

Igneous thermometers and barometers based on plagioclase + liquid equilibria: Tests of some existing models and new calibrations

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ABSTRACT

Although many formulations of plagioclase + liquid equilibria have been calibrated in the last decade, few models specifically address the issue of temperature (T) prediction. Moreover, for those that do, T error is not addressed, greatly limiting their use as geothermometers. Several recent models of plagioclase-liquid equilibria are thus tested for their ability to recover T from their calibration data, and predict T from experiments not used for calibration. The models of Sugawara (2001) and Ghiorso et al. (1995, 2002) outperform earlier calibrations. These models perform reasonably well at $T > 1100$ °C, though recovery and prediction of T is less precise for hydrous compositions. In addition, these models cannot be integrated with geo-hygrometers, or other mineral-melt thermometers and barometers; the following expression predicts T with up to 40% greater precision:

$$\begin{aligned} \frac{10^4}{T(\text{K})} = & 6.12 + 0.257 \ln \left[\frac{[\text{An}^{\text{pl}}]}{[\text{Ca}^{\text{liq}} (\text{Al}^{\text{liq}})^2 (\text{Si}^{\text{liq}})^2]} \right] - 3.166[\text{Ca}^{\text{liq}}] + 0.2166[\text{H}_2\text{O}^{\text{liq}}] \\ & - 3.137 \left[\frac{\text{Al}^{\text{liq}}}{\text{Al}^{\text{liq}} + \text{Si}^{\text{liq}}} \right] + 1.216[\text{Ab}^{\text{pl}}]^2 - 2.475 \times 10^{-2}[P(\text{kbar})] \end{aligned} \quad (1)$$

Because these thermometers are pressure (P) sensitive, a temperature-sensitive barometer was also developed:

$$\begin{aligned} P(\text{kbar}) = & -42.2 + 4.94 \times 10^{-2}[T(\text{K})] + 1.16 \times 10^{-2}T(\text{K}) \ln \left[\frac{[\text{Ab}^{\text{pl}}\text{Al}^{\text{liq}}\text{Ca}^{\text{liq}}]}{[\text{An}^{\text{pl}}\text{Na}^{\text{liq}}\text{Si}^{\text{liq}}]} \right] \\ & - 382.3[\text{Si}^{\text{liq}}]^2 + 514.2[\text{Si}^{\text{liq}}]^3 - 19.6 \ln[\text{Ab}^{\text{pl}}] - 139.8[\text{Ca}^{\text{liq}}] \\ & + 287.2[\text{Na}^{\text{liq}}] + 163.9[\text{K}^{\text{liq}}] \end{aligned} \quad (2)$$

In these models, T is in Kelvins and P is in kbar. An^{pl} and Ab^{pl} are the fractions of anorthite and albite in plagioclase, calculated as cation fractions: $\text{An} = \text{CaO}/(\text{CaO} + \text{NaO}_{0.5} + \text{KO}_{0.5})$ and $\text{Ab} = \text{NaO}_{0.5}/(\text{CaO} + \text{NaO}_{0.5} + \text{KO}_{0.5})$. Terms such as Al^{liq} refer to the anhydrous cation fraction of Al in the liquid; H_2O in Equation 1 is in units of wt%. Errors on these models are comparable to those for clinopyroxene thermobarometers: In Equation 1, $R = 0.99$ and the standard error of estimate (SEE) is 23 K; for Equation 2, $R = 0.94$ and the SEE is 1.8 kbar. The models successfully recover mean pressures for experimental data that are not used for calibration, and are furthermore able to recover near-1-atm P estimates for volcanic rocks from Kilauea, Hawaii, which are thought to have crystallized at or very near Earth's surface.

OVERVIEW

In igneous petrology, it is often crucial to determine the pressures (P) and temperatures (T) at which magmas partially crystallize, as such information is central to testing our ideas of magma transport and liquid evolution. For a geothermometer or geobarometer to be useful, though, it is no less crucial that errors on estimates of T and P be known. In the absence of some estimate of model uncertainty, calculated values are virtually meaningless. Below, several geothermometers based on plagioclase + liquid equilibria are tested for their ability to recover T from plagioclase-saturated partial melting experiments.

Plagioclase + liquid thermometers are among the earliest dedicated geothermometers formulated for igneous systems. Early efforts employed expressions relating T to plagioclase and liquid composition, and were calibrated using 1-atmosphere experimental data (Bowen 1913; Kudo and Weill 1970; Mathez 1973; Drake 1976). Subsequent studies augmented the P - T conditions, bulk compositions and thermodynamic treatments of these earlier efforts, in some cases emphasizing prediction of T (Loomis 1979; Glazner 1984; Ariskin and Barmina 1990), in others the prediction of plagioclase components [anorthite (An), albite (Ab), orthoclase (Or)] when a liquid composition, T , and/or P are given (e.g., Housh and Luhr 1991; Panjasawatwong et al. 1995; Danyushevsky et al. 1997). Following these efforts, Housh and Luhr (1991), Sugawara (2001), and Ghiorso

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et al. (1995, 2002) presented detailed thermodynamic models that allow calculation of plagioclase compositions and/or saturation temperatures, among other quantities. However, these models have yet to be tested for their capacity to recover T for their calibration data. Neither have these models been tested for their ability to predict T for experimental data not used for calibration. It is thus unclear to what extent these models can be used to calculate plagioclase crystallization temperatures reliably for natural samples.

The models of Housh and Luhr (1991), Ariskin (1999), Sugawara (2001), and Ghiorso et al. (1995, 2002) (MELTS/pMELTS) are singled out for testing for several reasons. First, Marsh et al. (1990) presented tests of several pre-1990 plagioclase + liquid thermometers. Second, unlike most other calibration efforts, the Housh and Luhr (1991), Ariskin (1999), Sugawara (2001), and Ghiorso et al. (1995, 2002) models were apparently intended to be used as igneous thermometers. Third, all these models include hydrous experimental calibration data. And finally, except for Ariskin (1999), these models employed comprehensive thermodynamic treatments of system components, which are suspected to enhance model precision and enable model extrapolation.

Several other models also were tested as geo-thermometers, but to anticipate certain of the results, the models of Sugawara (2001) and Ghiorso et al. (1995, 2002) provided more accurate T estimates than earlier calibrations. Models that utilize limited calibration data, or data with special restrictions (e.g., multiple phase saturation), or that rely on the inversion of a regression equation to obtain T , performed poorly. In addition, early calibrations that rely heavily on 1-atm experiments performed prior to the advent of techniques to minimize Na_2O loss from liquids (Tormey et al. 1987) do not perform well as geothermometers. One-atmosphere experiments that do not control Na_2O loss must be considered with caution: when such data dominate a calibration, $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{CaO})$ ratios of experimental glasses are almost assuredly skewed downward, and hence unlikely to represent equilibrium values (see also Putirka et al. 1996). Similarly, Na loss may occur during microbeam analysis of hydrous glasses (see Rutherford et al. 1985). Calibrations based on such experiments will necessarily yield poor results, no matter how sophisticated the thermodynamic or numerical treatment. Conversely, calibrations based on sound experimental data will always be useful, even if only over a limited P - T - X range.

