The validity of plagioclase-melt geothermometry for degassing-driven magma crystallisation.

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Abstract

Any quantitative interpretation of the formation conditions of igneous rocks requires methods for determining crystallisation temperature. Accurate application of such thermobarometers relies on the attainment of equilibrium in the system to be studied. This may be particularly difficult in silicic magmas, where diffusivities are low and crystallisation kinetics sluggish. Moreover, progressive degassing of volatile-rich magmas during ascent can result in continuous changes in effective undercooling, causing particular problems in achieving equilibrium between melt and crystals that grow in response to decompression. We consider these problems in the context of plagioclase-melt equilibria for magmas undergoing decompression and degassing-driven crystallisation, using two published thermometers. The two thermometers show similar trends with key parameters but absolute temperatures can vary significantly. Analysis of decompression experiments conducted at constant temperature shows systematic variations in calculated temperature and equilibrium constant with varying decompression rate and quench pressure. This
indicates that an unrecognised lack of equilibration could result in significant temperature overestimates and potentially spurious results. This highlights the need to assess for equilibrium, and we discuss problems associated with some commonly used indicators of equilibration. Finally, retrospective analysis of published plagioclase-hosted melt inclusion suites from five subduction zone volcanoes shows systematic increases in calculated temperature and decreases in equilibrium constant with decreasing H\textsubscript{2}O concentration. While this could represent the signature of latent heat of crystallisation, we suggest that such patterns should be treated with caution unless there is clear evidence of sustained equilibrium between plagioclase and melt during decompression.

**Introduction**

Thermometry and thermobarometry underpin igneous petrology as a quantitative science. An ability to place quantitative estimates of temperature and pressure on mineral ± melt assemblages observed in igneous rocks is fundamental to understanding the conditions of magma storage, fractionation, ascent and eruption, as well as melt generation processes, in any tectonic setting. For example, clinopyroxene-melt thermobarometry was used to demonstrate that individual eruptions in the Springerville volcanic field, Arizona, USA were derived from different source regions in a vertically extensive mush reservoir, with magma ponding levels influenced by changes in crustal rheology or density (Putirka and Condit 2003). Cashman and Blundy (2013) used knowledge of plagioclase-melt equilibria to reconstruct the pressure-temperature histories of individual,
complexly zoned plagioclase phenocrysts from Mount St Helens, USA. Hornblende thermobarometry also appears to define vertically extensive crystallisation conditions for magmas from Redoubt volcano (Alaska) and El Reventador (Ecuador), amongst others (Ridolfi et al. 2010).

Although application of thermobarometry is now routine, it still has the potential to prompt new interpretations about the ways that magmas evolve and migrate. For example, Blundy et al. (2006) used the plagioclase-liquid thermometer of Putirka (2005) to determine entrapment temperatures for suites of plagioclase-hosted melt inclusions. The results showed strong increases in calculated temperature with decreasing melt H$_2$O contents, interpreted as the result of latent heat release during exothermic, decompression-driven crystallisation of volatile-saturated silicic magmas. This is significant because such release of latent heat could produce commonly observed petrographic features, such as reversely zoned phenocryst rims, that might otherwise be ascribed to late-stage mingling with hotter magma (Blundy et al. 2006). With the increasing availability of relatively large mineral and/or melt datasets from electron microprobe and other analytical techniques, thermometers are now routinely applied to whole datasets instead of carefully chosen individual analyses. This has the potential to uncover subtle details that are only apparent at the population level, but brings a risk of inadequate interrogation of equilibration within the full dataset.

An important limitation is that in volcanic systems, where the timescales of melt crystallisation, chemical diffusion or magma movement may be short, geochemical equilibration between melt and mineral may be kinetically inhibited.
For example, both the major element composition and the trace element contents of crystals are highly dependent on the degree of undercooling below the liquidus temperature (e.g. Gamble and Taylor 1980; Kennedy et al. 1993; Dunbar et al. 1995; Mollo et al. 2010, 2011b). Chemical diffusion rates can also be strongly dependent on the concentrations of species that are involved in the reaction(s). This is not a new problem and has been addressed by several authors historically, but is particularly important in the context of degassing-driven processes in volatile-rich magmas. In the context of thermobarometry, these factors represent varying degrees of disequilibrium and have the potential to produce biased or spurious temperatures if this is not recognised (e.g. Putirka 2008; Mollo et al. 2011b). In particular, Mollo et al. (2010) and Mollo et al. (2011b) showed that increasing the cooling rate of anhydrous basaltic melt from 0.5 to 15 °C/min could generate an overestimate in calculated temperature of up to 150 °C.

Here, we highlight the problems of not recognising incomplete equilibration in H2O-bearing magmas, many of which crystallise due to decompression rather than cooling (e.g. Geschwind and Rutherford 1995; Blundy and Cashman 2001), where diffusivities are low and crystallisation kinetics may be very sluggish. In this scenario, the thermal undercooling driving crystallisation may be negligible but substantial effective undercoolings are still readily achieved by decompression and water loss. We focus on plagioclase-melt thermometry and degassing-driven magma crystallisation, which is particularly sensitive to the kinetics of crystal nucleation and growth. Drawing on previously published natural datasets and experimental studies, we demonstrate that disequilibrium crystallisation during degassing can
result in large errors in thermometry, and that this can lead to potentially very significant problems with obtaining a unique interpretation of the resultant P-T conditions.

