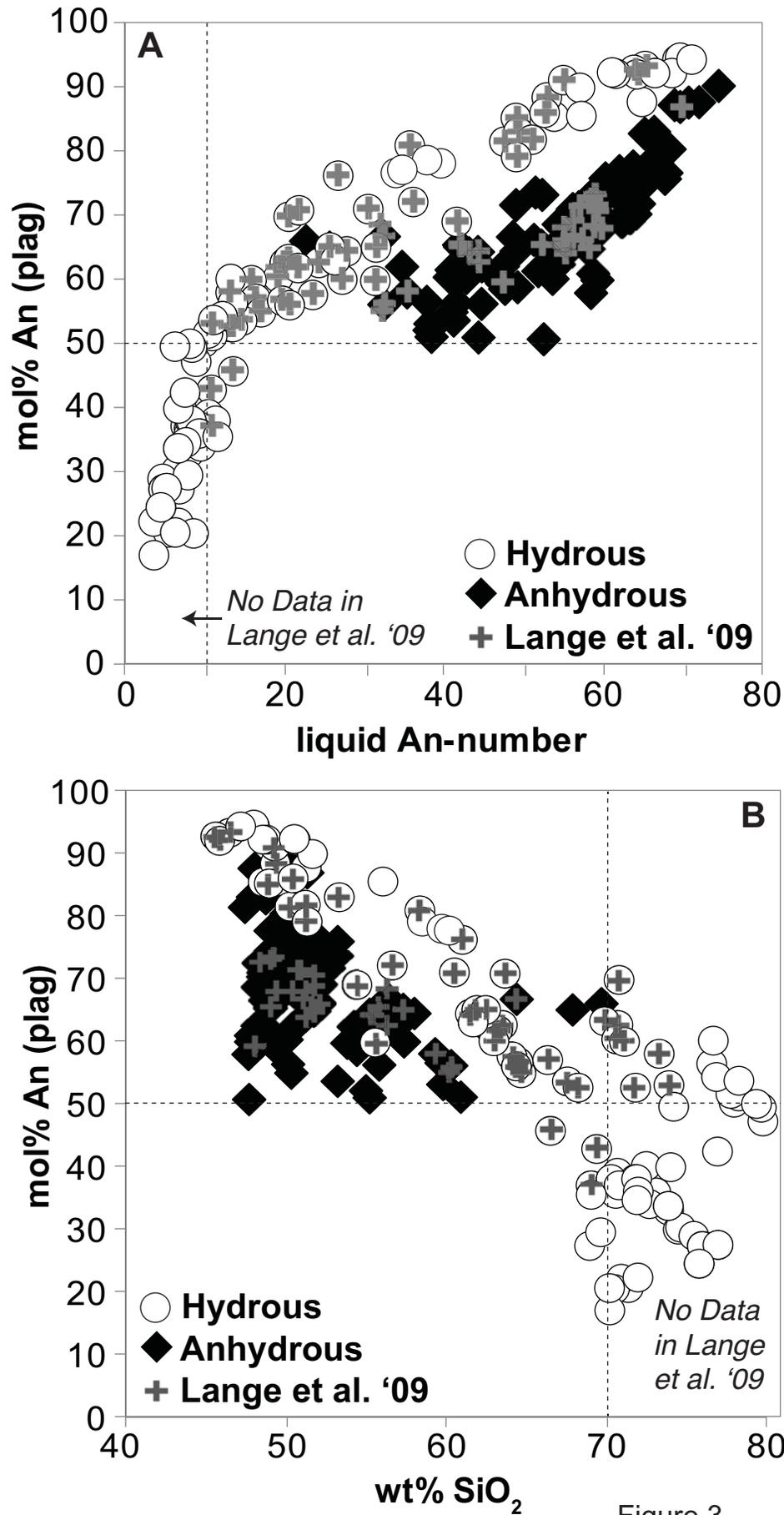
Figure 1

Figure 2

Figure 3
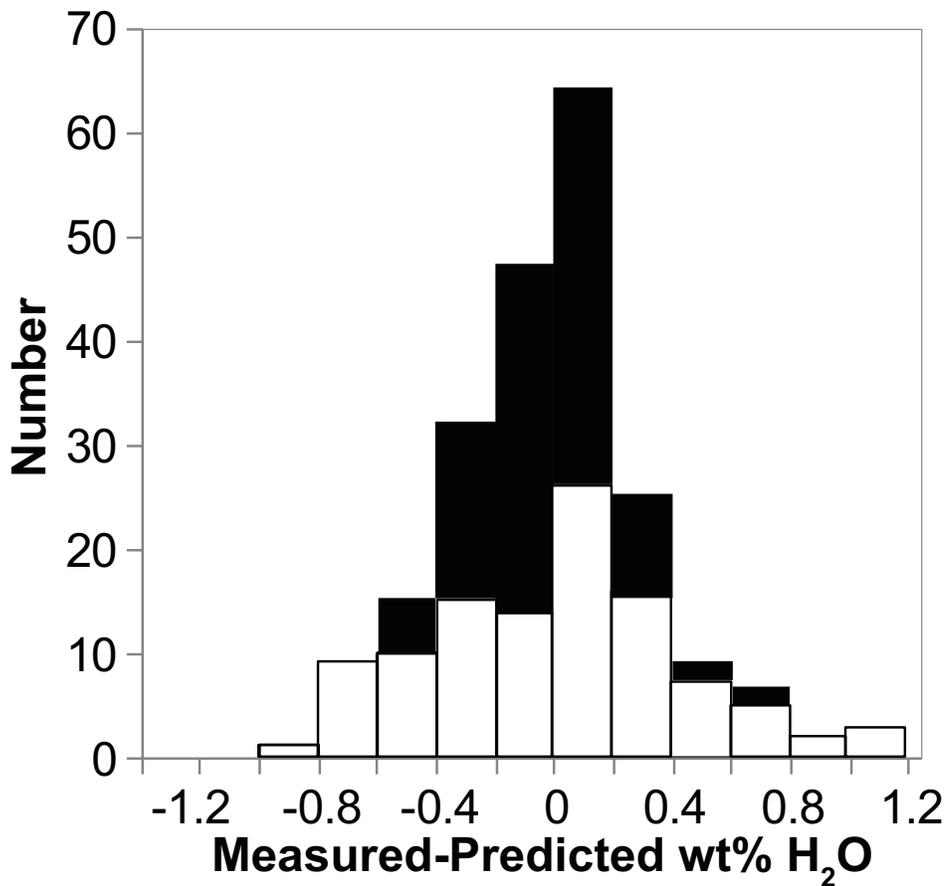