Although the pressure sensitivity of plagioclase-liquid equilibria has been noted (e.g., Panjasawatwong et al. 1995), and although the Sugawara (2001) and Ghiorso et al. (1995, 2002) models require P as input, these models provide no means of predicting P when a plagioclase and liquid composition are given. To remedy this deficiency, a temperature-sensitive plagioclase + liquid barometer has been calibrated. Finally, the effect of water contents on plagioclase-melt equilibria has long been recognized (e.g., Kudo and Weill 1970; Housh and Luhr 1991; Panjasawatwong et al. 1995) and has been thought to be responsible for the very high anorthite contents discovered in some arc lavas (Panjasawatwong et al. 1995). For this reason, an attempt was made to incorporate water as a variable in the geothermometers and -barometers, and to test the Housh and Luhr (1991) geo-hygrometer for its ability to predict water contents of experimental glasses. In such attempts, water contents of

experimentally derived glasses must be estimated. But only in a very few cases have water contents been determined directly (Table 1). Most experimental studies rely on solubility models, or otherwise make no attempt to quantify water concentrations. Indeed, because of the scarcity of direct H_2O measurements in experimental studies, prior attempts at the calibration of clinopyroxene-liquid thermometers (Putirka, et al. 2003) have purposely avoided including H_2O as a variable. However, as will be shown later, even crude estimates of water contents aid greatly in the calculation of plagioclase crystallization temperatures. Nonetheless, more highly refined thermometers await a larger experimental database where water contents are measured directly.

TESTS OF PRIOR MODELS

Data and methods

Experimental data spanning a wide P , T , and liquid composition range were used to test various thermometers (Table 1); these data range from 0.001–27 kbar and 850–1430 °C, with liquid compositions that range from 42–73 wt% SiO_2 . Of these data, some were used for calibration by Ariskin (1999), Sugawara (2001), and Ghiorso et al. (1995, 2002), as indicated in Table 1; all data not used for calibration comprise “test data,” which necessarily differ for each model. Table 1 also indicates which 1-atm experimental studies attempted to control for Na-loss, in the analysis of hydrous glass compositions.

Reported experimental P , glass and (where appropriate) coexisting plagioclase compositions were used as input for all models. For both Sugawara (2001) and Ghiorso et al. (1995, 2002) (MELTS/pMELTS), the expressions for T and plagioclase composition were not readily coded independently; computer programs provided at the authors' web sites were employed for T and plagioclase component calculations. The Sugawara (2001) model has the fortunate feature of yielding direct output of plagioclase saturation T and composition. In contrast, MELTS/pMELTS is not an intrinsic thermometer; plagioclase compositions and saturation T values must be ascertained after adjusting input. In the use of MELTS/pMELTS, glass compositions and P were used as input and the “find liquidus” feature was used. However, MELTS/pMELTS did not predict plagioclase to be on the liquidus for >50% of experimental observations. In such instances, input T was decreased in 10 °C increments until plagioclase saturation was achieved (see Tests of MELTS/pMELTS).

Tests of the Sugawara (2001) model

Unsurprisingly, when the Sugawara (2001) model was used to recover T for its calibration data, the model performed well (Fig. 1a). The standard error of estimate (SEE) for the Sugawara (2001) calibration data is 41 °C. Interestingly, the Sugawara (2001) model provided a poor fit to a substantial fraction of the Sugawara (2001) data. Also, it is worth noting that for those hydrous experiments that were not water saturated (e.g., Rutherford et al. 1985), T was best recovered when water was estimated as: $\text{H}_2\text{O} = 100 - \text{glass wt\% total}$.

When the Sugawara (2001) model was used to predict T for experimental data not used for calibration, predicted values are only slightly less precise, with an SEE of 45 °C. Interestingly, the correlation coefficient and slope and intercept are all much improved ($R = 0.96$; $m = 1.03$; $b = -23$ °C) (Fig. 1a). In addition, T estimates for hydrous experiments from Rutherford et al. (1985), Grove et al. (1997), and Helz (1976) are very good, even when water was estimated as the remainder of oxide sums less than 100 [$\text{H}_2\text{O} = (100 - \text{glass wt\% total})$]. On the whole, however, values of T from hydrous experiments are recovered with less precision (SEE = 46 °C) than for anhydrous experiments (SEE = 29 °C).

The Sugawara (2001) model was calibrated using only experiments performed between 1 atm and 2 kbar, but the model works surprisingly well for high- P experiments. For test data in the 5–27 kbar range, the SEE is 31 °C, and the $R = 0.82$. But some systematic error is evident in the slope and intercept, which are 0.65 and 450 °C respectively, although there is no correlation between T -error and P ($R = 0.015$).

Finally, with regard to the recovery and prediction of plagioclase compositions, the Sugawara (2001) model yields similar results for both the calibration and test data (Figs. 1b–1d). Correlation coefficients in each case approach 0.8, and the values of SEE are between 0.06 and 0.10 for Ab and An.

TABLE 1. Experimental studies used as test and calibration data

Source	Pressure range (kbar)	T range (Kelvins)	C = Calibration data*					This study
			Mitigate Na loss (Exp/Anal)? †	H = Hydrous data	Sugawara (2001)	Ariskin (1999)	MELTS/pMELTS	
Baker and Eggler (1987)	0.001–8	1273–1523	N/Y	H ^S	C		C	
Baker et al. (1994)	0.001	1413–1476	N/N	H			C	
Bartels et al. (1991)	10–15	1513–1563					C	C
Blatter and Carmichael (2001)	0.548–1.41	1182–1273	/Y	H ^S			C	C
Draper and Johnston (1992)	0.001–20	1423–1623	N/				C	C
Dunn and Sen (1994)	0.001	1373–1456	N/		C		C	
Fram and Longhi (1992)	0.001	1398	Y/				C	C
Gardner et al. (1995)	1–2.5	1123	/Y	H ^M			C	C
Grove et al. (1990)	0.001–8	1381–1506	Y/				C	C
Grove et al. (1992)	2–10	1399–1538					C	
Grove et al. (1997)	1–2	1153–1323	/Y				C	
Grove et al. (2003)	0.001–2	1213–1473	Y/Y	H			C	
Grove and Juster (1989)	0.001	1328–1445	Y/		C		C	
Helz (1976)	5	998–1148	N/N	H			C	
Housh and Luhr (1991)	2–4	1073–1223	/Y	H ^S			C	
Johnston (1986)	9.5–10	1506–1553					C	
Juster et al. (1989)	0.001	1313–1422	Y/				C	
Kinzler and Grove (1992)	9–13	1493–1568					C	C
Longhi et al. (1999)	6–13	1448–1573					C	
Moore and Carmichael (1998)	0.483–2.851	1173–1398	/Y	H ^S			C	C
Panjasawatwong et al. (1995)	5–10	1303–1565	/Y	H ^F			C	
Rutherford et al. (1985)	1–2.4	1148–1363	/Y	H			C	
Sack et al. (1987)	0.001	1337–1535	N/		C	C	C	C
Sisson and Grove (1993a)	1	1293–1355	/Y	H ^F	C		C	C
Sisson and Grove (1993b)	2	1198–1323	/Y	H ^F	C		C	C
Sugawara (2001)	0.001	1359–1529	N/		C		C	
Thy (1991)	0.001–15	1383–1513	N/				C	
Tormey et al. (1987)	0.001	1425–1478	Y/		C	C	C	
Vander Auwera and Longhi (1994)	0.001–13	1338–1463	Y/				C	C
Vander Auwera et al. (1998)	0.001–5	1323–1393	Y/				C	C
Walter and Presnall (1994)	7–13	1498–1583					C	C
Yang et al. (1996)	0.001	1383–1486	Y/		C		C	

Notes: The superscripts "F" denote studies where water contents of glasses were determined (or spot checked) by FTIR; superscript "M" denotes the use of Secondary Ion Mass Spectrometry. Experimental studies that report water contents solely from calculated water solubility models are noted with the superscript "S". All other studies do not quantify H₂O for individual experiments.