Plagioclase-melt thermobarometry

Plagioclase-melt thermometers are based on equilibrium exchange of albite (Ab) and anorthite (An) components between solid (s) and melt (m):

$$\text{An}(m) + \text{Ab}(s) = \text{An}(s) + \text{Ab}(m)$$  \[1\]

with the equilibrium constant for An-Ab exchange expressed as (Putirka 2005; Putirka 2008):

$$K_D = \frac{(X_{\text{An}}^{\text{pl}} \cdot \text{Ca}^{\text{L}} \cdot \text{Al}^{\text{L}})}{(X_{\text{Ab}}^{\text{pl}} \cdot \text{Na}^{\text{L}} \cdot \text{Si}^{\text{L}})}$$  \[2\]

where (e.g.) Ca$^L$ refers to the anhydrous cation fraction of Ca in the liquid and $X_{\text{An}}$ is the mole fraction of anorthite in plagioclase. The composition of plagioclase crystallising from a melt is controlled by temperature, melt composition and melt H$_2$O concentration. In anhydrous melts, the equilibrium plagioclase composition shifts systematically towards albite with decreasing temperature (e.g. (Bowen 1913; Kudo and Weill 1970; Drake 1976). In hydrous melts, the shape of the albite-anorthite binary loop in T-X space is broadened and shifted to lower temperature relative to anhydrous compositions (Kudo and Weill 1970; Drake 1976; Johannes 1984). This may be because OH tends to complex with Na and SiO$_4$ groups in preference to Ca and AlO$_4$, particularly at higher temperature (Lange et al. 2009). This means that addition of H$_2$O causes a decrease in activity of the albite component of the melt, $a_{\text{Ab}}(m)$, relative to $a_{\text{An}}(m)$ and the liquidus plagioclase...
composition therefore becomes more calcic (e.g. Arculus and Wills 1980; Housh and Luhr 1991; Sisson and Grove 1993; Panjasawatwong et al. 1995).

We focus on two of the most recently published plagioclase-melt thermometers: model A of Putirka (2005) and the plagioclase-melt hygrometer of Lange et al. (2009). The latter has been recalibrated and updated by Waters and Lange (in press). Both models are based on empirical regression of thermodynamically derived expressions. Calibration of both models was done using large databases of phase equilibrium experiments that crystallised plagioclase over a range of pressures, temperatures and H2O concentrations. A second set of experiments was used to test each model. The Putirka model (model A) was calibrated on basaltic to rhyolitic liquids that crystallised plagioclase from 0.001-13 kbar, 998-1623 K and H2O concentrations up to 15 wt%. According to the test data, the model returns temperature with a standard error estimate of ± 23 K (Putirka 2005). A later independent test using a larger dataset of additional experiments gave an average absolute deviation of ±19 °C and propagated uncertainty of ± 7 MPa for experiments on hydrous rhyolite at 750-995 °C and 15-313 MPa (Blundy et al. 2006). The Lange et al. (2009) hygrometer was calibrated on rhyolitic melts with <30 vol% crystals at 925-1100 °C, 48-300 MPa and 2.2-7.0 wt% H2O. Temperatures were recovered for the test data with an average uncertainty of ± 14 °C, while the standard error estimate for H2O was ± 0.32 wt% (Lange et al. 2009).

Comparison of the thermobaroimeters
We first used each of the two thermometers to predict the shape of constant-$X_{\text{An}}$ contours in $H_2O$-$T$ space (figure 1) for a representative rhyolitic matrix glass composition from Soufrière Hills volcano, Montserrat (table 1), for comparison with the experimental study of Couch et al. (2003). For the Lange thermometer, this involved supplying $X_{\text{An}}$, $T$, $P$ and melt composition to the model and retrieving melt $H_2O$ over a range of temperatures. We ran these calculations using pressures of 10 MPa and 200 MPa, but this made little difference to the absolute $H_2O$ concentrations retrieved and had no effect on the shape of the $X_{\text{An}}$ contours. We therefore subsequently assumed $H_2O$-saturated conditions and calculated $P_{\text{tot}} = p_{H2O}$ using VolatileCalc (Newman and Lowenstern 2002) (we define $p_{H2O}$ as the partial pressure of $H_2O$, which for a pure $H_2O$ magmatic component is the total confining pressure at volatile saturation for a given $H_2O$ concentration). For the Putirka thermometer we supplied $X_{\text{An}}$, $H_2O$ content, $P$ and melt composition and retrieved temperature, again assuming that $P_{\text{tot}} = p_{H2O}$.

Both models calculate an increase in temperature with decreasing $H_2O$ concentration at constant $X_{\text{An}}$ and fixed melt composition (figure 1a), as expected. Equivalent calculations using a basaltic-andesite melt from Hamada & Fujii (2007; see table 1) produce parallel curves offset to higher temperature at the same $H_2O$ concentration. However, the overall results are highly model-dependent, particularly at low $H_2O$ concentrations where there are big disparities between temperatures predicted for a given $X_{\text{An}}$. For example, at 20 MPa (1.3 wt% $H_2O$, volatile-saturated) plagioclase of composition An$_{70}$ is predicted to occur in $H_2O$-
saturated melt at 951 °C using Putirka (2005) but at >1300 °C using Lange et al. (2009) (figure 1a). This indicates that application of plagioclase-melt equilibria to give absolute temperature estimates must be subject to at least some uncertainty.