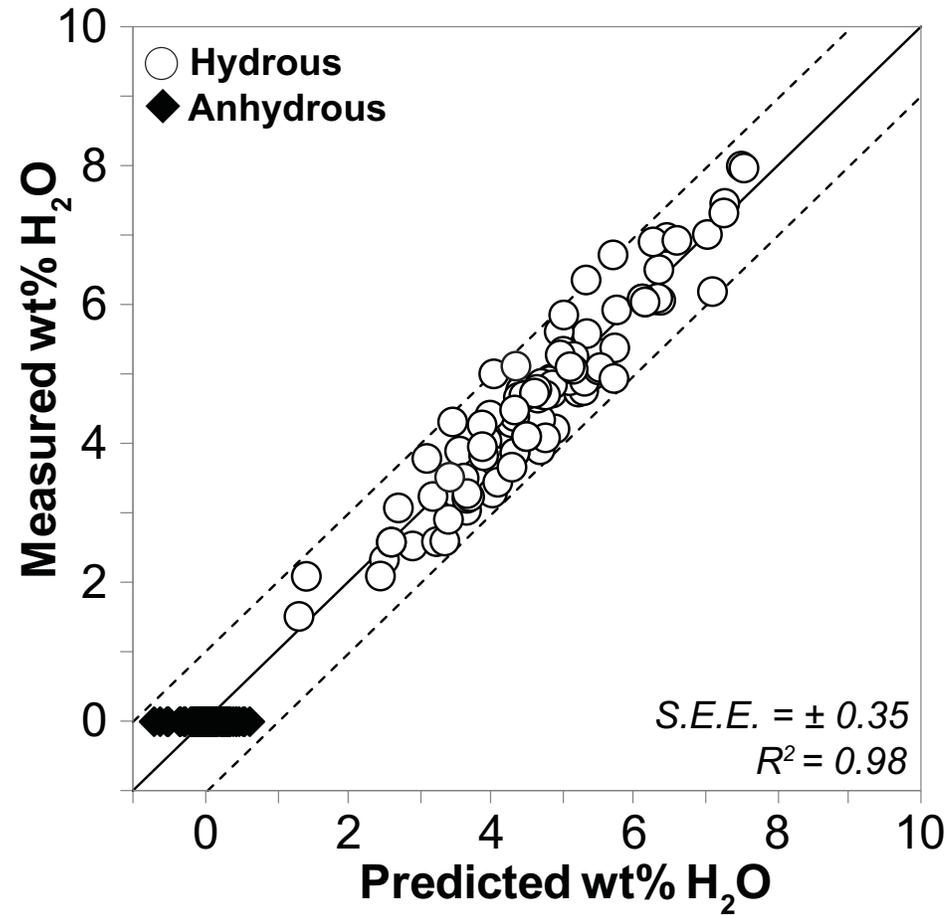
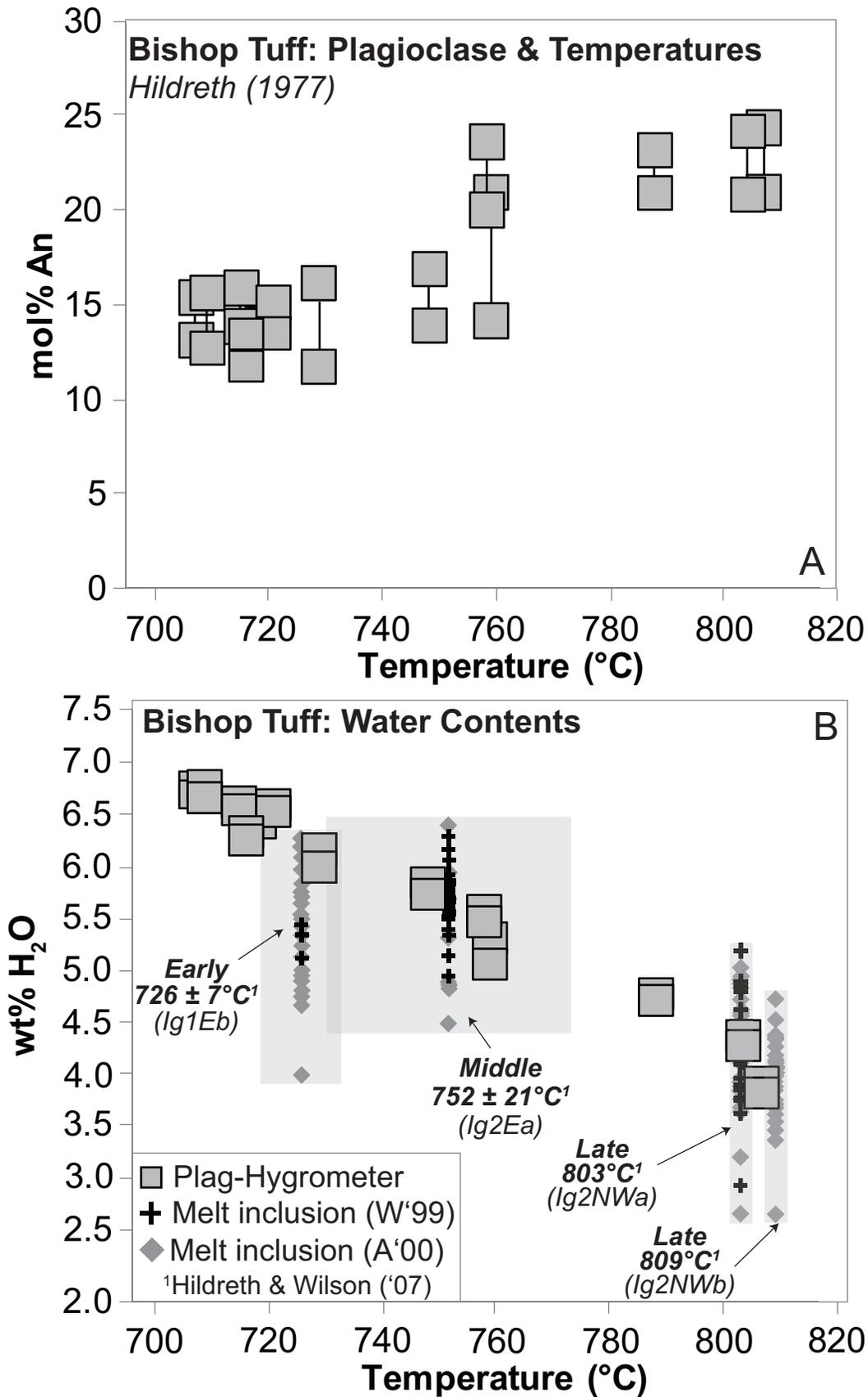Figure 4