* These columns note (with a C) which experimental data were used for calibration by various models; none of these data were used for the calibration of the Housh and Luhr (1991) coefficients.

† This column indicates which of the experimental studies note attention to Na loss during either 1-atm experimental runs, or during the microbeam analysis of hydrous glasses (Y = Yes, N = No); this is not an evaluation of effectiveness (see Tormey et al., 1987; Rutherford et al., 1985). Blank spaces indicate "not applicable".

Tests of the MELTS/pMELTS models of Ghiorso et al. (1995, 2002)

In the analysis of MELTS/pMELTS, experimental glass composition were used as input (as with all other models tested). Because all experimental glasses used for this study were plagioclase saturated, any model that purports to predict liquidus T and phase composition should yield plagioclase at the liquidus, at the reported experimental T . However, the "find liquidus" feature of MELTS/pMELTS failed to place plagioclase on the liquidus for over half the test and calibration data, and with predicted values of liquidus T that exceeded experimental values by as much as 317 °C for the calibration data (43 °C average) and up to 270 °C for the test data (46 °C average). Overall, MELTS/pMELTS failed to place plagioclase within 10 °C of the liquidus for 66% of experiments, and was more than 30 °C in error for 45% of all experiments. However, by lowering T in 10 °C increments, and selecting the highest T at which MELTS/pMELTS recorded plagioclase saturation, much closer matches to experimental temperatures were achieved (with much less systematic error). These latter values of T will be referred to as the "plagioclase saturation temperatures," and are shown in Figure 2.

In recovering values of plagioclase saturation T , the MELTS/pMELTS models of Ghiorso et al. (1995, 2002) performed equally as well as Sugawara (2001), with a SEE of 44 °C (Fig. 2a). As in Sugawara (2001), temperatures for a portion of their calibration data (Baker and Eggler 1987) were also curiously not well reproduced.

Temperature predictions for the test data for MELTS/pMELTS were only slightly worse (Fig. 2a), but predicted T values for the hydrous test data were significantly worse with an SEE of 52 °C, and an R of 0.79. Interestingly, although the MELTS/pMELTS models utilized the 850 °C data from Gardner et al. (1985) for calibration, and encompassed experimental liquid compositions that approach 80 wt% SiO₂, these models captured little of the temperature variation within the

Rutherford et al. (1985) data set (875–1090 °C; 62.8–74.4 wt% SiO₂). Temperatures for some samples from Sugawara (2001) also are not well predicted. It does not appear that any attempt was employed to limit Na₂O loss from the Sugawara (2001) 1 atm experiments, which may account for the difficulty with which both MELTS/pMELTS and the Sugawara (2001) models have in recovering T for these experiments. It also should be noted that the total number of calibration and test data for MELTS/pMELTS is considerably less than that used to test Sugawara (2001). The reason is that MELTS/pMELTS failed to predict T for 22% of its calibration data and 25% of the test data; this high failure rate clearly poses limitations on model implementation.

Regarding the prediction of plagioclase compositions, predictions of An and Ab fall off sharply for the test data compared to the calibration data (Figs. 2b–2d). For both An and Ab, values of SEE increase by a factor of 3 from the calibration to the test data, while R values are nearly half.

Finally, one might inquire as to why the "find liquidus" feature of MELTS/pMELTS did not perform well in predicting T . Interestingly, in MELTS/pMELTS, plagioclase saturation in many cases was preceded by the precipitation of olivine, clinopyroxene, or rhombohedral oxides. Moreover, error on values of plagioclase saturation T are moderately correlated with error on predicted liquidus T values for both calibration ($R_{\text{cal}} = 0.51$) and test data ($R_{\text{test}} = 0.75$), but uncorrelated with other quantities, such as P ($R_{\text{cal}} = 0.03$; $R_{\text{test}} = 0.03$), T ($R_{\text{cal}} = -0.06$; $R_{\text{test}} = -0.37$), wt% SiO₂ ($R_{\text{cal}} = 0.06$; $R_{\text{test}} = -0.15$), and wt% Na₂O ($R_{\text{cal}} = -0.02$; $R_{\text{test}} = 0.03$). One possible source of error may reside within the MELTS/pMELTS calibration of other mineral saturation surfaces. That other mineral-melt equilibria might be described inadequately by MELTS/pMELTS is illustrated in Figure 2e, which shows T -calculated vs. T -measured for experimental clinopyroxene-saturated glasses. Similarly, MELTS and pMELTS are poor predictors of clinopyroxene compositions when P , T , and bulk composition are used as input (e.g., Putirka et al. 2003).