Data from the phase equilibrium experiments of Couch et al. (2003), which were used as a calibration dataset for Lange et al. (2009) but not for Putirka (2005), lie between the two models (figure 1a).

Figure 1

Secondly, we calculated temperature contours in H₂O – XAn space, which show a positive correlation of XAn with H₂O concentration at constant temperature (figure 1b). The results are similarly model-dependent, with only minor variations in slope of the temperature contours but significant variations in the absolute H₂O concentration predicted to be in equilibrium with a given plagioclase composition. In comparison, RhyoliteMELTS (Gualda et al. 2012) isothermal decompression runs and the data from Couch et al. (2003) show a much steeper variation of XAn with H₂O (figure 1b).

Figure 2

Finally, we calculated isobaric contours for H₂O-saturated rhyolite in T-XAn space; these define a positive correlation of temperature with XAn (figure 2). The two models agree well at lower temperature and more sodic plagioclase compositions.
but diverge with increasing temperature and $X_{An}$. RhyoliteMELTS isobaric cooling runs are offset towards lower temperature and lower $X_{An}$, and with steeper slope in T-$X_{An}$ space, than either of the other two thermobarometers (figure 2). The data from Couch et al. (2003) are offset to higher $X_{An}$ relative to the Lange model and have a steeper slope than the Putirka model (figure 2).

Figure 3

As a possible test for equilibrium in the system Ca$_2$Al$_2$Si$_2$O$_8$ – NaAlSi$_3$O$_8$ – H$_2$O – silicate melt, the equilibrium constant for Ab-An exchange, $K_D$ (equation [2]) is reported to be normally distributed with values of 0.10 ± 0.05 for $T < 1050$ °C (mostly hydrous) and 0.27 ± 0.11 for $T \geq 1050$ °C, for a global compilation of test data (Putirka 2008). To assess the significance of individual external parameters in contributing to this variation, we retrieved $K_D$ from the equilibrium calculations described above, using the Putirka thermometer. Importantly, the results show that for a fixed melt composition and fixed H$_2$O concentration at equilibrium conditions, variations in $X_{An}$ cause $K_D$ to decrease systematically with increasing temperature (figure 3a). Similarly, for a fixed melt composition at equilibrium at a constant calculated temperature, the link between $X_{An}$ and pH$_2$O means that $K_D$ decreases systematically with increasing $X_{An}$ or increasing pH$_2$O (figure 3b,c). These variations mean that the equilibrium constant cannot easily be used to assess whether equilibrium has been achieved.
pH2O – T profiles of decompression experiments

Both thermobarometers were originally calibrated and tested using phase equilibrium studies at fixed P, T conditions. However, many of their potential applications are for magmas that have experienced more dynamic conditions, including degassing-induced crystallisation. To test the applicability of the thermobarometers for these conditions in natural volatile-rich magmas, we used the results of three sets of decompression experiments that crystallised plagioclase from hydrous, silicic melt at variable decompression rates representative of typical intermediate magma ascent. Cichy et al. (2011) performed isothermal decompression experiments on a synthetic, H2O-bearing Unzen rhyodacite melt composition at 850 °C and at decompression rates from 0.0002 to 20 MPa/s. Glass H2O contents were analysed by FTIR but represent incomplete (disequilibrium) degassing due to retarded bubble nucleation (Cichy et al. 2011). Secondly, Martel and Schmidt (2003) ran both isobaric and decompression experiments on H2O-saturated, synthetic rhyolitic melt at 860 °C and 15-170 MPa, at decompression rates from 0.000017 – 16 MPa/s. Thirdly, Brugger and Hammer (2010) performed two series of experiments using used a crushed natural rhyodacitic starting material: one set of experiments was quenched along a decompression path (‘snapshots’) and the other set was allowed to anneal at the final pressure. Decompression rates varied between 0.008 and 0.17 MPa/s. For each experimental dataset, we took the glass composition, H2O concentration of the glass (either calculated as volatiles by difference or from published measurements, see supplementary data table) and coexisting plagioclase composition to calculate the
equilibrium temperature ($T_{\text{calc}}$, see supplementary data table). Except for mixed volatile (H$_2$O+CO$_2$) experiments we assumed melt H$_2$O saturation, and used VolatileCalc (Newman and Lowenstern 2002) to convert H$_2$O concentration to pH$_2$O in MPa. This is important because in all three experimental studies, H$_2$O degassing was retarded relative to equilibrium, showing higher concentrations in the glass than the solubility at the experimental quench pressure (figure 4). Treating the data in this way as volatile-saturated ‘unknowns’ therefore results in anomalously high estimates of $P_{\text{tot}}$.