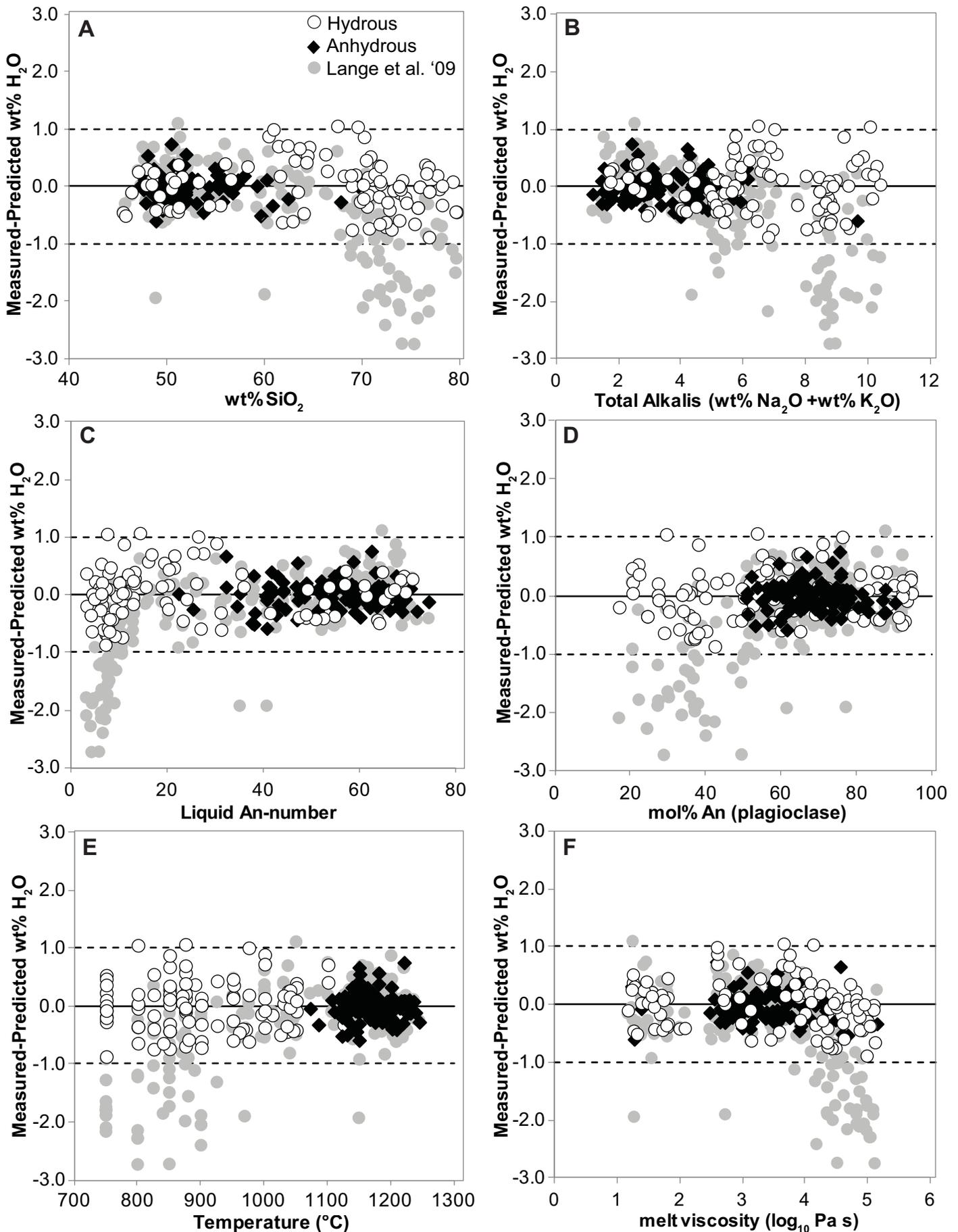
Figure 5
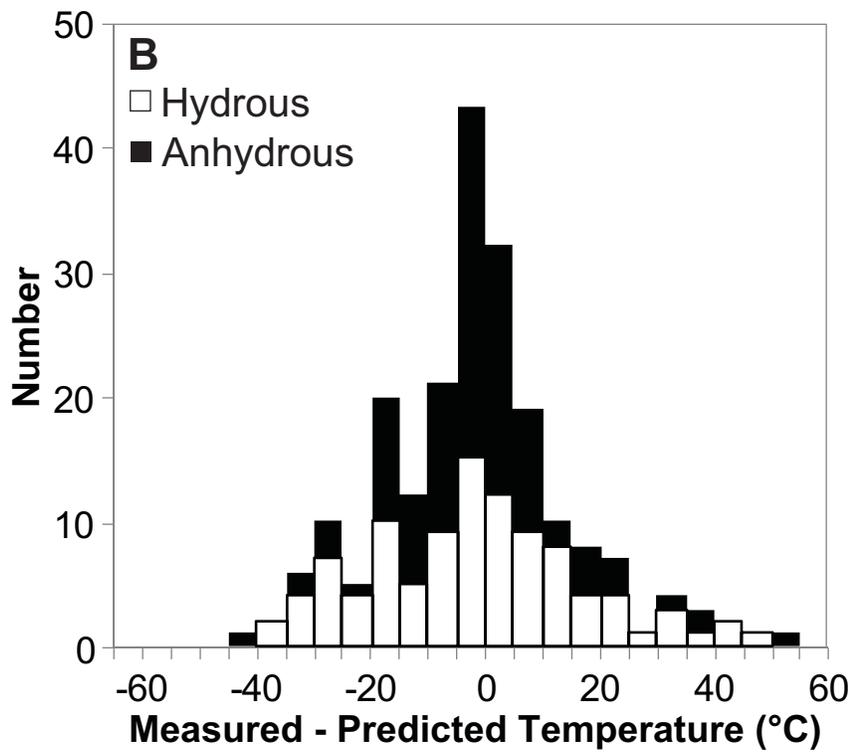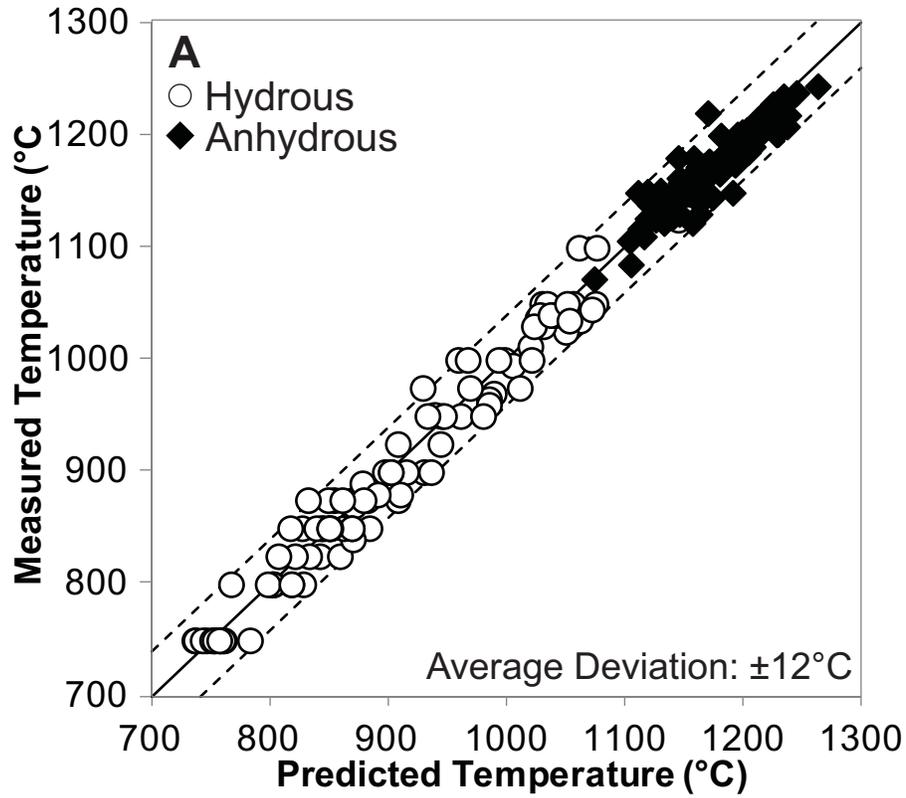