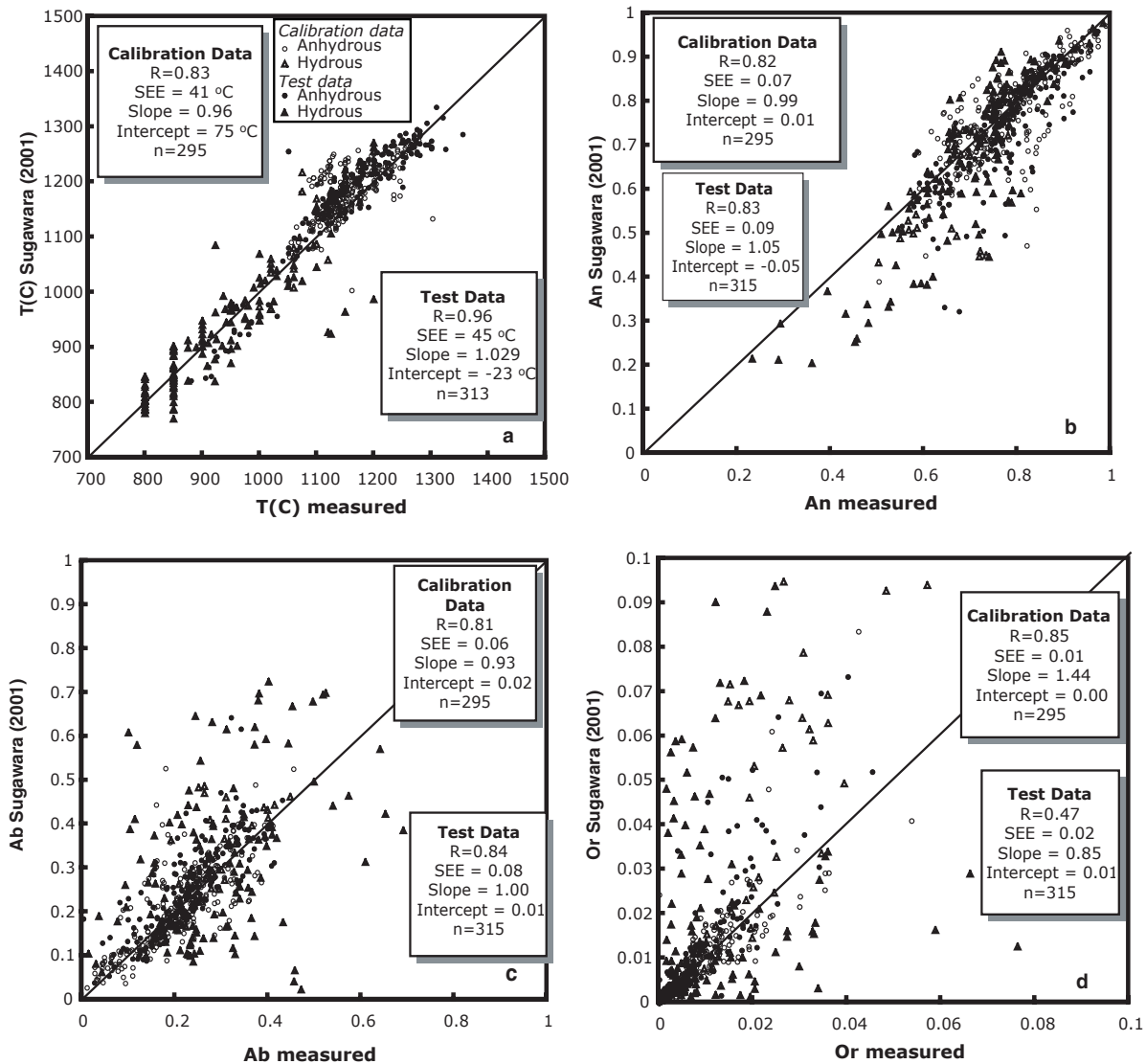


FIGURE 1. The Sugawara (2001) model was used to predict (a) T , (b) anorthite (An), (c) albite (Ab), and (d) orthoclase (Or) for experimental data (Table 1).

Tests of the Housh and Luhr (1991) and Ariskin (1999) models

The models of Housh and Luhr (1991) were originally intended to be used as geo-hygrometers, rather than thermometers (T. Housh, pers. comm.). Nonetheless, their Equation 6 is expressed as a thermometer, and might be used as such. When used to predict T of experimental data (Fig. 3a), their model performs remarkably well for the hydrous data but poorly for the anhydrous data. Because the Housh and Luhr (1991) models were intended as geo-hygrometers, their Equation 6 also was used to recover water contents for hydrous experiments. The Housh and Luhr (1991) Equation 6 recovers water contents with an SEE of 1.35 wt%, with $R = 0.83$ and a slope and intercept of 0.89 and -0.04 wt% respectively, when measured T is used as input. Unfortunately, their model tends to overestimate water contents of some nominally anhydrous experiments (Fig. 3b).

Ariskin (1999) developed a FORTRAN program, COMAGAT, which contains expressions developed by Ariskin and Barmina (1990) to calculate plagioclase crystallization temperatures for anhydrous data, and expressions from Ariskin (1999) correct for the freezing point depression effect of water. These models employ only a few adjustable parameters [compared with Sugawara (2001) and MELTS/pMELTS], and yet the SEE on the test data are similar. But clearly, the Ariskin (1999) models yield significant systematic error for anhydrous and hydrous data, as is evident in the distribution of data compared to the one-to-one line.

SUMMARY OBSERVATIONS

The Sugawara (2001) and the MELTS/pMELTS models of Ghiorso et al. (1995, 2002) appear to predict values of plagioclase saturation T successfully for both anhydrous and hydrous experiments performed over the P range 1 atm to 27 kbar with errors in the range 41–46 $^{\circ}\text{C}$ for calibration and test data. Temperature estimates for hydrous data are less precise, with SEE between 46–52 $^{\circ}\text{C}$.

The Sugawara (2001) model has the advantage over MELTS/pMELTS that values of plagioclase saturation T can be computed rapidly. In addition, the Sugawara (2001) model failed to calculate a T for 13% of the experimental data compared to a failure rate of nearly 25% for MELTS/pMELTS. Both MELTS/pMELTS and Sugawara (2001) suffer the deficiency that they cannot be integrated with other models—for example, the plagioclase geo-hygrometer of Housh and Luhr (1991), which greatly limits the kinds

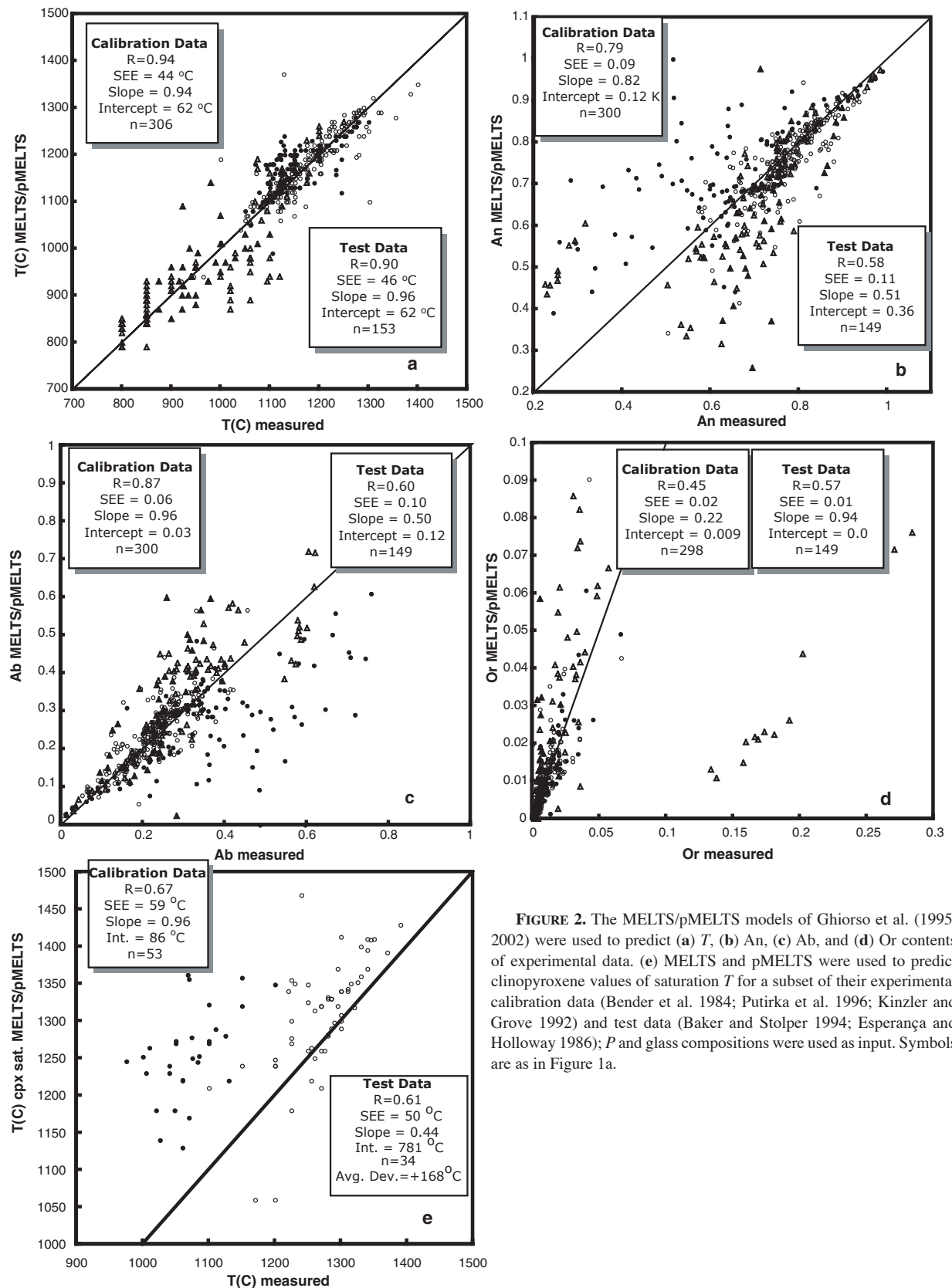
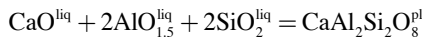