Figure 4

Application of the Putirka thermometer to data from the Martel and Schmidt (2003) and Brugger and Hammer (2010) experimental series shows a general pattern of increasing $T_{\text{calc}}$ and decreasing $K_D$ with decreasing pH$_2$O (figure 5), even though the experiments were run at controlled temperature. Temperatures calculated from the ‘low pressure’ experiments of Martel and Schmidt (2003) are scattered within ±45 °C of the experimental run temperature (860 ± 5 °C, Martel and Schmidt 2003), whereas the ‘high pressure’ experiments are systematically offset to significantly higher calculated temperatures, up to 84 °C greater than the experimental run temperature (figure 5). Their isobaric experiments also show an increase of $T_{\text{calc}}$ with lower H$_2$O measurements (see supplementary data table). In contrast, temperatures for data from the Brugger and Hammer (2010) experiments are typically lower than the experimental run temperature (figure 5). The glass
compositions in all experiments show clear trends of increasing K$_2$O and decreasing CaO content as pH$_2$O decreases due to progressive decompression, degassing and crystallisation (see supplementary data table). The annealed experiments from Brugger and Hammer (2010) had a more Al-poor, K-rich and Si-rich residual melt composition and crystallised more albitic plagioclase; consequently temperatures calculated from these data are slightly lower at a given pH$_2$O than the snapshot experiments.

**Figure 5**

Temperatures calculated from Martel and Schmidt (2003) generally show an increase with increasing decompression rate except at the very highest decompression rates (>10 MPa/s); calculated K$_D$s increase systematically with increasing decompression rate (figure 6) and with $T_{\text{calc}}$ (supplementary data table). In contrast, the Brugger & Hammer data show no variation of either $T_{\text{calc}}$ or K$_D$ with decompression rate (figure 6), and no variation of K$_D$ with $T_{\text{calc}}$ over the more limited range of decompression rates (see supplementary data table).

**Figure 6**

Fewer data are available for the Cichy et al. (2011) experiments but the available data give higher (and more scattered) calculated temperatures and lower K$_D$ at lower pH$_2$O (figure 5). In contrast, there are clear increases in both $T_{\text{calc}}$ and K$_D$ with
increasing decompression rate, similar to calculations from the experiments of Martel & Schmidt (figure 6), and $K_D$ increases systematically with $T_{\text{calc}}$ (see supplementary data table). The glass compositions also change systematically as a function of both $\text{pH}_2\text{O}$ and decompression rate (supplementary data table).

The same patterns of $T_{\text{calc}}$ are also seen using the Lange et al. (2009) thermometer. The two sets of calculated temperatures correlate reasonably well but those calculated using Lange et al. (2009) are typically significantly higher. Meaningful temperatures commonly cannot be returned for evolved melts with low $\text{H}_2\text{O}$ content. This is due to an instability in the calculation of $a \text{Ab(m)}$ for temperatures $\geq 1200 \, ^\circ\text{C}$, which has been corrected by the recalibrated version of the hygrometer (Waters and Lange in press; Lange & Waters, personal communication). For this reason, and because the same trends were observed with both models, we only used the Putirka thermometer for subsequent analysis of natural datasets (see below).

**$\text{pH}_2\text{O}$-$T$ profiles of magmas recorded in melt inclusions**

We applied a similar approach to populations of plagioclase-hosted melt inclusions where the composition of coexisting melt and feldspar and the $\text{H}_2\text{O}$ content of the melt are both known, following Blundy et al. (2006). This allowed us to calculate the apparent equilibrium temperature of entrapment for each melt inclusion and plagioclase host pair, resulting in arrays of $\text{pH}_2\text{O}$-$T$ coordinates (see supplementary data table) and thus apparent magma ascent paths in $\text{pH}_2\text{O}$-$T$ space. We examined
suites of melt inclusion data from the literature for Mount St Helens, USA (Blundy et al. 2006); Shiveluch Volcano, Kamchatka (Blundy et al. 2006); Soufrière Hills, Montserrat (Humphreys et al. 2009a, 2010); Unzen, Japan (Botcharnikov et al. 2008) and Izu-Oshima, Japan (Hamada and Fujii 2007). All datasets show a clear increase in $T_{\text{calc}}$ with decreasing melt H$_2$O (figure 7), approximately parallel to constant-$X_{\text{An}}$ contours shown in figure 1, as previously reported for Mount St Helens and Shiveluch by Blundy et al. (2006). There is a slight positive correlation of $T_{\text{calc}}$ with $X_{\text{An}}$ for the dataset as a whole (figure 7). For the rhyolitic melts (Soufrière Hills, Mount St Helens and Shiveluch), calculated $K_D$s are low and typically decrease systematically with increasing $X_{\text{An}}$ in the host plagioclase and increase systematically with increasing melt H$_2$O concentration (figure 8); the latter is the opposite to the trend observed for the equilibrium calculations (see figure 3). Calculated $K_D$s are higher for the andesitic (Unzen) and basaltic andesite (Izu Oshima) melts but the same trends are observed (figure 8).