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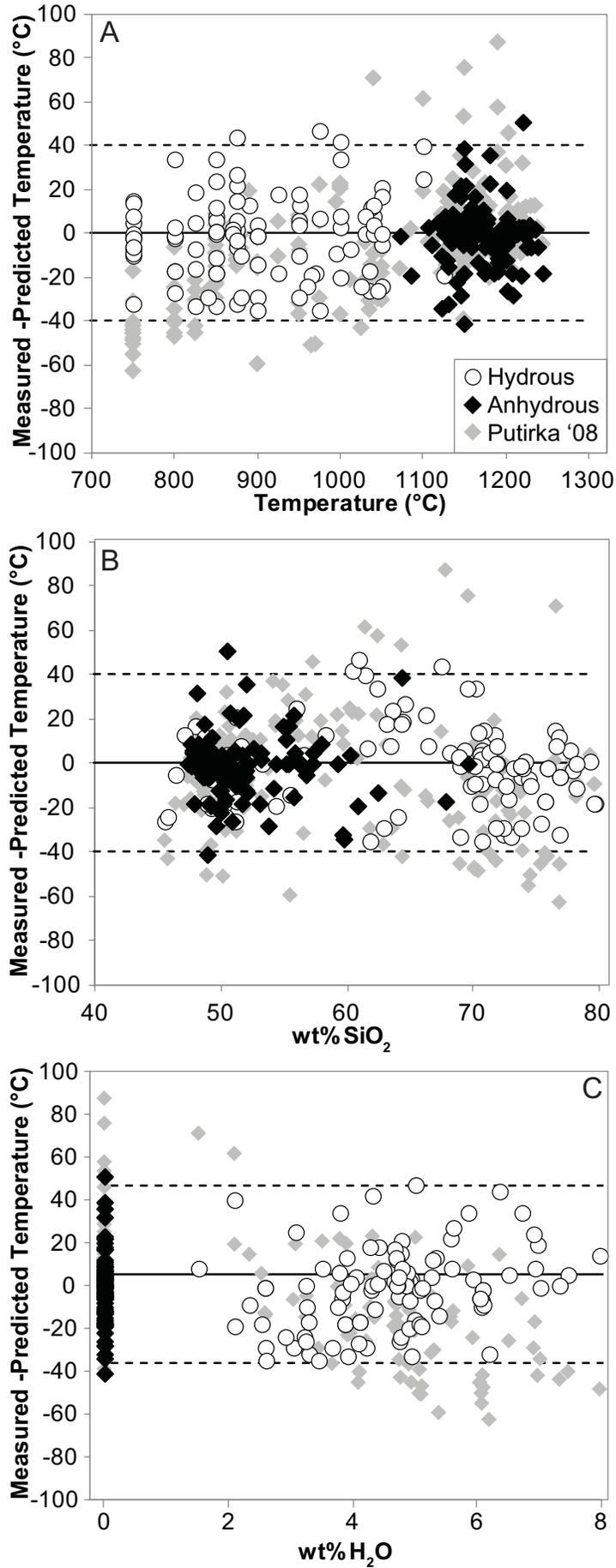