FIGURE 2. The MELTS/pMELTS models of Ghiorso et al. (1995, 2002) were used to predict (a) T , (b) An, (c) Ab, and (d) Or contents of experimental data. (e) MELTS and pMELTS were used to predict clinopyroxene values of saturation T for a subset of their experimental calibration data (Bender et al. 1984; Putirka et al. 1996; Kinzler and Grove 1992) and test data (Baker and Stolper 1994; Esperança and Holloway 1986); P and glass compositions were used as input. Symbols are as in Figure 1a.

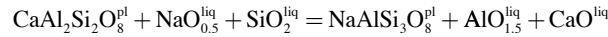
of petrologic questions that can be addressed with these models. The Ariskin (1999) models interestingly approach the precision of MELTS/pMELTS with an empirical model having very few adjustable parameters; however, these models indicate significant systematic error for both anhydrous and hydrous data sets.

New calibrations

As with the calibration of clinopyroxene-liquid thermobarometers (Putirka et al. 1996, 2003), new plagioclase-liquid models are based on regression analysis of partial melting experiments where plagioclase crystals were grown at a range of pressures and temperatures, from a range of liquid compositions. For a pressure-sensitive thermometer, the equilibrium constant (K_{eq}) based on An crystallization equilibrium is used:



For a temperature-sensitive barometer, the K_{eq} based on an An-Ab exchange reaction is employed,



The superscripts pl and liq refer to the phases plagioclase and

liquid (glass) respectively.

The new thermobarometers were calibrated using the same regression strategies outlined in detail in Putirka et al. (2003). Data for calibration and test data were selected from the same data as used to test the Sugawara (2001) and the MELTS/pMELTS models. As in earlier calibrations, data for which Na₂O loss is a suspected problem (Table 1) were not used for calibration or testing.

Component calculations

Liquid components have been treated as cation fractions of the oxides SiO₂, TiO₂, AlO_{1.5}, FeO, MnO, MgO, CaO, NaO_{0.5}, KO_{0.5}, and CrO_{1.5}; H₂O was excluded from the calculation and was added to the models in units of wt% (Table 2; see following discussion). Oxide weight percentages were not renormalized prior to the calculation of cation fractions. (In calculating cation fractions, the weight percentages of oxides that have more than one cation per formula unit such as Al₂O₃, were divided by the molecular weight of the single cation unit, i.e., 50.981 for AlO_{1.5}; see Table 3). The amounts of plagioclase components An, Ab, and Or were calculated from cation fractions: An = Ca/(Ca + Na + K); Ab = Na/(Ca + Na + K); Or = K/(Ca + Na + K). Other plagioclase component calculation schemes were explored (Fuhrman

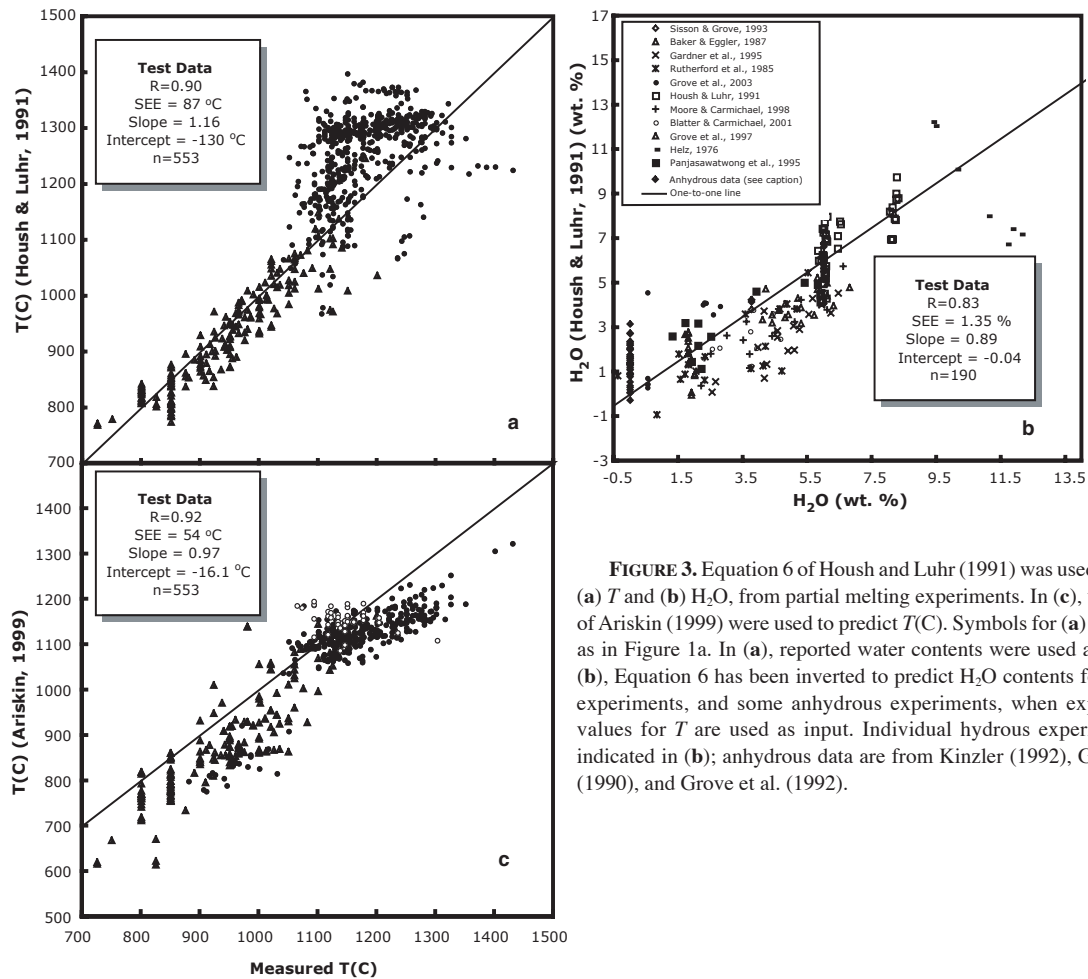


FIGURE 3. Equation 6 of Housh and Luhr (1991) was used to predict (a) T and (b) H_2O , from partial melting experiments. In (c), the models of Ariskin (1999) were used to predict $T(C)$. Symbols for (a) and (c) are as in Figure 1a. In (a), reported water contents were used as input; in (b), Equation 6 has been inverted to predict H_2O contents for hydrous experiments, and some anhydrous experiments, when experimental values for T are used as input. Individual hydrous experiments are indicated in (b); anhydrous data are from Kinzler (1992), Grove et al. (1990), and Grove et al. (1992).