Regression of $T_{\text{calc}}$ for each dataset with the individual parameters that contribute to the temperature calculation typically gives $R^2 \leq 0.92$ for correlation of $T_{\text{calc}}$ with H$_2$O and low to insignificant $R^2$ (typically $\leq 0.25$) for other parameters (figures 9, 10). This indicates that up to 92% of the total variability in $T_{\text{calc}}$ from each case study results from variability in melt H$_2$O concentrations, typically with little effect of changing melt or plagioclase composition. This is reinforced by the fact that
‘ruptured’ melt inclusions (those known from their major element composition to have leaked H$_2$O, Blundy and Cashman 2005; Blundy et al. 2008) give anomalously high calculated temperatures, some in excess of 1000 °C (figure 7; supplementary data table). In fact, the full range of $T_{\text{calc}}$ recorded by each dataset can be reproduced by manually changing the H$_2$O concentration of any individual inclusion, whereas the host plagioclase composition has relatively little effect on $T_{\text{calc}}$.

Figures 9, 10

Discussion

Degassing-induced crystallisation under disequilibrium conditions?

Our analysis shows that many arc magmas (all those examined) show evidence of apparent heating during degassing-induced crystallisation driven by decompression. Decreasing melt H$_2$O concentration is the primary factor that drives the increase in calculated temperature, accounting for up to 92% of the observed variations in $T_{\text{calc}}$. Experimental studies where volatile-saturated melt is decompressed at constant temperature also show the same effect, giving systematic increases in $T_{\text{calc}}$ with decreasing melt H$_2$O concentration. Studies that covered a wide range of decompression rates also show a systematic increase of $T_{\text{calc}}$ with increasing decompression rate, although the Brugger & Hammer dataset shows that absolute temperature may not always be overestimated (see below). Finally, the equilibrium constant for reaction of plagioclase and melt also varies systematically with both melt H$_2$O concentration and decompression rate. These observations
suggest that the calculated temperatures in the systems examined may reflect a
disequilibrium process of volatile degassing and melt crystallisation. This could
arise because crystal and bubble nucleation and growth at low pH$_2$O is hindered by
the increasing diffusivities of components within the melt, which are intimately
linked to degassing kinetics and temperature (e.g. Cashman and Blundy 2000;
Hammer and Rutherford 2002; Couch et al. 2003b; Brugger and Hammer 2010). A
lack of equilibrium in the decompression experiments is evidenced by variations in
 crystal size distribution and degree of plagioclase saturation, and progressive
changes towards disequilibrium crystal morphologies with increasing
decompression rate (Brugger and Hammer 2010). The slow equilibration process is
also indicated by the slightly lower calculated temperatures retrieved (see figure 5)
and more Ab-rich plagioclase crystallised in their series of experiments that were
annealed at constant temperature following decompression, and by the failure of
the MELTS algorithm to predict melt compositions for experiments quenched at
<45 MPa (Brugger and Hammer 2010). Finally, the systematic variations of K$_D$
with temperature, pH$_2$O and decompression rate in the experimental studies clearly
show that these do not represent equilibrium conditions.

All the experimental studies examined here report a range of plagioclase
compositions for each run. Plagioclase compositions closest to equilibrium are
typically found at the crystal rim, with early-formed, more calcic plagioclase
preserved in the cores (Martel and Schmidt 2003; Brugger and Hammer 2010;
Waters 2013). This is explained by crystallisation during increasing extents of
effective undercooling, $\Delta T_{\text{eff}}$ (defined as $T_{\text{liquidus}} - T_{\text{magma}}$, see Crabtree and Lange 2011). Initially, crystallisation is inhibited relative to the equilibrium case, resulting in lower volumes of plagioclase growth; insufficient time available for complete re-equilibration means that as melt $\text{H}_2\text{O}$ continues to change, new growth is added as more Ab-rich plagioclase, closer to equilibrium compositions (Brugger and Hammer 2010).

**How accurate are calculated temperatures?**

There is poor agreement between the two thermometers examined here, except for $\text{H}_2\text{O}$-rich melts and more albitic plagioclase (see figures 1 and 2). This means that it is difficult to be confident about the significance of absolute calculated temperatures, although relative variations appear robust. Secondly, crystallisation temperatures can be significantly over-estimated in the system plagioclase-melt-$\text{H}_2\text{O}$ if disequilibrium is not recognised. This is consistent with observations of (Mollo et al. 2010, 2011) for both plagioclase and clinopyroxene in anhydrous basalt. Such disequilibrium would most likely take the form of hindered $\text{H}_2\text{O}$ degassing into vesicles, disequilibrium crystallisation of anomalously An-rich plagioclase, or (for melt inclusions) variable loss of H from the inclusions after entrapment (see later). Our analysis shows that increases in $T_{\text{calc}}$ can reflect increasing $\Delta T_{\text{eff}}$ due to changes in melt $\text{H}_2\text{O}$ during decompression, as the melt viscosity increases and the kinetics of crystallisation become sluggish, rather than real increases in magma temperature. This means that, without an independent measure of $\Delta T_{\text{eff}}$, it is difficult to interpret significant increases in calculated
Substantial release of latent heat is, however, predicted on theoretical grounds, because the primary driving force for crystallisation during decompression of volatile-saturated magma is H₂O loss from the melt (Blundy et al. 2006). Thermodynamic calculations indicate that plagioclase crystallisation from an anhydrous melt would result in temperature increase of ~2.3 °C per 1% crystallisation (Couch et al. 2001), while the assemblage plagioclase + orthopyroxene + oxides would give ~3.2 °C per 1% (Blundy et al. 2006). For the natural datasets studied here, the temperatures estimated from plagioclase-liquid thermometry are typically well matched by two-oxide temperatures, including for Mount St Helens and Shiveluch (Blundy et al. 2006) and Soufrière Hills, Montserrat (two-oxide microphenocryst or microlite temperatures 958-1017 °C, Humphreys et al. 2009b; temperatures up to ~968 °C from plagioclase-liquid thermometry, this study). For Unzen, oxide equilibria indicate that the pre-eruptive magma was stored at ~790 °C whereas groundmass oxides give temperatures of ~890 °C (Venezky & Rutherford 1999), and plagioclase-liquid temperatures are significantly higher (900–1080 °C, see figure 10). However, we note that even though in some cases plagioclase-liquid temperatures calculated from Putirka (2005) and 2-oxide temperatures are very similar, the available two-oxide temperatures would not be in agreement with any of the plagioclase-liquid temperatures calculated using the Lange et al. (2009) model. Variably high 2-oxide temperatures may otherwise be
ascribed to magma mixing immediately prior to eruption (e.g. Devine et al. 2003; Blundy et al. 2006).