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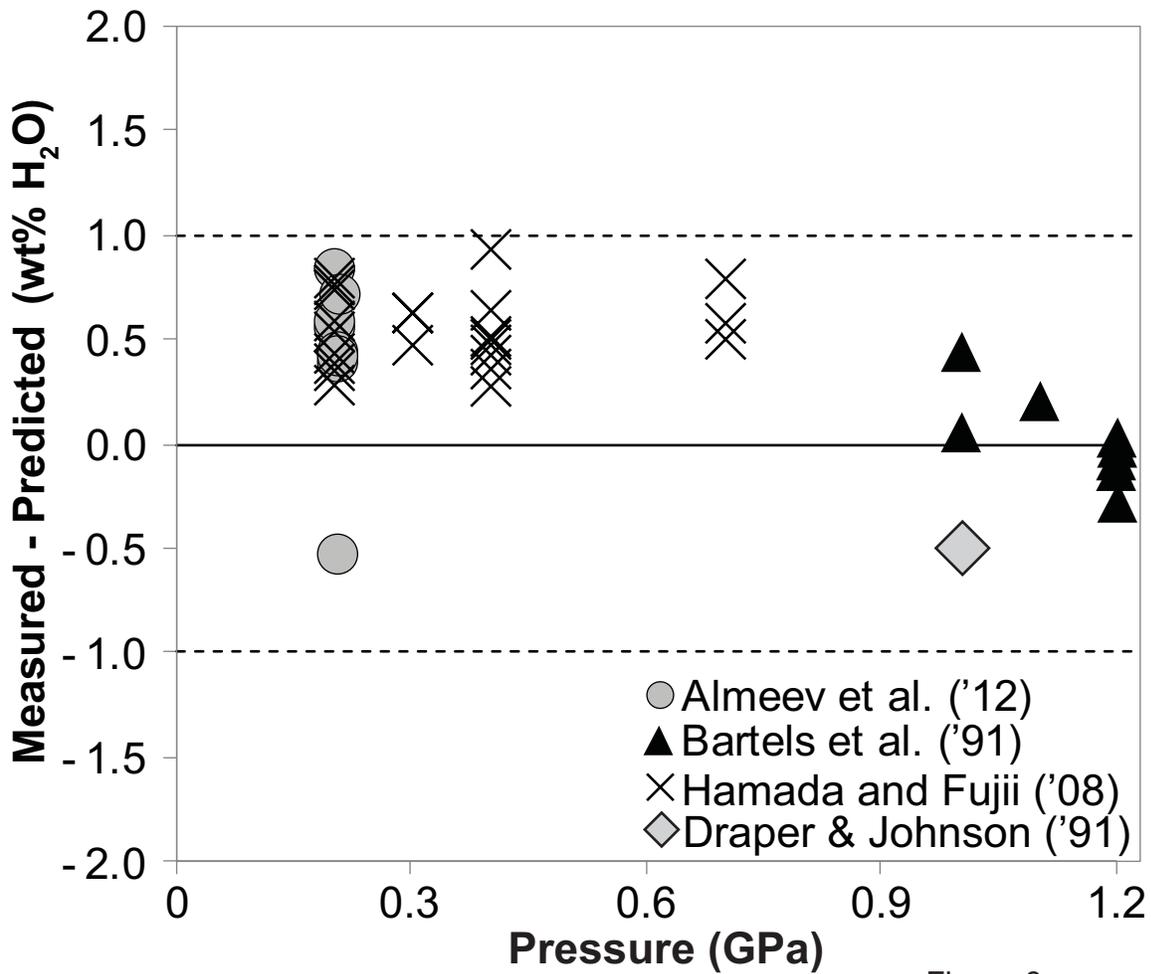