TABLE 2. Plagioclase-liquid thermobarometers and saturation surface models

Equation	Model
Plagioclase + Liquid Thermobarometers	
$\frac{10^4}{T(K)} = 6.12 + 0.257 \ln \left[\frac{[An^{pl}]}{[Ca^{liq} (Al^{liq})^2 (Si^{liq})^2]} \right] - 3.166 [Ca^{liq}] + 0.2166 [H_2O^{liq}]$ $- 3.137 \left[\frac{Al^{liq}}{Al^{liq} + Si^{liq}} \right] + 1.216 [Ab^{pl}]^2 - 2.475 \times 10^{-2} [P(kbar)]$	(A)
$\frac{10^4}{T(K)} = 68.8 - 0.86 \ln \left[\frac{[An^p]}{[Ca^{liq} (Al^{liq})^2 (Si^{liq})^2]} \right] + 179 [Al^{liq}] - 113 \left[\frac{Al}{Al + Si} \right]^{liq} - 7.92 [AbAn^p]$ $- 6.13 \times 10^{-2} [P(kbar)] - 91.6 [CaAl^{liq}] - 155 [Si^{liq}] + 110.3 [Si^{liq}]^2 - 149 [Al^{liq}]^2$	(B)
$P(kbar) = -42.2 + 4.94 \times 10^{-2} [T(K)] + 1.16 \times 10^{-2} T(K) \ln \left[\frac{[Ab^{pl} Al^{liq} Ca^{liq}]}{[An^{pl} Na^{liq} Si^{liq}]} \right]$ $- 382.3 [Si^{liq}]^2 + 514.2 [Si^{liq}]^3 - 19.6 \ln [Ab^{pl}] - 139.8 [Ca^{liq}]$ $+ 287.2 [Na^{liq}] + 163.9 [K^{liq}]$	(C)
Plagioclase Saturation Surface Models	
$\frac{10^4}{T(K)} = 8.759 - 6.396 [Ca^{liq}] + 0.2147 [H_2O^{liq}] + 1.221 [Si^{liq}]^3 - 1.751 \times 10^{-2} [P(kbar)]$ $- 8.043 [Al^{liq}]$	(D)
$\ln(An) = -3.485 + 22.93 [Ca^{liq}] + 0.0805 [H_2O^{liq}] + 1.0925 \left[\frac{Ca^{liq}}{Ca^{liq} + Na^{liq}} \right]$ $+ 13.11 \left[\frac{Al^{liq}}{Al^{liq} + Si^{liq}} \right] + 5.59258 [Si^{liq}]^3 - 38.786 \left[\frac{P(kb)}{T(K)} \right] - 125.04 [Ca^{liq} Al^{liq}]$ $+ 8.958 [Si^{liq} K^{liq}] - \frac{2589.27}{T(K)}$	(E)
$\ln(Ab) = -2.748 - 0.1553 [H_2O^{liq}] + 1.017 [Mg\#^{liq}] - 1.997 [Si^{liq}]^3 + 54.556 [P(kb)/T(K)]$ $- 67.878 [K^{liq} Al^{liq}] - 99.03 [Ca^{liq} Al^{liq}] + \frac{4175.307}{T(K)}$	(F)
$\ln(Or) = 19.42 - 12.5 [Mg^{liq}] - 161.4 [Na^{liq}] - 16.65 \left[\frac{Ca^{liq}}{Ca^{liq} + Na^{liq}} \right] - 528.1 [K^{liq} Al^{liq}] - \frac{10190}{T(K)}$ $- 19.38 [Si^{liq}]^3 + 168.2 [Si^{liq} Na^{liq}] - 1951.2 [Ca^{liq} K^{liq}]$	(G)
$H_2O(wt\%) = 24.757 - 2.26 \times 10^{-3} T(K) \ln \left[\frac{[An^{pl}]}{[Ca^{liq} (Al^{liq})^2 (Si^{liq})^2]} \right] - 3.847 [Ab^{pl}] + 1.927 \left[\frac{An^{pl}}{Ca^{liq}} \right]$ $\left[\frac{Ca^{liq}}{(Ca^{liq} + Na^{liq})} \right]$	(H)

Note: Superscripts pl and liq refer to plagioclase and liquid phases respectively. Liquid components are calculated as cation fractions. T is in Kelvins and P is in kbar. Plagioclase components are calculated from cation fractions as follows: $An = CaO/(CaO + NaO_{0.5} + KO_{0.5})$; $Ab = NaO_{0.5}/(CaO + NaO_{0.5} + KO_{0.5})$; $Or = KO_{0.5}/(CaO + NaO_{0.5} + KO_{0.5})$. Terms such as Si^{liq} refer to the anhydrous cation fraction of SiO_2 in the liquid, and terms such as $CaAl^{liq}$ refer to the product of liquid cation fractions CaO and $AlO_{1.5}$. H_2O is in units of weight percent, and is not part of the cation fraction calculation.

TABLE 3A. Example calculations based on Fissure A, 1849 glass, Plg mph/glm core Episode 54*

	Input		Cation fractions		Plagioclase components Plag.
	Glass	Plag.	Glass	Plag.	
SiO ₂	50.6	51.45	0.488	0.47152	
TiO ₂	3.04		0.022	0	
Al ₂ O ₃	12.98	29.96			
AlO _{3/2}			0.147	0.324	
FeO	11.84	0.82	0.095	0.006	
MnO	0.17		0.001	0	
MgO	6.06		0.087	0	
CaO	10.07	13.61	0.104	0.134	
Na ₂ O	2.53	3.59			
NaO _{1/2}			0.047	0.064	
K ₂ O	0.64	0.1			
KO _{1/2}			0.008	0.001	
Cr ₂ O ₃					
CrO _{3/2}			0	0	
An					0.673
Ab					0.321
Or					0.006

Note: Plag. = Plagioclase

* Data are from Tables 5 and 6 of Thornber et al. (2003): Glass = Fissure A, KE54-no.: 1849, Table 6; Plagioclase = 5, plg, mph/glm, core, Table 5.

and Lindsley 1988; Elkins and Grove 1990). However, adoption of such strategies did not lead to improvement in the ability to predict T , P , or X_i for the test data. Similarly, although the thermometers were much more precise when H₂O was added as a parameter, P and Or were recovered more precisely—even for hydrous test data—when these models did not employ a hydrous term (Models C and G respectively). To maintain consistency with the treatment of liquid components between the barometer and other models, all liquid components were treated as above, and all models in Table 2 that included H₂O as an independent variable utilized H₂O in units of wt%, similar to the approach of Ariskin (1999).