We are not aware of any further temperature estimates for Izu Oshima volcano, but Hamada and Fujii (2007) interpreted the variations in H$_2$O concentration in their melt inclusion suite as the result of variable H$_2$O loss from the inclusions. A similar interpretation has been proposed to explain the variable H$_2$O contents of plagioclase-hosted melt inclusions from Soufriere Hills Volcano, as a result of rapid diffusional re-equilibration of H$_2$O through the phenocryst host (Mann et al. 2013). If this were the case, then the significant increase in calculated temperature seen in both datasets would result from disequilibrium driven by diffusive H loss from the inclusions, with the inclusion and host unable to re-equilibrate except on much longer timescales. This is effectively equivalent to the ‘ruptured’ melt inclusions from Mount St Helens (Blundy et al. 2008), which are known to have undergone syneruptive leakage of H$_2$O and which give anomalously high calculated temperatures (see figure 7).

Although overall the data from the decompression experiments show similar patterns of calculated temperature, there are also clear differences between studies. The experiments of Martel and Schmidt (2003) and Cichy et al. (2011) give calculated temperatures that are mostly too high, and are consistent with experimental run conditions only at high pH$_2$O (figure 5c, e) and for the ‘low pressure’ series of Martel & Schmidt (2003). However, the Brugger and Hammer
dataset consistently underestimates the known experimental run conditions, even though the same pattern of increasing temperature with decreasing pH$_2$O is still observed (figure 5a). A potentially significant difference between these studies is that Brugger and Hammer (2010) used a crushed natural starting material while both Martel and Schmidt (2003) and Cichy et al. (2011) used synthetic starting materials made from mixed powders. The use of different starting materials could affect the degree of approach to equilibrium during the experiments, particularly for experiments that cover a broad range of P-T-H$_2$O conditions (Pichavant et al. 2007).

An important final question is how to assess the accuracy of calculated temperatures, or $\Delta T_{\text{eff}}$, in natural magmas. For the experiments, accuracy is simple to gauge by comparison with the known experimental temperature. However, for natural melt inclusion datasets (or crystal rim – host melt pairs) this is impossible without an independent measure of temperature and/or $\Delta T_{\text{eff}}$. Any calculated temperature using the plagioclase-liquid thermometer should therefore be considered as a maximum unless there is clear evidence of equilibrium (see below). Ideally, $\Delta T_{\text{eff}}$ should be constrained independently, but in practice this is difficult. Integration of quantitative or qualitative textural studies with minor or trace element partitioning, which is known to be strongly dependent on $\Delta T$ (e.g. Gamble and Taylor 1980), may represent one path towards obtaining a less equivocal measure of the degree of disequilibrium in natural systems. However, we suggest that calculated K$_D$ that are within the ‘equilibrium range’ of 0.10 ± 0.05 (for
temperatures < 1050 °C, Putirka 2008) are not sufficient to indicate complete
equilibration. Even the isobaric experiments of Martel and Schmidt (2003) show a
small but systematic decrease in $K_D$ from 0.06 to 0.03 for a pressure range of 170 to
50 MPa, and this also reflects our calculations at fixed pH$_2$O and melt composition
(see figure 3; supplementary data table).

Broader constraints on determining equilibrium in melt inclusions

It is commonly assumed that melt inclusion glass is in equilibrium with the host
mineral, based on observing whether the inclusions have euhedral ‘negative crystal’
shapes or are rounded. The faceted negative crystal shapes are typically interpreted
as equilibrated, but in fact the texturally equilibrated shape moves towards rounded
surfaces with constant mean curvature in an attempt to minimise interfacial energy
(e.g. Bulau et al. 1979). Chemically, equilibrium in melt inclusions is commonly
tested by calculating the apparent mineral-melt $K_D$ for the inclusion and its host
phenocryst, as described above for plagioclase-hosted melt inclusions. For slowly
equilibrating crystals, complex zoning textures in the host phase around the
inclusion may be clearly obvious using light microscopy or scanning electron
microscopy. However, in more rapidly equilibrating systems (e.g. olivine-hosted
inclusions) the major element Mg-Fe profiles may appear equilibrated while
significant chemical zoning of minor or trace components (e.g. Cr, Ni, P, Al) may still
be present, either within the host grain (e.g. Milman-Barris et al. 2008) or at the
margins of the melt inclusions (Newcombe et al. 2014). This is demonstrated by P
mapping of slowly cooled cumulate olivines that retained compositional zoning.
features from a primary dendritic crystal architecture (Welsch et al. 2014).