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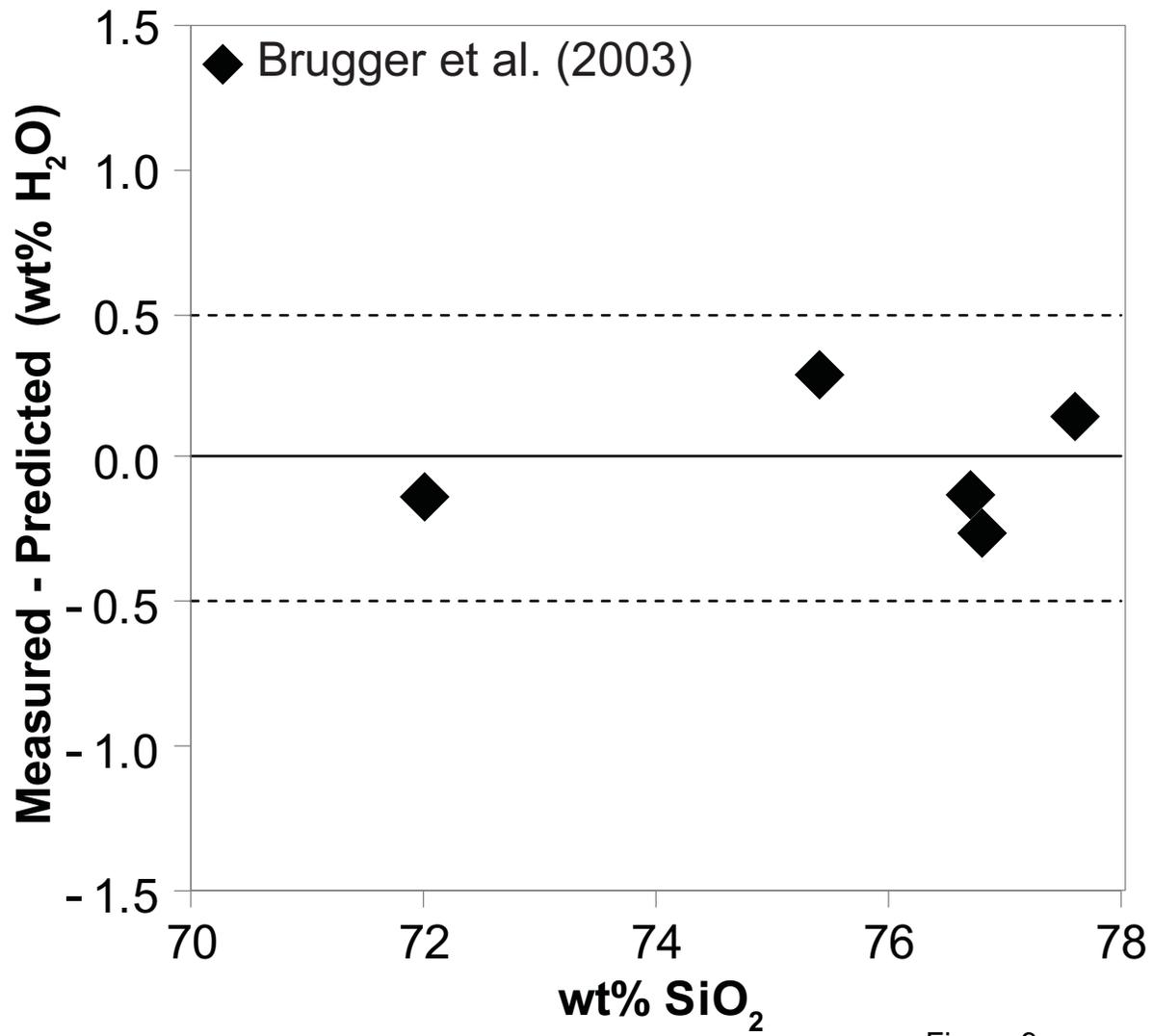