RESULTS AND DISCUSSION

The models of Sugawara (2001) and Ghorso et al. (1995, 2002) can be used to calculate crystallization temperatures for plagioclase, with errors on the order of 41 to 52 °C. These models are P dependent, but do not provide means for estimating P , nor can they be integrated with other petrologic models. New plagioclase-liquid thermobarometers are presented in Table 2, with example calculations in Table 3. Compared to the models of Sugawara (2001) and Ghorso et al. (1995, 2002), the much more simple expression, Model A, yields an error on T (SEE) that is 30–40% lower: for the calibration data, the SEE for anhydrous and hydrous data are 24 and 19 °C respectively; for the test data, the SEE for anhydrous and hydrous data are 24 and 33 °C respectively. In addition, since a pre-coded program is not needed, the failure rate problem of the Sugawara (2001) and MELTS/pMELTS is avoided, and the geothermometer can be combined with other petrologic models, such as the Housh and Luhr (1991) geo-hygrometer. A T -sensitive plagioclase + liquid barometer (model C, Table 2) also was calibrated and recovers P with a level of precision similar to that of clinopyroxene-liquid barometers (Putirka et al. 1996, 2003) (Figs. 3c and 3d). Experimental P values for the test data are predicted with an SEE of 2.2 kbar, and mean values are recovered to ± 1.0 kbar. As it is useful in many cases to be able to calculate a plagioclase

TABLE 3B. Result calculations based on Fissure A, 1849 glass, and Plg mph/glm core Episode 54*,†

Models	P (kbar)‡	T (K)‡	An	Ab	Or	H ₂ O
A & C	0.62	1427				
B & C	-0.28	1402				
D & C	0.34	1420				
E (B&C)	(0.62)	(1427)	0.69			
F (B&C)	(0.62)	(1427)		0.32		
G (B&C)	(0.62)	(1427)			0.0	
H	(0.62)	(1427)			0.2	
Housh and Luhr (1991)§		1564(1409)				2.4
MgO $T(K) $		1409				2.5

* Data are from Tables 5 and 6 of Thornber et al. (2003): Glass = Fissure A, KE54-no.: 1849, Table 6; Plagioclase = 5, plg, mph/glm, core, Table 5.

† First column indicates models that were solved to obtain values for P , T , An, Ab, Or, and H₂O. "A & B" means that models A and B were solved simultaneously to obtain T and P .

‡ Parentheses indicate values that were used as input.

§ 1564 K = T assuming glass is anhydrous; 2.5 wt% water calculated using 1409 K as input for T .

|| $T(K)$ is from Thornber et al. (2003), estimated from MgO content of glass.

composition and saturation T when P and a liquid composition are given, Models D-G (Table 2) were calibrated to predict such quantities (Fig. 5).

Although one advantage of the expressions of Table 2 is that they can be combined with other models, one must be wary of model cross-correlation. For example, there is a very high degree of correlation between T and H₂O, and when model A and Equation 6 of Housh and Luhr (1991) are solved simultaneously, water contents from experimental data are poorly recovered (Fig. 6a). Model B, which does not use a water term, is more suitable for integration with either the Housh and Luhr (1991) geo-hygrometer, or model H (Fig. 6b). Model H recovers lower mean water contents for anhydrous experimental data compared to Housh and Luhr (1991), but both models yield similarly high water contents (Table 3B) for a nominally dry basalt from Kilauea (Thornber et al. 2003).

Tests of the barometer using lava tube flows from Kilauea

As an additional test of the barometer (model C), P was calculated for lava tube (skylight) samples from Kilauea. Plagioclase crystals from these samples are thought to have crystallized at the surface based on field and petrographic observations (Thornber et al. 2003). This test is valuable because, although the mean value of predicted values of P for 1-atm experimental data are close to 1-atm, these P estimates range to ± 5 kbar (as is also the case for clinopyroxene-liquid barometers; see Putirka et al. 1996, 2003). A key issue is whether estimates of P from natural samples might be averaged—in the same way as experimental values of Figure 4d were averaged—to yield a more precise estimate of P (see Putirka et al. 2003). If the error on such barometers is random, a mean P obtained from multiple phenocrysts should yield a more accurate P estimate. Crystals from a Kilauea lava tube, allow a natural test of this strategy.

Model C was used to calculate P using 28 coexisting plagioclase and glass compositions from Tables 5 and 6 of Thornber et al. (2003). When Model B is used to obtain T for these 28 plagioclase-glass pairs (mean = 1132 \pm 46 °C), the range of calculated

FIGURE 4. The thermometers, Models A (a) and B (b) were used to recover T for the calibration data and to predict T for the test data. Thermometer A incorporates a term for water, whereas Model B does not. (c) Model C was used to calculate P for test and regression data. (d) Mean P values from model C were calculated for experimental data divided into isobaric sets (combined test and calibration data). Open-square is the mean pressure (calculated using models B and C) for 32 Kilauea lava tube-derived plagioclase phenocrysts, which presumably crystallized near 1-atm (Thornber et al. 2003). Symbols are as in Figure 1a.

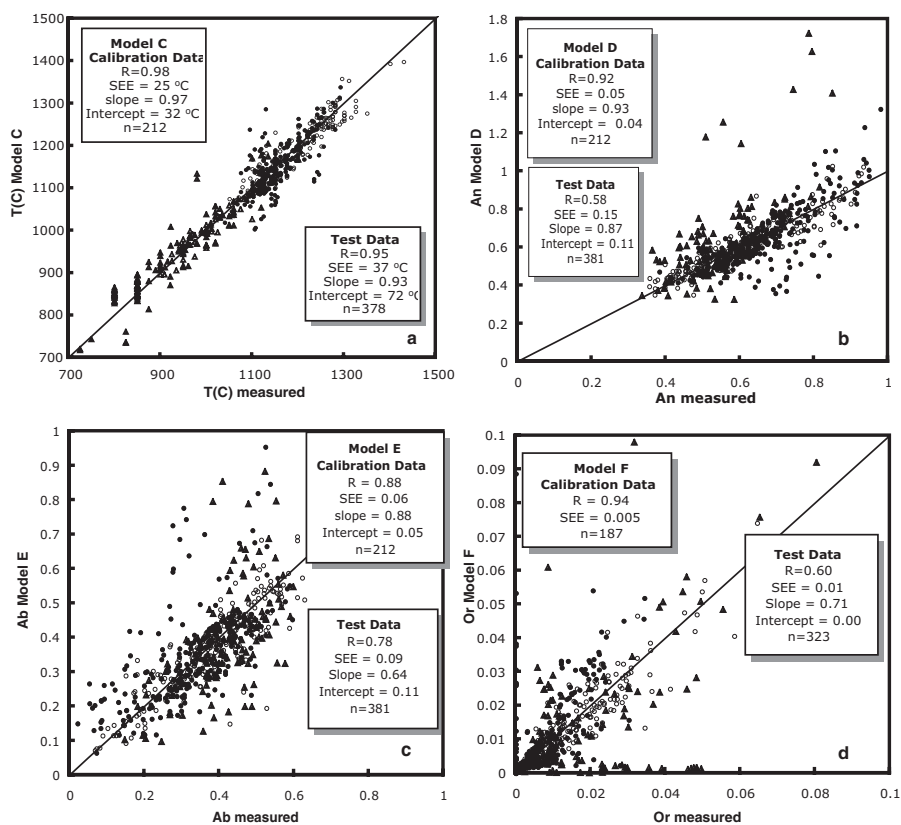
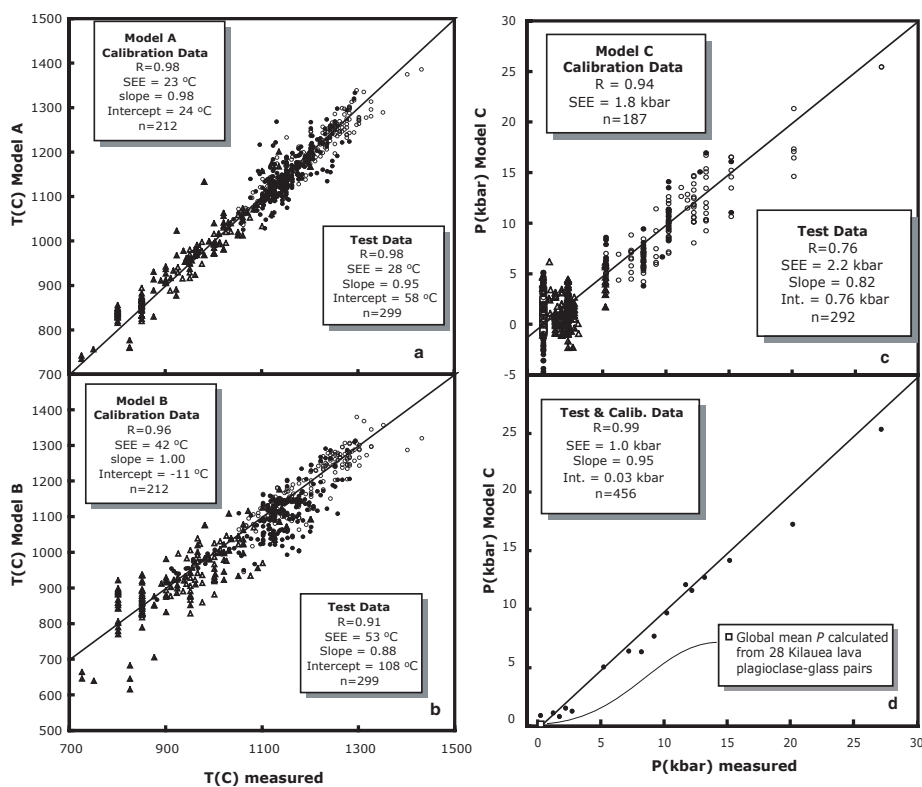