Depending on whether the thermometer of choice involves major elements or trace components, these issues may be significant or unimportant.

Figure 11

For plagioclase, diffusivities are overall much lower than in olivine, so major element zonation is usually clearly evident (figure 11). Melt inclusions in plagioclase commonly appear to be linked to periods of partial dissolution of the crystal, suggesting that formation of a rough interface predisposes the crystals towards melt entrapment. The main problem is usually to deduce which part of the host crystal most likely represents ‘equilibrium’ host plagioclase; in some cases this may be possible from careful examination of the plagioclase zoning textures (figure 11; Blundy and Cashman 2005; Humphreys et al. 2008). In other cases, petrographic examination shows that melt inclusions form an irregular, interconnected network in 3D, linked to either significant partial dissolution of the crystal during its evolution (reaction-controlled entrapment), or skeletal or hopper growth forms (growth entrapment). It may be very difficult to distinguish these two processes, particularly in crystals where partial textural equilibration has occurred leading to rounding of primary skeletal facets. Similar textures to those observed in plagioclase are also seen in both hornblende-hosted and pyroxene-hosted melt inclusions, and we suggest that further careful X-ray mapping in olivine is likely to show that these same processes are also present in olivine-hosted melt inclusions.
Implications

An analysis of variations in temperature calculated using two published plagioclase-liquid thermometers shows that disequilibrium conditions can result in significant temperature overestimates for the system melt-plagioclase-H₂O. Differences in temperature calculated by the different models imply that absolute temperatures returned by the models should not be used with too much certainty. Systematic variations in both calculated temperature and K₀ are observed with increasing decompression rate in isothermal decompression experiments. This implies that disequilibrium degassing of H₂O from the melt is an important control on calculated temperatures, and/or that growth of the equilibrium feldspar composition becomes impeded during H₂O degassing as melt viscosity and species diffusivities increase. Several natural melt inclusions datasets were examined and each shows a clear trend of apparent heating with decreasing melt H₂O content. This could imply that significant latent heating during degassing-induced crystallisation is a generic feature of subduction zone volcanoes, or that syn-eruptive or post-entrapment H₂O loss from melt inclusions during disequilibrium crystallisation is a significant process in degassing magmas. We suggest that the calculated temperatures should be treated as maxima unless there is direct evidence of equilibrium between plagioclase and melt.

Acknowledgements
MCSH acknowledges support from a Royal Society University Research Fellowship. We are grateful to Caroline Martel for provision of unpublished glass compositional data and to Becky Lange and Laura Waters for discussion and advance access to their recalibrated hygrometer. We acknowledge useful discussions with Jon Blundy, Kathy Cashman, Keith Putirka, Tom Sisson and Julia Hammer, and journal reviews from Fidel Costa and an anonymous reviewer.

References


Humphreys, M., Christopher, T., and Hards, V. (2009b) Microlite transfer by disaggregation of mafic inclusions following magma mixing at Soufriere Hills volcano, Montserrat. Contributions to Mineralogy and Petrology, 157, 609–624.


Equilibrium relationships between rhyolitic melt H$_2$O, temperature and plagioclase XAn, calculated using Putirka (2005) and Lange et al. (2009). (a) Contours of constant plagioclase composition in H$_2$O-T space. Large grey diamonds are interpolated from the phase diagram of Couch et al. (2003). (b) Contours of constant temperature in H$_2$O-XAn space. Also shown is RhyoliteMELTS modelling of isothermal decompression for rhyolitic melt (bold lines, 825-875 °C) and basaltic andesite melt (thin black lines, 1000-1100 °C).

Contours of constant pressure (assuming H$_2$O saturation, i.e. P$_{tot}$ = pH$_2$O) in T-XAn space, calculated for rhyolitic melt using Putirka (2005) and Lange et al. (2009). Large circles are interpolated from the phase diagram of Couch et al. (2003) for 160 MPa (black) and 200 MPa (grey). Also shown is RhyoliteMELTS modelling of isobaric cooling in rhyolitic melt (25-200 MPa).

Theoretical variation of plagioclase-liquid K$_D$ for rhyolitic melt (as defined by Putirka 2005; 2008) with calculated temperature (T$_{calc}$) as a function of pressure (assuming H$_2$O saturation, i.e. P$_{tot}$ = pH$_2$O) (a), and with pH$_2$O as a function of temperature (b). Points in (a) represent increments of 10 mol% XAn.
H₂O concentration in experimentally decompressed glasses from Martel & Schmidt (2003), Brugger & Hammer (2010) and Cichy et al. (2011), in comparison with isobaric (solubility) data from Mangan & Sisson (2000). Also shown is rhyolite solubility curve from VolatileCalc (Newman & Lowenstern 2002). All data have H₂O concentrations in excess of the solubility limit for the experimental quench pressure, indicating kinetically inhibited degassing.