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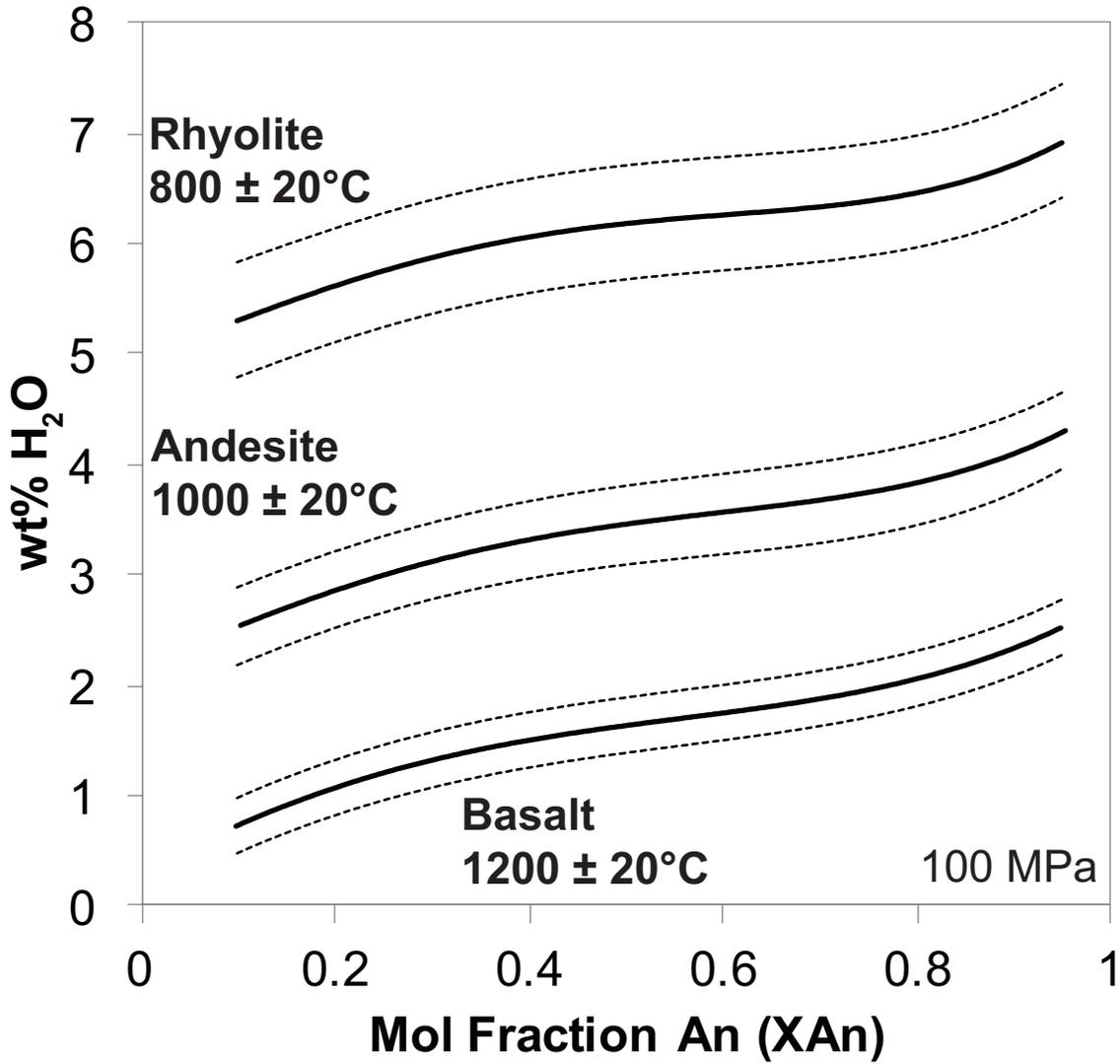
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