FIGURE 5. (a) Model D (Table 2) was used to predict plagioclase saturation temperatures for test and regression data. Plagioclase components An (b), Ab (c), and Or (d), were calculated for test and regression data using models E, F, and G respectively (Table 2). Symbols are as in Figure 1a.

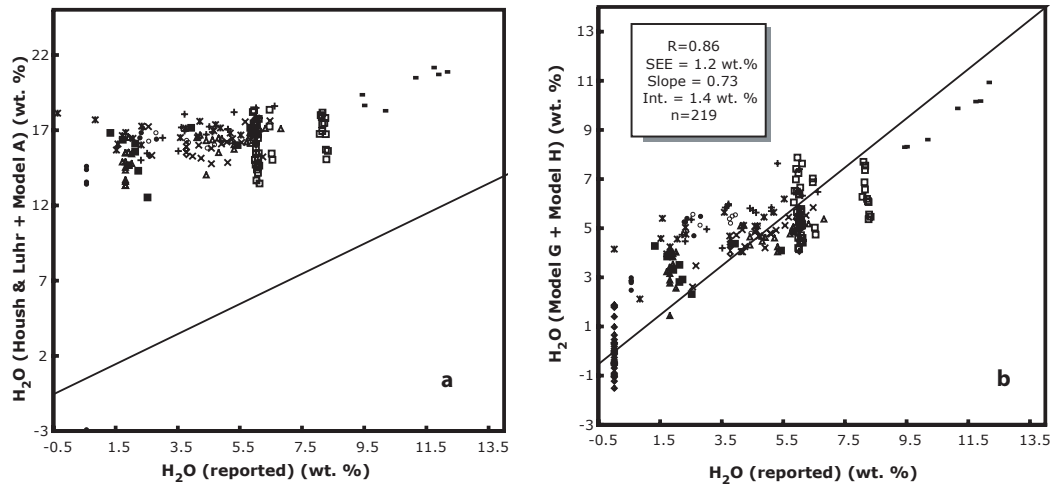


FIGURE 6. In (a), Equation 6 of Housh and Luhr (1991) was solved simultaneously with Model A (Table 2) to obtain estimates for H_2O for hydrous experiments. In (b), models B and H (Table 2) were solved simultaneously to predict H_2O . Model H has the advantage of yielding lower mean water contents for nominally anhydrous experiments (same data as in Figure 3b), but both model H and Housh and Luhr (1991) yield high H_2O contents for a nominally anhydrous basalt from Kilauea (see Table 3B). Symbols are as in Figure 3b

P values is -5.4 to 3.1 kbar, with a median of 0.4 kbar and a mean and standard deviation of -0.1 ± 2.3 kbar. When using Model A to obtain T for these same data (mean = 1142 ± 20 °C), model C yields a range of -2.5 to 2.9 kbar, with a median of 0.3 kbar, and mean and standard deviation of 0.2 ± 1.6 kbar respectively. These distributions of P values are quantitatively similar to 1-atm experimental studies; predicted values are remarkably close to the anticipated 1-atm value, and well within 1-atm given error on means of 1.0 kbar (Fig. 3d). It thus appears that mineral compositional error is indeed random, and that mean P values obtained from averaging multiple, nominally isobaric, plagioclase grains, should more closely approach true crystallization pressures.

SUMMARY REMARKS

Our views of what a magma plumbing system might look like, and how it might evolve, hinge precisely on our interpretation of the depths and temperatures at which magmas stagnate and partially crystallize. Minerals provide an archive of these P - T conditions and hence the calculation of crystallization temperatures and pressures is crucial to our appraisal of the evolution of igneous systems. For geo-thermometers and -barometers to be useful, however, it is essential that such models be accompanied by estimates of error, and hence several existing geo-thermometers were tested for their ability to recover T for their calibration data, and to predict T for data not used for calibration.

Compared to other prior calibrations of plagioclase-liquid equilibria, the models of Sugawara (2001) and Ghiorso et al. (1995, 2002) (MELTS/pMELTS) provided the better estimates of T , with standard errors of estimate between 41 and 46 °C. However, the much more simple expressions, presented as Models A and D in Table 2, yield errors on T that are significantly less, with SEEs between 23 and 37 °C. In general, better estimates were obtained for anhydrous compared to hydrous compositions. Because the Sugawara (2001) and Ghiorso et al. (1995, 2002) models do not allow P to be calculated, a temperature sensitive geo-barometer also was calibrated (Model C of Table 2), whose

precision approaches that of clinopyroxene-melt geo-thermometers (Putirka et al. 2003). Significantly, simultaneous solutions of Models A and C, using natural plagioclase compositions from Kilauea lava tube samples (ostensibly crystallized at 1 atm), suggest that error on P may be random and that improved estimates of P can be recovered as the mean of multiple P estimates (Fig. 4d). Finally, as water is known to provide a considerable influence on plagioclase-melt equilibria, an attempt was made to test the prediction of water contents based on plagioclase-melt compositions. The Housh and Luhr (1991) models performed well when experimental T is used as input (Fig. 3b), but if T is calculated (Fig. 6a and Table 3B, Results), as would be the usual case for natural samples, water contents are poorly recovered for both Housh and Luhr (1991), and Model H of Table 2. Improvement in the prediction of water contents undoubtedly will require a larger experimental database where water contents have been determined precisely.

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