Figure 5

Variation of calculated temperature (T<sub>calc</sub>, using model A from Putirka, 2005) and K<sub>D</sub> with pH<sub>2O</sub> in experimentally decompressed glasses from Brugger & Hammer (2010; a, b), Cichy et al. (2011; c, d) and Martel & Schmidt (2003; e, f). Grey bar with black line shows the experimental run temperature in each case ± 5 °C. See supplementary data table for original data and calculated values.

Figure 6

Variation of calculated temperature (T<sub>calc</sub>, using model A from Putirka, 2005) and K<sub>D</sub> with decompression rate in experimentally decompressed glasses from Brugger & Hammer (2010; a, b), Cichy et al. (2011; c, d) and Martel & Schmidt (2003; e, f). Grey bar with black line shows the experimental run temperature in each case ± 5 °C. See supplementary data table for original data and calculated values.

Figure 7
(a) Variation of calculated temperature ($T_{\text{calc}}$) using model A from Putirka, 2005) with H$_2$O concentration reported for plagioclase-hosted melt inclusions from Soufrière Hills, Montserrat (Humphreys et al. 2009); Mt Unzen, Japan (Botcharnikov et al. 2007); Mount St Helens, USA (Blundy et al. 2006); Shiveluch, Kamchatka (Blundy et al. 2006) and Izu Oshima (Hamada & Fujii 2007). Constant-X$_{\text{An}}$ contours are shown for comparison (symbols as figure 1). (b) Variations of calculated temperature with reported X$_{\text{An}}$ of the host plagioclase phenocryst for the same melt inclusion suites. Constant-pH$_2$O contours are shown for comparison (symbols as figure 2). See supplementary data table for original data and calculated values.

Figure 8

Variation of calculated K$_D$ with (a) plagioclase X$_{\text{An}}$ and (b) glass H$_2$O concentration reported for melt inclusion datasets from the literature. Dark circles – Mount St Helens (Blundy et al. 2006); grey squares – Shiveluch (Blundy et al. 2006); dashes – Soufrière Hills, Montserrat (Humphreys et al. 2009); crosses - Izu Oshima (Hamada & Fujii 2007); dark triangles - Mt Unzen (Botcharnikov et al. 2007). See supplementary data table for original data and calculated values.

Figure 9

Regression of calculated temperature with each of the parameters that make up the ‘model A’ calculation (Putirka 2005), (a) Ca$_L$, (b) Na$_L$, (c) Al$_L$, (d) Si$_L$, (e) H$_2$O and (f) X$_{\text{An}}$. Dark circles – Mount St Helens, grey squares – Shiveluch (Blundy et al. 2006). Linear regression trends and equations are given for any significant regressions ($R^2$
≥ 0.15), with Mount St Helens regressions in black and Shiveluch in grey. The most significant parameter controlling $T_{\text{calc}}$ is the H$_2$O content of the glass. See supplementary data table for original data and calculated values.

Figure 10

Regression of calculated temperature with each of the parameters that make up the 'model A' calculation (Putirka 2005), (a) Ca$_L$, (b) Na$_L$, (c) Al$_L$, (d) Si$_L$, (e) H$_2$O and (f) X$_{\text{An}}$. Dashes – Soufriere Hills, Montserrat (Humphreys et al. 2009); crosses - Izu Oshima (Hamada & Fujii 2007); dark triangles - Mt Unzen (Botcharnikov et al. 2008). Linear regression trends and equations are given for any significant regressions ($R^2 \geq 0.15$) in each dataset. The most significant parameter controlling $T_{\text{calc}}$ is the H$_2$O content of the glass. See supplementary data table for original data and calculated values.

Figure 11

Back-scattered SEM image illustrating the complexity of plagioclase zoning that is common in intermediate calc-alkaline lavas. Melt inclusions are dark blebs (some annotated ‘MI’). White dashed lines outline clear resorptive zoning ‘events’ that leave irregular boundaries and may entrap melt inclusions.
Figure 1
Figure 2

Lange 160 MPa
Lange 100 MPa
Putirka 100 MPa
Putirka 160 MPa
MELTS 25 100 200

Couch et al. (2003), 160 MPa
Couch et al. (2003), 200 MPa

Temperature °C
XAn

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
Figure 3
Figure 4
Figure 6
Figure 8
Figure 9
Figure 10

(a) (c) (e)  
(b) (d) (f)

Izu Oshima  
Montserrat  
Unzen

Calculating T °C

y = -44.6x + 1136
R² = 0.90

y = -24.0x + 970
R² = 0.92

y = -26.14x + 1055
R² = 0.89

y = -3034x + 1297
R² = 0.27

y = -6014x + 992
R² = 0.15

Calculated T °C
Figure 11
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Table 1.
Composition of rhyolite melt inclusion (MVO1524b_112, from Humphreys et al. 2009) and basaltic andesite melt (ol101mi1, from Hamada & Fujii 2007) used for MELTS modelling and calculations shown in figures 1-4.