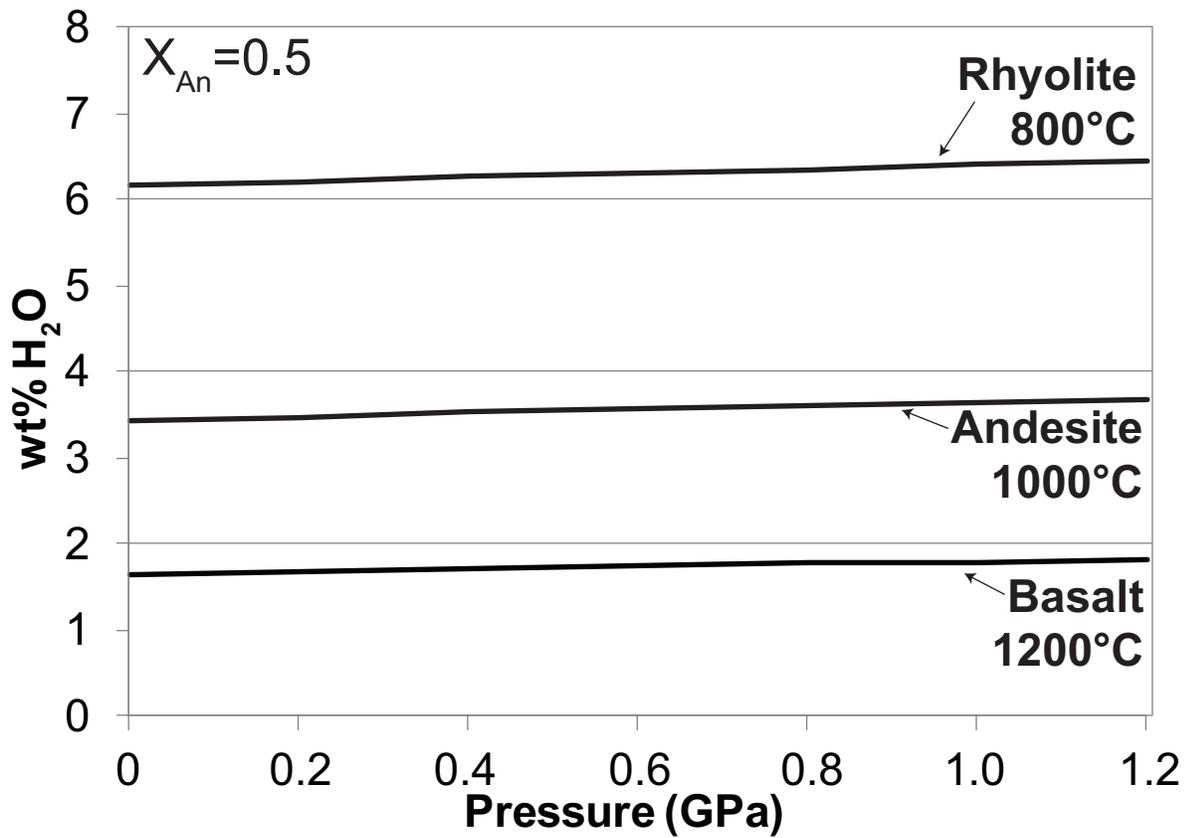
Figure 11

Figure 12

Figure 13

Figure 14